

"EFFECT OF SOLVENTS ON THE POTENTIAL OF ION-SELECTIVE  
ELECTRODES: A COMPARATIVE STUDY"

BY

H.A. AKE

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To my parents, wife and sons

The author received the degrees of Bachelor of Science and Master of Science (Analytical Chemistry) at the University of Ibadan, Nigeria.

He has also worked for three years as a chemist in the Public Health Laboratory, Ministry of Health, Ilorin, Nigeria.



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### SUMMARY

Ion-selective electrodes, reference electrodes and the effect of solvents on the cell potential are reviewed.

Direct potentiometry of ion, X (  $X = F^-$ ,  $Cl^-$ ,  $Ag^+$ ,  $Pb^{2+}$ ,  $Na^+$  and  $H^+$  ) is carried out in methanol/solvent and water/solvent systems ( solvent = MeOH, EtOH, HOAc, n-PrOH, i-PrOH, acetone and 1,4-dioxan ) for 0-99% m/m solvent.

Solvent effect is shown to exist for the Beckman sodium-selective glass electrode.

Measurements by direct and 'indirect' methods are compared.

A qualitative approach is made to explain non-Nernstian behaviour of electrode slopes.

The use of ion-selective electrodes for monitoring the production of vinegar from ethanol is proposed.

## INTRODUCTION

## 1. INTRODUCTION

### 1.1 ION-SELECTIVE ELECTRODES

Ion-selective electrodes are electrochemical sensors which sense the activity, rather than the concentrations of ions in solution. The oldest and perhaps the best behaved ion-selective electrode is the glass electrode for pH measurements, which was discovered by Cremer<sup>1</sup> in 1906. This discovery was shortly followed by a more detailed investigation by Haber and Klemensiewicz<sup>2</sup> who showed that this electrode responded to hydrogen ions according to the Nernst equation (see section 1.1.2). Early attempts to develop glass electrodes selective for other ions were made<sup>3,4,5</sup>, and presently glass electrode selective for cations, chiefly silver, the alkali metal and ammonium ions are commercially available.

In the late 1950s and early 1960s, research teams led by Nicolsky<sup>6</sup> in the U.S.S.R. and Eisenman<sup>7-10</sup> in the U.S.A. developed theories from their studies of properties of many families of glasses to account for the origin of the glass electrode potential. Isard<sup>11</sup> presented a review of the development of the composition of glasses sensitive to hydrogen ions and other cations.

Kolthoff, Sanders<sup>12</sup> and Tendeloo<sup>13,14</sup> were the first to make ion-selective electrodes from materials other than glass

in the 1930s. The former authors prepared halide-selective electrodes from pellets of silver halide, but unfortunately the performance of the electrodes was not sufficiently good. In the late 1950s, a calcium-sensing electrode from a membrane of paraffin impregnated with calcium oxalate was developed<sup>15,16</sup>, but its performance was not satisfactory in several respects. In the early 1960s, Pungor and Hollo's - Rokosinyi<sup>17</sup> developed an electrode membrane by embedding silver iodide in paraffin and demonstrated the selectivity of the electrode to iodide ions in the presence of chloride ions. Subsequent to their encouraging achievements, they developed a whole range of electrodes of good selectivity and giving Nernstian response, all of which had heterogeneous membranes consisting of an active material supported in an inert matrix of silicone rubber. These electrodes were considered the first truly selective ion-selective electrodes<sup>18a</sup> other than glass, to be developed which gave a response which is thermodynamically reversible with respect to the primary ions. The silver halide-selective electrode became commercially available in Hungary in 1965.

The year 1966 witnessed a major breakthrough in the development of a highly selective electrode for fluoride ion by Frant and Ross<sup>19</sup> because of the following reasons:

- (a) The satisfactory performance of the electrode and consequently its rapidly wide acceptability.
- (b) The importance of fluoride determination, primarily in the analysis of potable water.
- (c) The difficulties associated with alternative analytical methods of fluoride determination.
- (d) Perhaps, most importantly is the fact that a new lease of optimism was ushered to what had proved before then, more or less a fruitless research endeavour. Thus the emergence of other electrodes<sup>20</sup> selective to copper, lead, cadmium, etc, started flourishing shortly afterwards.

Since then, rapid progress has been made and the field has been further broadened by introduction of liquid ion-exchange membranes<sup>21,22</sup> and membranes containing electro-neutral macrocyclic compounds<sup>23</sup>.

Also, a notable contribution has been made through the development and investigation of water-insoluble basic dye salts as ion-exchanger for use in ion-selective electrodes<sup>24-27,63</sup>

Gas sensors<sup>28</sup> otherwise known as gas probes and enzyme electrodes<sup>29</sup> have been developed. However, it is important not to confuse the former with ion-selective electrodes since they have their reference electrodes incorporated and are

thus complete cells, whereas ion-selective electrodes are not. Other useful but less encountered electrodes include the surfactant electrodes, which are similar to the electrode based on organic ion-exchanger and ion-sensitive field effect transistors<sup>18</sup> (ISEFETS).

The analytical application of ion-selective electrodes is widespread. Many branches of science have benefited tremendously from their commercial availability, versatility and ease of operation. Their impact on solution chemistry has been likened to that of laser on optics<sup>30</sup>.

Because of their ever-increasing importance and applications, ion-selective electrodes have been a subject of reviews by many prominent researchers<sup>31-34</sup>. Two of the very important and most recent reviews include that of Buck<sup>35</sup> and and Thomas et al<sup>36</sup> giving a wide coverage with 434 references in the former and 177 references in the latter. A few others, on practice and theory of ion-selective electrodes and new books are by Bailey<sup>18</sup>, Vessely, Weiss and Stulik<sup>37</sup>.

Applied analysis using ion-selective electrodes in specific fields include clinical medicine<sup>38</sup>, food<sup>39</sup>, agriculture<sup>40</sup>, tobacco and smoke<sup>41</sup>, fuel gases<sup>43</sup> waste-water and pollution control<sup>43,44</sup>, paper industry<sup>45</sup>, metal finishing<sup>46</sup>, oceanography<sup>47</sup> and process stream<sup>48</sup>. Recent applications include their use in nonaqueous analysis<sup>30</sup>. The compatibility

of ion-selective electrodes with organic solvents coupled with interesting findings in these solvents have stimulated a momentuous interest in this field<sup>49-52</sup>. Recent work in this department has afforded a rapid method of solvent analysis of some organo-aqueous binary mixtures<sup>53</sup>.

Another recent and novel application of ion-selective electrodes is their use as detector for gas chromatography. A dual ion-selective electrode gas chromatographic detector which allows the simultaneous detection of chloride and bromide containing compounds through two-channel operation has been reported<sup>54</sup>.

#### 1.1.1 THEORY OF ION-SELECTIVE ELECTRODE POTENTIAL

When two phases containing electrically charged particles are brought into contact, an electrical potential difference develops at their interface. Each phase can be associated with an electrochemical potential,  $\mu_i$ , the values of which must be equal if the system is in equilibrium.

For the  $i$ th charge distributed in phases 1 and 2.

$$\mu_i(1) = \mu_i(2) \quad \dots\dots\dots (1.1)$$

under ion-selective electrode conditions, it can be assumed that the chemical properties of the phases are independent of the electrical charges involved, and thus equation (1.1) can be rewritten in terms of the standard chemical potentials

$\mu_i^0$ , the activities,  $a_i$ , the charges,  $z_i$ , and the inner electrical potentials of the phases,  $E$ , say;

$$\mu_i^0(1) + RT \ln a_i(1) + z_i F E(1) = \mu_i^0(2) + RT \ln a_i(2) + z_i F E(2) \dots (1.2)$$

where  $R$  is the universal gas constant,  $T$  is the temperature expressed on the absolute scale and  $F$  is the Faraday. Thus for the potential difference at the interface,

$$\begin{aligned} E = E(2) - E(1) &= \frac{\mu_i^0(1) - \mu_i^0(2)}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)} \\ &= \text{const} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)} \dots \dots \dots (1.3) \end{aligned}$$

if the activity of the  $i$ th species in one phase is known and/or fixed, the activity of the  $i$ th ion can be determined by measuring  $E$ . In fact the design of ion-selective electrodes is such that the activity of the internal reference is fixed, thus equation (1.3) becomes.

$$\begin{aligned} E = \text{Constant} - \frac{RT}{z_i F} \ln a_i(2) + \frac{RT}{z_i F} \ln a_i(1) \\ = \text{Constant} + \frac{RT}{z_i F} \ln a_i(1) \dots \dots \dots (1.4) \end{aligned}$$

which reduces to the familiar form of Nernst's equation.

And hence we see that the change in electrode potential is directly proportional to the logarithm of the activity of the determinand.



From the foregoing it can be seen that an immense number of systems can be used as electrodes for determining the activities of various species in solution. However, in practical measurements, not only sensitivity to the particular species, but also satisfactory selectivity, accuracy and reproducibility of the measurements will be required, thus implying considerable limitations on the selection of useful systems.

#### 1.1.2 DIRECT POTENTIOMETRY

Potential measurements with the aid of ion-selective electrodes are generally referred to as potentiometric technique which can be broadly divided into two groups-direct potentiometry and potentiometric titration.

Direct potentiometry involves the measurement of the e.m.f. of a cell consisting of an electrode selective to the ion of interest and a suitable electrode, which ideally, should maintain a constant potential, regardless of any variation of the activity of the determinand. When the two electrodes are immersed in a sample solution, they will indicate a potential given by the Nernst equation.

$$E = \text{Constant} + \frac{2.303RT}{nF} \log a_x \dots\dots\dots (1.5)$$

The constant term depends on the choice of reference electrode used, and its associated liquid junction potential.

E is the potential in mV ( $10^{-3}$ V) developed by the system

R is the gas constant =  $8.314 \text{ joules deg}^{-1} \text{ mole}^{-1}$   
( $\text{JK}^{-1} \text{ mol}^{-1}$ ).

T is the absolute temperature.

F is the Faraday =  $9.65 \times 10^4 \text{ coulomb g-equiv (C mol}^{-1}\text{)}$

$a_x$  is the activity of the determinand X in mole litre $^{-1}$   
( $\text{mol dm}^{-3}$ ) or mole per 1000 g. ( $\text{mol kg}^{-1}$ ).

n being its ionic charge.

The term  $\frac{RT}{F}$  is defined as the Nernst factor. A plot of electrode potential Vs. logarithm of activity of standard solutions is used as a working curve to determine the unknown sample activities. For most analysis, however, determination of concentration, rather than activity, are of interest, but a knowledge of the activity coefficient of the species under the particular situation is required to evaluate concentration. In fact, if necessary precautions are taken, a plot of electrode potential versus logarithm of concentration will give a working curve, and hence concentration can be evaluated directly. This point will be discussed further in section 1.1.4.

### 1.1.3 POTENTIOMETRIC TITRATIONS

In its everyday usage, direct potentiometry with an ion-selective electrode is most frequently encountered. However, in many applications, direct potentiometry with ion-selective electrode is not sufficiently accurate and precise<sup>55</sup>. This is evident from the fact that potential change only bears a useful analytical relationship with the logarithm of activity (concentration), and consequently the technique is insufficiently sensitive to a small change in concentration. Substantial improvement can be achieved by performing a titrimetric determination. Series of sample of similar concentration are better analysed by titration. In principle, any type of titration can be performed with an ion-selective electrode. Acid-base titrations are the domain of  $\text{pH}$ -selective glass electrodes; the other ion-selective electrodes are virtually exclusively used in precipitation and complexometric titrations, as suitable electrodes for systems which are best analysed by redox are not as yet available<sup>48</sup>.

The increased accuracy and precision (at the expense of time and simplicity) of potentiometric titration over direct potentiometry can be attributed to the following reasons.

- (a) Measured potential are used to detect rapid changes in concentration (activity) that occur at the equivalence

point of the titration, a point at which the rate of potential change is considerably greater than the response slope which limits precision and accuracy in direct potentiometry.

(b) Because it is the relative magnitude of potential change, rather than its absolute magnitude which is of interest, the influence of liquid junction potential and activity coefficient have little or no effect.

The technique involves addition of a standard titrant in relatively large initial increments in succession, allowing the system to attain equilibrium and then recording the corresponding potential reading, until around the equivalence point, when the titrant is added only in small increments just before and after the equivalence point. From a plot of potential change against volume of titrant added, the equivalence point is determined.

#### 1.1.4 ACTIVITY AND ACTIVITY COEFFICIENT

Although in recent years, there has been a growing awareness<sup>56</sup> of activity measurement for some chemical species, (e.g, the hardness of water depends on the calcium ion activity in the sample, and not on the concentration; also the role of calcium ion in biological processes such as nerve conduction, muscle contraction, and blood clotting is determined

by calcium ion activity in the system) which may vary considerably from the total ion concentration; most analytical problems involve concentration measurements since in general concentration is much simpler to determine analytically than activity.

It has been mentioned earlier that ion-selective electrodes sense activities rather than the concentration of ions in solution. Activity in this context is better considered as the apparent concentration of a free ion in solution<sup>57</sup>, since the chemical effectiveness of an ion is influenced by the amount and type of other ions in the solution.

The activity,  $a_x$ , of an ion, X, in solution may be related to its concentration  $[X]$  expressed as molarity by the equation.

$$a_x = \gamma_x [X] \dots\dots\dots (1.6)$$

where  $\gamma_x$  is the activity coefficient of ion, X. In general for an ion X in solution with a counter ion, Y, the mean activity coefficient  $\bar{\gamma}_{XY}$  is the important quantity, rather than  $\gamma_x$ , since it is not possible to determine the latter in solution in isolation. The mean activity coefficient depends, not only on the electrolyte of which the ions are composed, but also on the other ionic species in solution (ionic strength).

According to Debye - Huckel theory, this dependence may be expressed in the form<sup>18b</sup>.

$$\log \gamma_{XY} = - \frac{A |n_X n_Y| I^{\frac{1}{2}}}{I + B d I^{\frac{1}{2}}} \dots\dots\dots (1.7)$$

where A and B are conditional constants, depending upon temperature, dielectric constant of the solvent and the density;  $n_X$ ,  $n_Y$  are the charges carried by X and Y; d is the average effective diameter of the ions and I, the ionic strength, defined by:

$$I = \frac{1}{2} \sum [X] n_X^2 \dots\dots\dots (1.8)$$

where the summation is taken over all ions in the solution.

Substituting concentration for activity in the Nernst equation, we obtain for a cation:

$$E = E^0 + \frac{2.303RT}{n_X F} \log_{10} \gamma[X]$$

ie

$$E = E^0 + \frac{2.303RT}{n_X F} \log_{10} \gamma + \frac{2.303RT}{n_X F} \log_{10} [X] \dots\dots (1.9)$$

For pure solution of monovalent ions XY of concentration less than about  $10^{-4}M$ , the activity coefficient is close to unity, and differences between activity coefficients and concentrations may be ignored, in which case the middle term of the right hand side of the above equation vanishes. However, as concentrations increases above  $10^{-4}M$ , the activity coefficient

decreases and these differences become progressively larger.

In practice, an excess inert electrolyte is added as background (usually 10 to 100 fold times the determinand's concentration) to swamp out variation of  $\gamma$  in routine analysis involving ion-selective electrodes. This allows concentration to be measured directly.

#### 1.1.5 SELECTIVITY OF ELECTRODES

There is no ion-selective electrode which responds exclusively to the ion (primary ion) for which it is designed. To some extent, though it may be negligible in many cases, any foreign ion is capable of interfering. Thus in general, the electrode response will have contributions from the primary, as well as from the interfering ions (secondary ions). For a given primary ion, A, the degree of selectivity of its electrode, with respect to an interfering ion, B, is expressed by the selectivity coefficient,  $K_{AB}$ , which is defined by the general equation<sup>18b</sup> for the electrode potential:

$$E = E^{\circ} \pm \frac{2.303RT}{n_A F} \log_{10} [a_A + K_{AB} (a_B)^{n_A/n_B}] \dots\dots (1.10)$$

where  $n_A$  and  $n_B$  are the charges on ions, A, and B, respectively;  $E^{\circ}$  is the standard electrode potential. The +ve and the -ve signs in the equation hold when A is a cation and an anion

respectively. In essence  $K_{AB}$  is a measure of the performance of the electrode for A in the presence of B. The smaller the value of  $K_{AB}$ , the better the performance of the electrode for A.

It has been pointed<sup>58</sup> out that the nomenclature "selectivity constant" instead of selectivity coefficient is inappropriate because  $K_{AB}$  is never constant for all activities of A and B, although it may be, sometimes, constant for a given ratio of the activity of A and B. Another point is that,  $K_{AB}$ , should only be used with caution to assess the possible determination of A in the presence of B, since its numerical value is often quoted for a given A and B. When B is by far in excess of A, though,  $K_{AB}$  may be small, the contribution from  $K_{AB} a_B^{n_A/n_B}$  may be significant.

#### 1.1.6 CLASSIFICATION OF ION-SELECTIVE ELECTRODES

Many different classifications of ion-selective electrodes have been presented, but perhaps, the most logical from both practical and theoretical point of view, is that based on the type of active material used to make the membrane. In this way, the majority of ion-selective electrodes fall into three main classes, and a fourth may be used to account for the rest. If other types of electrochemical sensors (e.g gas-probe) are taken into consideration, then five classes of sensors may be presented as follows:<sup>18a</sup>



(1) Glass electrodes - containing a cation selective glass membrane.

(2) Electrodes based on organic ion-exchangers and neutral carriers - the former are made with organic ion-exchanger with liquid or solid membranes, whereas the latter are composed of macrotetrolide antibiotics or cyclic polyethers as membrane.

(3) Gas-sensing probes - these are complete electrochemical cells and are thus quite distinct in their properties of operation and performance from ion-selective electrodes.

(4) Solid-state electrodes - based on inorganic salts of which their membranes have been produced in a variety of homogeneous and heterogeneous forms, ranging from single crystals to dispersion of active material in an inert matrix, such as silicone rubber or polythene.

(5) Miscellaneous electrodes - these are sensors which do not fall within the other classes, despite similarities in some cases. Sensors in this class include the enzyme and, surfactant electrodes and ion-sensitive field effect transistors (ISEFETS).

Whatever type it may be, for a resonable performance, an ion-selective electrode is expected to meet the following requirements.

- (i) membrane must be substantially non-porous.
- (ii) solicit the minimum photoelectric response.
- (iii) membrane must have good mechanical strength and not be readily scratched or abraded.
- (iv) be water-insoluble, the smaller the solubility product the better.
- (v) show good selectivity.
- (vi) have good response time.
- (vii) be easy to handle.
- (viii) give stable, reproducible and meaningful readings within the optimum range of activity of the primary ion.

#### 1.1.6.1 GLASS ELECTRODES

Since the late 1930s, glass electrodes selective to hydrogen ions have been standard item of laboratory equipment<sup>1,2</sup>. In strongly alkaline solutions, they show response which deviates from Nernst equation<sup>5</sup>, known as the "alkaline error", which increases with increasing aluminium oxide content of the glass. This phenomenon was attributed to the electrode responding to alkali metal ions. The alkaline error has been exploited to an advantage, thus with modified composition and optimization for selectivity, glass electrodes responsive to alkali metals have been manufactured. However, at the

moment all glass electrodes manufactured for alkali metal ions show to a considerable extent greater selectivity for proton. The sodium-ion electrode, for instance, has by far greater selectivity for silver and hydrogen ions than for sodium ion.

There are three types of commercially available glass electrodes, characterised as follows<sup>59</sup>:

- (a)  $pH$  type, with selective order:  $H^+ \gg Na^+ > K^+, Rb^+, Cs^+ \gg Ca^{2+}$
- (b) cation type, with selective order:  $H^+ > K^+ > Na^+ > NH_4^+$
- (c) sodium sensitive type, with selective order:  $Ag^+ > H^+ > Na^+ \gg K^+, Li^+ \dots \gg Ca^{2+}$

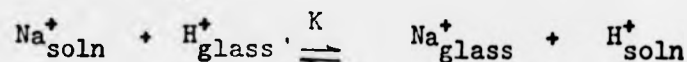
The origin of the glass electrode potential is generally accepted to involve an ion-exchange process mechanism<sup>10</sup>.

A cross-section through the membrane of a functioning glass electrode comprises several discrete regions and interfaces<sup>30b</sup>:

Internal	Hydrated	Dry Glass	Hydrated	External
Solution	Gel Layer	Layer	Gel Layer	Solution
	0.05-1 $\mu m$	50 $\mu m$	0.05-1 $\mu m$	

The dry glass layer constitutes the bulk of the membrane's thickness, sandwiched between much thinner hydrated layers, because the movement of ion is boosted by hydration of the glass.

For univalent cation, the diffusion coefficient is said to be about  $10^3$  times greater in hydrated glass than in dry glass<sup>61</sup>. For a sodium-responsive electrode, it was found that the hydrated glass surface undergoes cation exchange according to the equilibrium<sup>62</sup>.



It is noteworthy that, although hydrogen ion undergoes exchange across the solution/hydrated layer interface, these ions do not penetrate the glass membrane. This has been demonstrated by coulometric experiments involving prolonged electrolysis in glass electrode bulbs filled with tritium-labelled sample solutions<sup>62</sup>.

#### 1.1.6.2 ELECTRODES BASED ON ORGANIC ION-EXCHANGERS AND NEUTRAL CARRIERS

Many ion-selective electrodes based on organic ion-exchangers have been reported<sup>18c</sup>. Judging by the number of ion-exchange systems available, this vast number is easily anticipated. Many they are though, not all are equally satisfactory, or exhibit good selectivities. The number of ions for which neutral carriers are available is quite limited. Those reported so far include calcium, potassium, barium, sodium and ammonium. Generally speaking, these neutral

carrier electrodes are more selective than the ion-exchange electrodes.

Initially the ion-exchange electrodes flourished under the name "liquid ion-exchange electrodes" but this nomenclature is becoming obsolete because, unlike in the past, when the ion-exchanger was usually incorporated into the electrode dissolved in an organic solvent, it is now fashionable to incorporate the ion-exchanger in an inert matrix, such as PVC, polythene or silicone rubber<sup>63</sup>, to obtain a 'solid' membrane<sup>18c</sup>. Thus the electrodes are now simply called "ion-exchange electrodes"<sup>18c</sup>.

The advantages and disadvantages of the liquid and solid membranes for electrodes in this class have been argued at length in the literature<sup>18c</sup>. In Bailey's word, "the proponents of the solid membranes have succeeded in filling more journal pages with this discussions, but reports of applications refer almost entirely to electrodes with the liquid membranes".

Table 1<sup>18c</sup> shows a comparison of liquid and solid membranes.

TABLE 1

	Liquid membrane	Solid membrane
Wt of active material incorporated	about 100 mg	about 1 mg
Ease of electrode assembly	depending on design	easy
Selectivity	as solid	as liquid
Effect of strong interferences	prolonged drift	short drift or failure
Typical $E^0$ drift	$1\text{mV day}^{-1}$	$1\text{mV week}^{-1}$
Sample contamination by electrode	slight	negligible
Lifetime	1 - 2 months	1 week- 2 months

Perhaps, the most fundamental difference between the liquid and the solid membranes arises from the greater mobility of the species and the larger quantity of active material present in the liquid membranes. While these types of electrodes are only slightly soluble in water, they are not necessarily so in organic solvents, thus they are most successful in aqueous analysis. Because of their finite solubility in water, one obvious advantage of liquid membrane over solid membrane emerges - in the former, more ion-exchanger can diffuse from the reservoir to the surface of the membrane to replace that which has dissolved and also, if the electrode surface becomes contaminated, the surface can be wiped with, say, cotton wool, to produce a fresh surface, whereas for solid membranes, when the ion-exchanger has dissolved out of the

surface, the membrane must be discarded.

The theory of these ion-exchange electrode has been developed in detail by Eisenman and his coworkers<sup>67</sup>.

The most important discovery among liquid ion-exchange electrode is that of the calcium electrode by Ross<sup>22</sup>. Considerable significance is also attached to the nitrate ion-exchange electrode. Others worth mentioning are: perchlorate, tetrafluoroborate, 'water hardness', carbonate and chloride.

The other type of electrodes in this broad classification are those based on neutral carrier. As has been mentioned earlier, the neutral carriers used in these electrodes are usually macrotetrolide antibiotics, cyclic polyethers (crown compounds) etc; molecules, which have closely packed structures with a central cavity. By a suitable choice of neutral carrier and solvent, electrodes have been made with high selectivity for the appropriate determinand. Again, it was Eisenman and his co-workers who developed the theory for electrodes of this kind<sup>67</sup>.

#### 1.1.6.3 GAS-SENSING PROBES

The development of gas-sensing probes has increased the range of species which may be analysed by potentiometry. Since it is the partial pressure of gases that is sensed in

solution, probes suffer no interference from ions<sup>18d</sup>. Also, because samples are unlikely to contain more than a few gases to which they can respond, the probes are generally more selective than ion-selective electrodes. At the moment, gas sensing probes are available for carbon dioxide, ammonia, sulphur dioxide, hydrogen sulphide and nitrous oxides. In addition, because of the ease of conversion to their respective gases by either acid or alkali, ions such as carbonate, ammonium and sulphites can be determined by gas sensing probes.

Two types of gas-sensing probes have been reported<sup>64</sup>, those without membrane, known as "air-gap electrodes" and those with membrane. In the former, the membrane is replaced by an air-gap of several millimetres and the probe assembly is suspended above the sample in a specially sealed container, whereas the latter contains a glass electrode with a flat or slightly convex pH-sensitive tip. It is however, the gas-sensing membrane probes that have been independently assessed and generally used<sup>18d</sup>.

The principle on which a probe operates is based on the diffusion of the determinand gas in the sample through the membrane of the probe and then reaching the internal solution to form the ion which is sensed by the ion-selective electrode component of the probe. The activity



of the ion sensed is then related to the partial pressure or concentration of the gas in the sample.

The cell potential is related to gas concentration by the Nernstian equation, e.g. for ammonia by<sup>18d</sup>

$$E = E^1 - \frac{-2.303RT}{F} \log_{10} \text{NH}_3 \dots\dots\dots(1.11)$$

Analogous equations may be written for other probes, with the negative sign replaced by positive sign for acidic gases.

#### 1.1.6.4 SOLID-STATE ELECTRODES

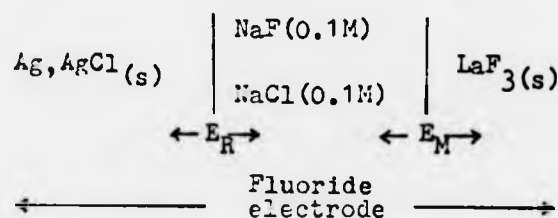
Solid-state or inorganic salt-based electrodes were the first new generation of ion-selective electrodes which succeeded the glass electrodes. A review of their development has been presented in section 1.1. Since they are many in number, only those used in this particular piece of work will be discussed in some detail.

The mechanisms to which these inorganic salt-based electrodes owe their response have been theorised by several workers<sup>65-67</sup>. In general, for all of them, it is assumed that when an electrode in this class is immersed in a sample solution, interfacial potentials are developed which are attributable to the ion-exchange processes on the membrane surface, and at the same time, there is an onset of diffusion

potential arising from the diffusion of the various ionic species across the membrane<sup>18e</sup>.

#### 1.1.6.4.1 LANTHANUM FLUORIDE ELECTRODE

The Lanthanum Fluoride electrode is the most successful of the solid-state electrodes. The half-cell representation of the electrode can be given by<sup>68</sup>:

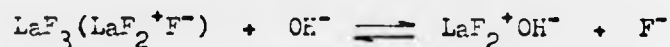


where  $E_R$  and  $E_M$  are the reference electrode potential and membrane potential respectively.

It has an inner reference electrode made of silver with silver chloride solid coating, immersed in an equimolar (decimolar) solution of sodium chloride and fluoride. The chloride ion fixes the potential of the reference electrode and the fluoride controls the potential of the inner surface of the membrane. The internal reference system sits in a PTFE casing with Lanthanum Fluoride sometimes, doped with europium (II) (to enhance conductivity) as a single crystal sandwiched and firmly cemented between the internal reference compartment through the PTFE casing, exposing the crystal as a window at the bottom.

The electrode has a reasonably low limit of detection, about  $10^{-6} M F^-$  in water and lower limits have been achieved in organic solvent-water mixtures. This has been quantitatively related to the solubility of the membrane.

The major interference is from hydroxide ion which perhaps occurs in the following way<sup>69</sup>:

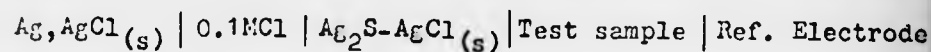


This is not too strange if it is borne in mind that  $OH^-$  and  $F^-$  have comparable size.

#### 1.1.6.4.2 SILVER CHLORIDE ELECTRODE

This is one of the three silver halide electrodes, all of which are ion-conducting materials in which silver ion is the mobile species. The improved model<sup>70</sup> incorporates silver sulphide, a chemically inert matrix which enhances the conductance and obviates difficulties due to light sensitivity of silver halides, since  $AgCl$  and  $AgBr$  are known to exhibit photoelectric potential. Thus the modern chloride electrode is an intimate mixture of  $Ag_2S - AgCl$ .

A functioning chloride electrode can be represented in the following way:



The overall potential for the above is given by:-

$$E = E^0 + \frac{2.303RT}{F} \log_{10} a_{\text{Ag}}^+ \dots\dots\dots (1.12)$$

Because the silver chloride membrane has a finite solubility, silver chloride will always be in equilibrium with its ions, and thus  $\text{Ag}^+$  will always be present .

And hence<sup>70</sup>:

$$a_{\text{Ag}}^+ = S_{\text{AgCl}} / a_{\text{Cl}}^- \dots\dots\dots (1.13)$$

sub. into equation, (1.12)

$$E = E^0 + \frac{2.303RT}{F} \log \frac{S_{\text{AgCl}}}{a_{\text{Cl}}^-} \dots\dots\dots (1.14)$$

expanding:

$$E = \underbrace{E^0 + \frac{2.303RT}{F} \log_{10} S_{\text{AgCl}}}_{E^0 1} - \frac{2.303RT}{F} \log_{10} a_{\text{Cl}}^- \dots\dots\dots (1.15)$$

but  $S_{\text{AgCl}}$  is constant for a given temperature thus the above equation becomes.

$$E = E^0 1 - \frac{2.303RT}{F} \log_{10} a_{\text{Cl}}^- \dots\dots\dots (1.16)$$

It can be seen, therefore, that the, electrode can be used either as a silver ion or a chloride ion sensor.

Like the fluoride electrode the lower limit of

detection is governed by membrane solubility, and again, it is also found to decrease in organo-aqueous mixtures<sup>161</sup>.

The principal interfering ions are bromide, iodide, hydroxide, thiosulphate and especially cyanide and sulphide.

#### 1.1.6.4.3 LEAD SULPHIDE ELECTRODE

The electrode consists of an unbreakable epoxy plastic body, well suited for use in most of the common solvents. The electrode membrane consists of Lead Sulphide dispersed in an inert matrix of Silver (I) Sulphide ( $Ag_2S/PbS$ ). Because the surface of the electrode membrane passivates with time, the electrode tend to suffer from drift and consequently exhibits poor reproducibility<sup>71</sup>. It is therefore necessary to polish the surface of the membrane from time to time with a plastic abrasive.

The limit of detection of the ion activity in neutral solution is as low as  $10^{-7}$  M, however, special care is necessary for measurement below  $10^{-5}$  M since significant loss of lead ion may occur due to adsorption of sample lead ions on the container.

Presence of oxidants in the sample solution destroys the electrode response.

#### 1.1.6.5 MISCELLANEOUS ELECTRODES

These are ion-selective electrodes which do not exactly fit into the broad classification so far treated, among which are the following:

(a) Enzyme Electrodes - incorporate the enzyme (for substrate analysis) or the substrate (for enzyme analysis) as the active species immobilized in an inert matrix in a thin layer of gel coated on the surface of the sensor. Their advantages and disadvantages have been thoroughly discussed<sup>18f</sup>.

(b) Chalcogenide Glass Electrodes - this type of electrodes has been reported<sup>72</sup> for sensing ferric and cupric ions. Those selective to ferric ions are prepared from the glass of  $\text{Fe}_n\text{Se}_{60}\text{Ge}_{20}\text{Sb}_{12}$ , and those for cupric are made from a  $\text{Cu-As}_2\text{S}_2$  glass containing sinnerite ( $\text{Cu}_6\text{As}_4\text{S}_9$ ) as the active species. Their uses are quite limited because they suffer too many analytical disadvantages.

(c) Surfactant Electrodes - both anionic and cationic surfactant electrodes have been reported<sup>73,74</sup>. In essence they are liquid ion-exchanger electrodes responding to anionic and cationic surfactants. They are useful for detergent analysis.

Other electrodes which have been reported and vividly described are, acetylcholine<sup>75</sup>. Chirality-sensing electrode<sup>76</sup> and ion-sensitive field effect transistors<sup>77</sup>.

#### 1.1.6.6 SELECTRODES "The Universal Ion-Selective Electrodes"

The vast number of ion-selective electrodes available, especially different types by different manufacturers for a given species has its drawback, as this makes the choice of an electrode for a given task increasingly difficult. For instance, about ten different types, four of which are available commercially, have been reported for copper (II) ion<sup>79</sup>. The membranes of all these electrodes are made in different ways and also of different materials, and therefore their vital properties like stability, selectivity and sensitivity differ considerably. As a consequence, in order to get the best type for a particular purpose, a prospective user would be inclined to test all the available types, and this inevitably could be very expensive!

The concept and construction of a multi-purpose electrode (selectrode), the selectivity of which can be varied at will was described by Ruzicka et al <sup>78,79</sup>. According to them, the change of electrode response is achieved by using various electroactive materials, which can either be solid (solid-state selectrode) or liquid (liquid-state selectrode). A number of electroactive materials was discussed for various selectrodes with respect to their sensitivities and characteristic potentials. In addition, a reference selectrode which employs a

humidified solid salt instead of the saturated solution of an electrolyte was also described and discussed.

## 1.2 REFERENCE ELECTRODES

Normally, electrochemical measurements involve two electrodes, but interest is usually directed more towards the indicator electrode; while the other electrode, which usually receives less attention, is the reference electrode. Thus a reference electrode may be defined as the electrode which is not of primary interest in the cell<sup>20a</sup>.

In spite of the rapid progress in the field of potentiometry within the last fifteen years, brought about by a host of different types of ion-selective electrodes, coupled with new electrochemical findings in nonaqueous solvents by their applications, their 'silent partners' (reference electrodes) seemed to be completely overshadowed. This according to Caton<sup>80</sup>, is rather unfortunate and should not be, since investigations, especially in nonaqueous solvent, have revealed that the search for and testing of a suitable reference electrode may occupy a significant portion of the research, if it is not a separate problem in its own right. Thus he pointed out that in any event, the correct choice of a reference electrode for a particular experiment, a firm respect for its function, and some concern for its



maintenance will greatly enhance the reliability of electrochemical measurements.

Different types of reference electrodes are in use, but basically all have three basic features in common: the internal reference element, the reference element electrolyte and the porous plug through which the inner electrolyte is brought into contact with the sample solution (except for the double junction design).

Ideally, a reference electrode should possess the following properties<sup>20a</sup>:

- (1) reversibility - of which the quantitative measure is exchange current: unless a reference electrode has a high exchange current, its potential will depart from its equilibrium value when current demands are made upon it.
- (2) return to its fixed reference potential after accidental polarisation.
- (3) obey Nernst equation for some species in solution without showing concentration - (or temperature) hysteresis.
- (4) have a stable potential

The degree to which these requirements must be obeyed depend on the particular circumstance of the measurements required.

Covington<sup>20a</sup> has given a broadly based classification of reference electrodes and their usage, whereas Caton<sup>80</sup> and Hill<sup>81</sup> have given their own classifications based on aqueous and nonaqueous reference electrodes. However the rest of of the discussion in this section will be centred on those reference electrodes that have been used for this piece of work, except for the Normal hydrogen electrode (NHE) which will be discussed in addition because of its importance. These include: the saturated calomel (SCE); the mercury-mercurous sulphate; silver-silver chloride, both the single and the double junction types and the calomel-lithium chloride reference electrodes.

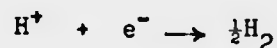
#### 1.2.1 THE REVERSIBLE HYDROGEN ELECTRODE (NHE)

The hydrogen electrode is important for two main reasons<sup>20a</sup>.

(1) It is the electrode whose standard potential is conventionally set at zero at all temperatures in order to tabulate standard potential of the electrodes.

(2) It is considered to be the most reproducible electrode available with bias potential of the order of a few  $\mu\text{V}$  for a freshly prepared electrode.

In essence, the hydrogen electrode consists of a platinum foil, the surface of which is able to catalyse the reaction:



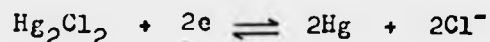
which is not known to occur in the solution phase. Platinum black, the most useful catalyst, is usually deposited from a 1-3% solution of chloroplatinic acid in the presence of a small quantity of lead acetate. Although, the lead acetate is not essential it is desirable as it gives the electrode made in this way a longer life and less susceptibility to poisoning by traces of sulphide and cyanide. Its disadvantage is that, it is not very easy to handle.

#### 1.2.2 MERCURY-MERCUROUS CHLORIDE ELECTRODE (SCE)

Calomel electrode was extensively use up to 1930, when silver-silver chloride began to gain ground. There are three common types of calomel electrodes, which differ essentially in the strength (with respect to KCl) of their reference filling solutions: the saturated (w.r.t. KCl), 1M and 0.1MKCl solutions. However the saturated calomel is the commonest in use.

In its simple form, the electrode is composed of a pool of mercury covered with a layer of mercurous chloride (calomel) and a solution of saturated potassium chloride. A platinum wire fused through the glass wall of the containing vessel touches onto the pool of mercury, serving as the electrical

point of contact for the electrode. The electrode reaction is represented as follow.



Although, the electrode is still used as a reference for widely varied electrochemical measurements, it is most commonly used with glass electrodes and also with the fluoride electrode. It is not very suitable ordinarily, for low level determination of species which are capable of reacting with chloride, such as  $\text{Pb}^{2+}$  or  $\text{Ag}^+$ , because of contamination by its reference filling solution. Also, the electrode shows temperature hysteresis, the reason of which is attributed to the disproportionation of mercurous chloride to mercury and mercuric chloride<sup>81a</sup>.

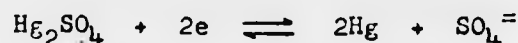


### 1.2.3 MERCURY-MERCUROUS SULPHATE ELECTRODE

This consists of a mercury electrode in contact with a sulphate solution that is saturated with excess mercurous sulphate. The electrode is known for its outstanding reproducibility: its performance favourably compares with the hydrogen electrode<sup>81c</sup>. It is very suitable for chloride determination, since the reference filling solution does not

make use of a chloride-containing electrolyte. Thus for aqueous measurements it is often the electrode of choice for chloride and silver ions.

The electrode half-cell reaction may be represented by:



#### 1.2.4. SILVER-SILVER CHLORIDE ELECTRODE

The silver-silver chloride electrode has been described as the most satisfactory of all reference electrodes in many respects and it is undoubtedly the simplest<sup>96</sup>. The electrode consists of a silver wire or plate coated with silver chloride in contact with a solution of chloride ions saturated with silver chloride. Many ion-selective electrode use this electrode as the internal reference electrode. From the hazard point of view, it does not release toxic chemicals as do mercury-based electrodes, if accidentally broken. The major problem with this electrode however is the relatively high solubility of the silver chloride coating in the strong potassium chloride solution due to the formation of silver chloride complexes (e.g.  $\text{AgCl}_3^{2-}$ ). A second disadvantage is that as the temperature rises, the solubility of the electrode increases: and thus at high temperature a sufficient excess of solid silver chloride must be added to the bridge solution

to maintain saturation, otherwise the electrode will show temperature hysteresis, characterised by potential drift and eventual shortening of the electrodes's life. There has been much discussion about this electrode in the literature, concerning its different methods of preparation. A full discussion of these various methods has been given by Janz<sup>81b</sup>.

1.2.4.1 SILVER-SILVER CHLORIDE (ORION/SINGLE JUNCTION)  
ELECTRODE

This electrode is similar to the conventional silver-silver chloride electrode. The single junction reference electrode (Orion-type) is a sleeve-type silver-silver chloride reference electrode designed for precision measurement. According to Orion<sup>82</sup>, it is suitable for use in pH - and a wide range of ionic species measurements, except for species contained in the filling solution, or species which can react with either the constituents of the reference filling solution. Like the conventional silver-silver chloride electrode, it exhibits very good reproducibility. The silver-silver chloride electrode is contained in an unbreakable plastic, which is resistant to most acids, bases and solvents. The filling solution, usually an equitransferent solution containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions, saturated with  $\text{Ag}^+$  which is normally introduced through a hole on the plastic

body of the electrode.

The electrode reaction can be represented thus:



#### 1.2.4.2 SILVER-SILVER CHLORIDE ELECTRODE (ORION/DOUBLE JUNCTION)

Again this is a silver-silver chloride electrode. It has two concentric chambers, the inner and outer chambers, which are made of plastic walls. The inner chamber comprises the silver-silver chloride reference electrode and the reference filling solution of constitution similar to the single junction, but coloured green in order to enable the analyst to determine its level against the background of the filling solution of the outer compartment. The outer compartment can be filled with any suitable solutions, depending on the system under investigation provided<sup>83</sup>;

(1) the components of the filling solution do not interfere with the electrode response of the ion being measured.

(2) the constituents do not react with potassium, sodium ions, nitrate, chloride or silver which are the constituents of the inner chamber solution.

(3) it has a fairly high ionic strength, and as much as possible the anions and cations of the electrolyte should be equitransferent (e.g.  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$  are): and the filling solution should match the background of the sample as closely as possible.

(4) for samples with extreme pH, ie  $\text{pH} > 10$  or  $\text{pH} < 2$ , the filling solution is adjusted with NaOH or  $\text{HNO}_3$  to match the sample pH.

The development of the double-junction reference electrode is a major breakthrough:

(1) Until recently, neither calomel, conventional silver-silver chloride nor mercury-mercurous sulphate electrodes could be used directly for chloride determination in the presence of sulphate ion, without the cumbersome external agar salt bridge. But now, with the double junction and a suitable choice of the outer chamber electrolyte, this is easily overcome.

(2) Most determinations in organo-aqueous or pure organic media are easily achieved with the double junction which would have been otherwise difficult to achieve.

It is the recommended reference electrode for lead ion determination. Kakabadse et al<sup>84,85</sup> have reported the use of this electrode in organo-aqueous solutions to nearly pure organic media and found it to function very well. By varying the constitution of the outer chamber with respect to the concentration of the electrolyte and the solvent composition, they concluded that it is beneficial to keep the composition of the outer chamber constant for a given series



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of measurement rather than changing it continuously to match the composition of the test solution.

#### 1.2.5 THE CALOMEL-LITHIUM CHLORIDE ELECTRODE

The electrode is especially designed for use as a reference electrode in non-aqueous systems. Essentially, it is a calomel electrode with a salt bridge containing a saturated aqueous solution of lithium chloride. Because its electrode potential deviates from the standard calomel electrode by the order of 50 mV and several hundred millivolt in aqueous and non-aqueous solvents respectively, it is not recommended for accurate pH measurement in aqueous as well as non-aqueous media<sup>10f</sup>.

#### 1.3 LIQUID JUNCTION POTENTIAL

There are three types of cell which are commonly used in work with ion-selective electrodes<sup>18f</sup>:

- (1) Cells without liquid junction, simply designated by:  
Reference electrode | sample | ion-selective electrode
- (2) Cells with one liquid junction, J. designated by:  

$$\underbrace{\text{Reference electrode} \mid \text{bridge solution}}_{\text{Reference electrode assembly}} \mid \text{sample} \mid \text{ion-selective electrode}$$
- (3) Cells with two liquid junctions,  $J_1$  and  $J_2$  designated by:  

$$\underbrace{\text{Reference electrode} \mid \text{reference solution}}_{\text{Reference electrode assembly}} \overset{J_1}{\mid} \underbrace{\text{bridge solution}}_{\text{ion-selective electrode}} \overset{J_2}{\mid} \text{sample}$$

The first type simply uses another ion-selective electrode as a reference electrode and is therefore not associated with any liquid junction potential. In the second and the third types, liquid junction, bridge and reference solutions are usually contained in a single reference assembly, generally referred to as the reference electrode. Thus the reference electrode potential is usually a composite of the actual reference electrode potential ( $E_{\text{ref}}$ ) and that of the associated liquid junction potential ( $E_j$ ), i.e.<sup>18f</sup>

$$E_{\text{Ref}} = E_{\text{Ref}} + E_j$$

where  $E_{\text{Ref}}$  is the composite electrode potential of the reference assembly.

In almost all measurements where an electrode of this type can be made functional as a reference,  $E_{\text{ref}}$  can be assumed constant (indeed it should be constant for a suitable choice of parameter by the designer) whereas  $E_j$  is more temperamental and more often than not constitutes the source of error in ion-selective electrode measurements. This error can be minimized but cannot be totally eliminated unless cells without liquid junction are used.

The origin of the liquid junction potential is attributable to the diffusion of ions from two electrolyte solutions separated by a junction (porous junction).

Different ions have different mobilities and will diffuse at different rates; consequently a charge separation will occur, the extent of which depends on anion and cation type and their differences in mobilities.

In practice, the situation is simpler than this for reference electrodes, in that the bridge solution usually gives a slightly higher pressure than the sample solution by maintaining a liquid head (hydrostatic pressure), and in addition the reference solution is maintained at a higher ionic strength than the sample with the result that the solution in the reference electrode flows out relatively faster into the sample thereby impeding the back-diffusion, of the sample into the salt bridge and also the variations of the sample composition in the salt bridge is assumed swamped<sup>18f</sup>.

The parameters affecting the liquid junction potential were discussed by Bailey<sup>18f</sup>. The most important ones are the junction structure, the mobilities of ions involved, the constitution of the bridge solution, suspension and colloidal effects.

Some other workers have pointed out that deviations from the Nernst equation can sometimes be due to the presence of liquid junction potential<sup>20b</sup>. For example the potential of Lanthanum fluoride - saturated calomel couple could obey a Nernst equation of the form:

$$E = E^0 - \frac{2.303RT}{F} \log a_F^- + E_j \dots\dots\dots (1.17)$$

in which case if at all other factors favour a linear plot for  $E$  versus  $\log a_F^-$ , departure from linearity will be obtained because of the non-constancy of  $E_j$ .

Strange though it is, the liquid junction is, however, the most important variable which the analyst has under control, and therefore from the practical point of view, the following points should be considered in choosing the filling solution of the reference electrode<sup>87</sup>.

(1) The bridge solution (reference solution usually) should be at least ten times stronger with respect to ionic strength than the maximum ionic strength expected for the sample or the strongest of the standardizing solution.

(2) As much as possible, the filling solution should be equitransferent with respect to the anions and the cations i.e., the electrolyte chosen should satisfy the condition:

$$Z_+ C_+ \Lambda_+ = Z_- C_- \Lambda_-, \text{ where}$$

$Z$  = ionic charge,  $C$ , being the concentration in mole/litre and  $\Lambda$  is the equivalent conductance.

(3) The ionic constituents of the filling solution

should not react with the species of the sample.

(4) It should be borne in mind that, heavy precipitation usually resulting from potentiometric precipitation titration or otherwise is undesirable, since this may temporarily clog the junction outlet. Also formation of stable reaction product between the diffusate and some other species in the solution may offset the equitransferent condition.

(5) Ions in the filling solutions which are common to the determinand or which are able to interfere with the determinand should be avoided or used, if at all, with caution, since serious error may be introduced at low level concentration measurement of the determinand.

The liquid junction potential for several salts were calculated by Orion<sup>87</sup> using Henderson equation:

$$E_j = \frac{2.3RT}{F} \frac{\sum (\Lambda_i / z_i) (C_S - C_R)}{\Lambda_1 (C_S - C_R)} \log \frac{\sum C_S \Lambda_1}{C_R \Lambda_1}$$

where  $C_R$  and  $C_S$  are the concentrations of the  $i$ th ion in the reference and the sample solutions, respectively. For two solutions of two different electrolytes (partitioned by a junction) which are equally dissociated and having one of their ions in common, the associated liquid junction potential is given by the modified Planck equation<sup>88</sup>.

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$$E = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}$$

#### 1.4 SOLVENTS

##### 1.4.1 CLASSIFICATION

Different classifications of solvents are possible. However, a classification is only helpful when it serves to focus attention on the similarities and differences in the light of the objective in mind. And thus for our purpose here, it is convenient to classify solvents into two broad groups based on their dielectric constants. The dielectric constant of a solvent may be defined as a numerical measure of the ability of a solvent to dissociate an electrolyte put into it. There are therefore solvents of high dielectric constant, otherwise referred to as polar solvents, and those of low dielectric constant. In the former ion-pairing is minimal, whereas in the latter ion-pairing could be significant. Although it may not seem very reasonable to draw a sharp line between high and low, it is a common practice to consider solvents with dielectric constant ( $\epsilon_r$ )  $> 30$  as high, and those with ( $\epsilon_r$ )  $< 30$  as low<sup>89</sup>. Thus methanol with  $\epsilon_r$  value of 32.70 is classified under high and ethanol with  $\epsilon_r$  of 24.55 is classified under low.



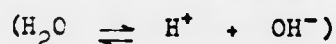
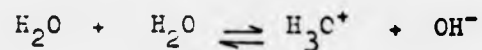
Each of the two groups can be further subdivided according to whether the solvents are hydrogen-bonded or not. Solvents which can donate or gain proton are therefore termed 'protic solvent' and those which cannot, donate, but may be able to accept are termed 'aprotic solvents'. Below is a table showing the classification for some common solvents<sup>85</sup>.

Table 1

High Dielectric Constant		Low Dielectric Constant	
Hydrogen bonded	Non-hydrogen bonded	Hydrogen bonded	Non-hydrogen bonded
Water	Acetonitrile	Ethanol	Acetic anhydride
Deuterium oxide	Dimethyl-acetamide	n-propanol	Acetone
Hydrogen peroxide	Nitrobenzene	1-propanol	Carbon tetrachloride
Methanol	Propylene-carbonate	tert-butanol	Cyclohexane
Ethanolamine		Acetic acid	diethylether
Ethylene glycol		Ammonia	n-hexane
Formic acid			Dioxan

Each subclass above can be further subdivided according to whether they have basic or acidic tendencies; for instance, both dimethylsulphoxide and ethanolamine are protophilic or

basic, whereas formic acid is acidic. Some solvents, however, exhibit both acidic as well as basic properties depending on the medium into which they are put - these are called amphiprotic solvents, of which a typical example is water. Such solvents are characterised by their ability to undergo self-ionisation or autoprotolysis: e.g. for  $\text{H}_2\text{O}$ .



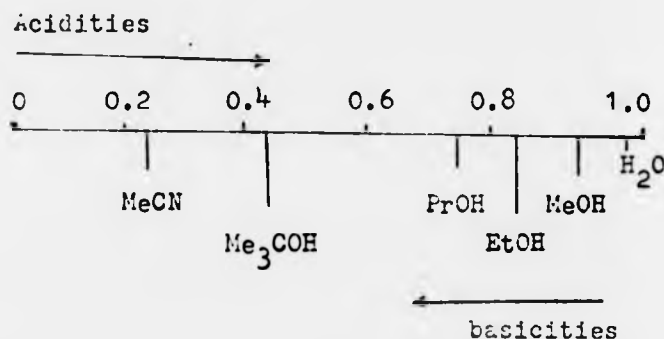
Symon<sup>90</sup> has given a very useful functionality classification of solvents based on the acidic proton available for donation or participation in hydrogen bonding and basic centres of lone pair electron available for bond participation. A logical inference which follows from his classification is that almost all solvents, if not all, can be associated with an expression of the form:  $n\text{A} + m\text{B}$ , where  $n$  and  $m$  take integral values and satisfying the condition  $n > 0$  and  $m \geq 0$  for protic solvents, and  $n = 0 \leq m$  for aprotic solvents.

where A = acidic proton

B = basic centre (lone-pair of electrons)

For example,  $\text{HCF}_3$ ,  $\text{ROH}$ ,  $\text{R}_3\text{N}$ ,  $\text{CCl}_4$  can be associated with  $1\text{A}$ ,  $1\text{A} + 2\text{B}$ ,  $1\text{B}$ ,  $0\text{A} + 0\text{B}$  respectively.

A simple scale constructed by Symons, of which the numerical values of the associated scale are attributed to Taft et al<sup>91</sup> is shown below.



Thus on this scale we see the relative acidities of some solvents, with their relative basicities in the reverse order.

The classification scheme by Symons can be easily correlated with the earlier one developed in the following way:

- (1) Solvents of  $nA(m = 0)$  type where  $n > 0$  contain 'available' proton and therefore may function as acid or base. However, there can be no intra - or intermolecular hydrogen bond in their pure solvents, but they may be involved in hydrogen bonding in the presence of a solute (solvent or electrolyte).
- (2) Solvent or  $mB (n = 0)$  type  $m \geq 0$  there is no available hydrogen for hydrogen bonding participation

and they are therefore basic; they can however, participate in intermolecular hydrogen bond formation in appropriate solvent mixtures.

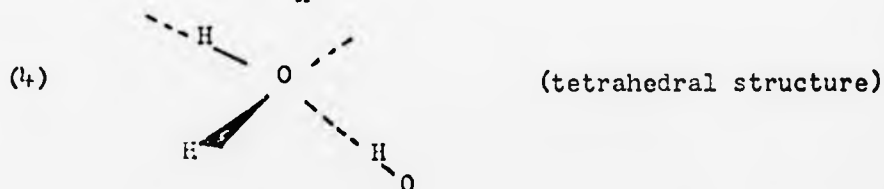
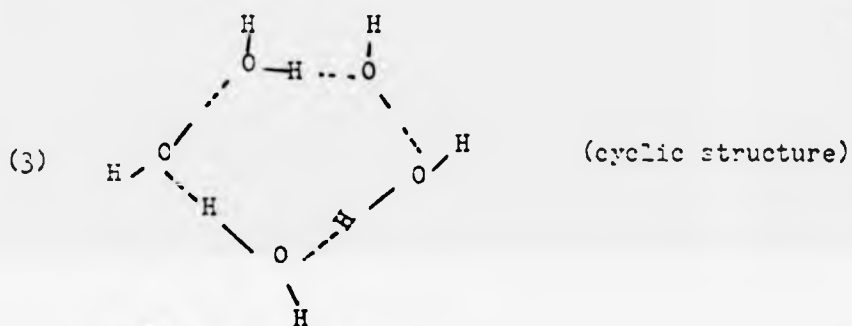
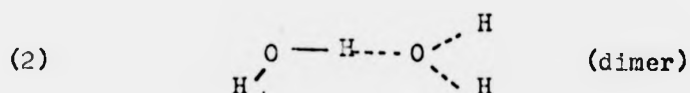
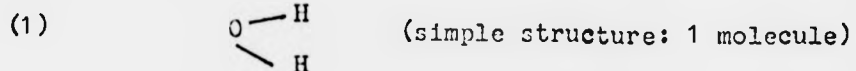
(3) Solvent of the  $nA + mB$  type where  $n, m > 0$ , these are capable of intermolecular and sometimes intramolecular hydrogen bond formation.

(4) Solvents for which  $n, m = 0$  are non-basic and non-hydrogen bonded neither in their pure solvents nor in mixed solvents.

#### 1.1.1.1 WATER

Water is undoubtedly by far the most abundant of all the solvents. It is a universal solvent with a widely varied usage. Chemically, it is a universal reference medium for almost all chemical systems.

Water is unique in several respects. One of such ways in which it is unique is in its structure. Whereas the liquid structure of some common protic solvent, e.g. alcohols, amines are known to be polymeric chains, that of water is three-dimensional<sup>92</sup>. Several structures have been advanced for water, some of which are:



According to Symons these structures ( and many more that are not drawn), should be considered as having very short life-times and are continuously interchanging. The solvation of ionic species by water is well known. On the simple empirical scheme mentioned earlier, water has a  $2A + 2B$  function, that is 2 acidic as well as 2 basic functions. Thus solvation of cation occur through coordination with the basic function in water whereas solvation of anions is achieved through

hydrogen bonding. In a mixed solvent system, of which the commonest type is organo-aqueous, there is always a tendency for preferential solvation<sup>93,94</sup> by one of the component (usually water) when a solute is added. For a general case in protic-aprotic mixtures, anion are expected to be preferentially solvated by the protic molecule, especially if they are basic. However, other factors, such as the relative proportion of the components may complicate the simple expectation.

#### 1.4.1.2 METHANOL

Methanol is obtained commercially in reasonable purity for most purposes, the principal impurity being water of the order of 0.05% which tends to increase in amount with handling. Water may be removed from it by distillation or the use of molecular sieves<sup>95</sup>. Methanol is one of the earliest used in physicochemical studies. Because of its similarities to water, it has been and still is being widely used both as pure as well as water-methanol medium for many chemical investigations.

With reference to the simple empirical expression developed in section 1.4, methanol can be associated with  $1A + 2B$ , that is, one acid function and two basic functions.

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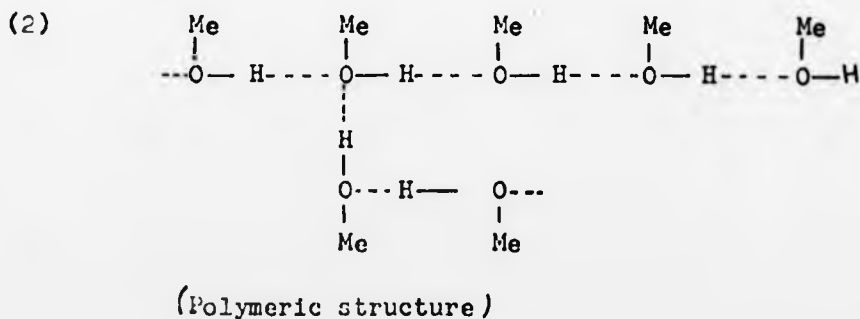
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With reference to the simple empirical expression developed in section 1.4, methanol can be associated with  $1A + 2B$ , that is, one acid function and two basic functions.

Thus when compared with water which is  $2A + 2B$ , it has a net  $1B$  function which therefore makes it more basic than water. Also it was suggested<sup>96</sup> that the inductive effect of the methyl group of methanol makes its more basic than water.

Spectroscopic evidence is available for the existence of intermolecular hydrogen bonding within the molecules of the pure solvent<sup>90</sup>. Thus the structures below have been advanced for the dimer and the polymeric molecules.



Like in water, ions are solvated in methanol, the cations coordinate to the basic function (lone pair of electron) and the anions form hydrogen bonds to acidic proton function.



#### 1.4.2 SOLVENT EFFECT

##### 1.4.2.1 MEMBRANE SOLUBILITY

The effect of solvent on membrane solubility is very important in inorganic salt-based electrodes. This is understandable, since this type of electrodes have membranes with finite solubilities in the media in which they are used, and therefore their ions resulting therefrom constitute the minimum background (for pure solvent) concentration, below which ordinarily, reasonable measurement cannot be made, for a given situation.

It is a well made known fact that inorganic salts are generally less soluble in organic solvents than in water. It follows that the solubility of these inorganic-based electrodes are expected to decrease from aqueous to organo-aqueous solvent mixtures, and even further in pure organic solvents.

Several workers<sup>97-99</sup> have measured solubility products of silver halides in various organo-aqueous solvent mixtures. Some of their results are shown in tables 2 and 3.

Table 2

Solubility Product of AgCl in Solvent Mixtures

Wt% non-aqueous Component	Dielectric Constant	- log $a_{H_2O}$	- log $K_s$
A. Methanol-Water Mixtures			
0.00	78.54	0.000	9.75
9.47	74.36	0.050	10.03
19.84	69.28	0.111	10.27
34.48	62.19	0.272	10.47
42.10	58.61	0.272	10.87
54.20	52.88	0.382	11.38
B. Acetone-Water Mixtures			
9.64	73.28	0.050	10.10
19.80	67.73	0.108	10.29
34.43	59.17	0.206	10.92
42.08	54.41	0.266	10.99
54.15	46.87	0.386	12.13
C. Dioxane-Water Mixture			
8.20	71.28	0.035	10.11
20.47	60.37	0.093	10.30
28.49	53.24	0.137	10.61
40.75	42.33	0.215	11.02
48.75	35.25	0.276	11.77
60.73	25.24	0.390	12.36

Table 3

Solubility of Silver Halide Salts in Aqueous-Alcohol Mixtures

Solvent	Ratio of Solvents (V/V%)	Mole fraction of solvents	Negative log of Solubility Product		
			AgI	AgBr	AgCl
H <sub>2</sub> O	100	0	15.96	12.36	9.82
MeOH	10	0.047	16.12	12.48	10.10
	40	0.228	16.48	13.00	10.40
	60	0.400	16.72	13.38	10.74
	90	0.802	17.42	14.40	11.50
	100	1.00	17.84	14.91	12.69
EtOH	10	0.032	16.16	12.54	10.20
	40	0.162	16.40	12.90	10.58
	60	0.298	16.60	13.26	10.82
	90	0.677	17.30	14.30	10.32
	100	1.00	18.96	-	13.77
n-PrOH	10	0.026	16.20	12.50	9.90
	20	0.056	16.24	12.66	9.92
	30	0.092	16.32	12.74	9.92
	40	0.137	16.40	12.82	10.00
1-PrOH	10	0.026	16.04	12.30	9.98
	20	0.056	16.12	12.48	10.16
	30	0.092	16.20	12.64	10.20
	40	0.137	16.28	12.78	10.28

From the two tables above, it can be seen that the solubility of silver halides decreases with increase in organic component in the various organo-aqueous mixtures, except for the slightly irregular results for silver chloride in ethanol in table 3.

#### 1.4.2.2 IONIC ACTIVITY AND ACTIVITY COEFFICIENT

A number of workers<sup>100-102</sup> have determined the mean molal activity coefficients in pure alcohols for various alkali metal halides. Akerlof<sup>96</sup>, using the Debye - Huckel activity function calculated the activity coefficients of alkali halides in various aqueous-alcohol solvent mixtures. From his data it can be seen that the activity coefficient for a given concentration of alkali halide decreases with increasing alcohol concentration. Furthermore it was observed that at infinite dilution, the logarithm of activity coefficient is directly proportional to the mole fraction of alcohol in the solvent mixture and also the logarithm of activity coefficient bears an inverse relation with the dielectric constant of the solvent mixture.

Tables 4-6 show the variation of mean molar activity coefficient for alkali halides in methanol, ethanol and methanol-water mixtures.

Table 4

Mean Molal activity coefficient  
of NaCl in Methanol

m/mole 1 Kg <sup>-1</sup>	$\gamma_{\pm}$
0.0001	0.943
0.0005	0.890
0.001	0.856
0.005	0.705
0.01	0.615
0.05	0.408
0.10	0.367

Table 5

Mean Molar Activity Coefficient for  
Alkali Metal Halides in Ethanol

m/mol Kg <sup>-1</sup>	NaBr	NaI
0.01	0.609	0.552
0.02	0.519	0.482
0.04	0.411	0.433
0.06	0.359	0.419
0.08	0.333	0.403

Table 6

Mean Molal Activity Coefficient of  
NaCl in MeOH-H<sub>2</sub>O Mixture

Wt% MeOH	NaCl		
	0.02 m	0.05 m	0.2 m
10	0.852	0.795	0.699
20	0.827	0.763	0.664
30	0.804	0.832	0.630
40	0.773	0.696	0.591
50	0.735	0.655	0.545
60	0.678	0.599	0.486
70	0.645	0.522	0.443
80	0.563	0.479	0.362
90	0.493	0.401	0.298

In the first two tables, the variation of activity coefficient (i.e decreasing with increasing concentration of electrolyte) can be seen in pure alcohol, while Table 6 shows the decreasing mean molal activity coefficient with increasing alcohol concentration in aqueous-alcohol mixtures.

#### 1.4.2.3 ELECTROLYTES

Most ions are known to be solvated in solutions, the degree of solvation depending on ion-type and medium<sup>190</sup>. Basic aprotic solvents are known to interact mainly with cations, and only exhibit feeble dipolar interaction with anions. Cations generally have solvation number between six and four depending on size of the ions involved. Protic solvents are, however, capable of solvating cations, using their ion-pair of electron for bonding, as well as anions with which they usually have hydrogen bond formation tendencies, and are thus good anion and good cation solvators. Hence, they have greater ability of dissolving electrolytes

A more complicated situation may arise in a mixed solvent system<sup>93,94</sup>. For instance, an added electrolyte may well be preferentially solvated by one component. Thus in protic-aprotic mixtures anions will be expected to be solvated by the protic solvent molecules in preference to the aprotic solvent molecules, especially if the former is basic.

Another common phenomenon of interaction between electrolytes and solvent is that of ion-pairs. Even in dilute solutions, numerous types of ion-pair can be envisaged<sup>103</sup>. Symon, in discussing ion-pair commented that if two ions are drawn together to give a solvent shared ion-pair, there is a strong tendency for anion to displace one of the solvent molecules to give a contact ion-pair, in which the anions becomes a part of the coordination shell of the cations, whereas for protic solvents, the solvent-shared ions are said to form extremely stable units since both ions reinforce the bonding to the shared solvent molecule, and hence ion-contact pairs are less probable, even for solvent mixtures, unless the protic solvent component is low.

Mayer<sup>104</sup>, in a well discussed article has shown that unlike in the aqueous counterpart, the association behaviour of many ionophores (electrolytes which form ionic lattices in the solid state) in nonaqueous solvents cannot be usually rationalized by a purely electrostatic model, and that a satisfactory interpretation is possible on the basis of a chemical coordination consideration which takes into account the specific nucleophilic and electrophilic properties of the solvents. The latter are characterized by such empirical parameters as "Acceptor Number" (AN), "Donor Number" (DN) or related parameters. In addition, differences in,

stabilization of ions by Born solvation must be taken into account in solvents with different dielectric constants. According to Mayer purely electrostatic models may however be successfully applied only in the case when the ions are either coordinately saturated, such as tetralkylammonium ion, or exhibit only poorly developed donor or acceptor properties, such as perchlorate ions or the high alkali metal ions. The results of his finding support the view that coordinative interactions are frequently involved in the formation of contact ion-pair which may be logically considered as unionized entities.

As it has been pointed out (in section 1.4.1), the behaviour of an electrolyte is affected by the dielectric constant of a medium. Below is a table showing the variation of dielectric constants with solvent composition for some organo-aqueous systems<sup>103</sup>.

Table 7

Wt% Organic Solvent	Dielectric Constant		
	Methanol	Ethanol	Dioxan
0	78.3	78.30	78.30
10	74.16	72.80	-
20	69.95	66.90	63.5
30	-	-	-
40	60.90	55.02	44.4
50	56.30	-	-
60	51.61	43.40	27.5
70	-	-	-
80	42.58	32.84	12.1
90	37.92	-	-
100	32.70	24.55	2.209



#### 1.4.2.4 LIQUID JUNCTION POTENTIAL

In non-aqueous solvents, the liquid junction potential ( $E_j$ ) between electrolyte solutions in different solvents can constitute an enormous problem worthy of attention. Many people have reported about this problem recently<sup>106-111</sup>.

Investigations carried out in this department have shown that the liquid junction potential between electrolyte solutions in different aqueous-alcohol mixtures increases with increasing alcohol concentration if other parameters are kept constant: Kakabadse and Khayat<sup>84</sup> measured the resistances in solutions of a series of constant alkali halide concentrations, but, varying methanol concentration with the aid of a conductivity bridge, and thus, in each case, evaluated the diffusion potential ( $E_d$ ), a quantity which though not identical with, is related to  $E_j$ <sup>84</sup>. In another investigation<sup>112</sup> a cell was used comprising two Orion double-junction reference electrodes, the two being identical with respect to electrolytes constitution but differing in the sense that one had an aqueous outer filling solution, whereas the other has the outer compartment filled with organo-aqueous solution. According to them there was hardly any effect except when the inner filling solution was modified. Table 8 shows the variation of  $E_d$  with methanol concentrations.

Table 8

Measured Resistance in Solutions of  $10^{-3}$  M  
NaCl and varying Methanol Concentrations in  
Methanol-Water Mixtures

Vol % MeOH	R/ohm (X 10 )	Ed/mV
0	0.2745	-1.38
20	0.389	7.54
40	0.474	12.54
60	0.535	15.71
80	0.512	14.59

Izutsu et al<sup>108</sup> have studied the liquid-junction potential between electrolyte solutions in different solvents. Their method involved keeping the concentration of the electrolyte on one side of a junction much larger than that on the other side in order to ensure that  $E_j$  was essentially determined by the more concentrated electrolyte solution. According to them the liquid junction potential can be expressed by the sum of three contributory factors:  $E_{j,ion} (cons)(I).$ ,  $E_{j,ion} (ion-solv)(II)$  and  $E_{j,sov} III$ , of which I and II are contributions from ionic species: I, being the concentration, which can be evaluated from the Henderson equation and II is the term due to the difference in ionic solvations in water and organic solvents; and III

is the contribution from the transfer of solvent molecules. Furthermore, the change of  $\Delta G$  with the anion  $X^-$ , say, is said to be linearly related to the free energy of transfer of  $X^-$  from water to organic solvent.

Cox et al.<sup>109,110</sup> investigated the factors influencing the liquid junction potential, and showed that a good correlation exists between the free energy of transfer of solvent across the junction and the solvent component of the liquid junction potential.

#### 1.4.2.5 DIRECT POTENTIOMETRY

Studies of electrochemical systems in aqueous solution have been extensively pursued, and a considerable amount of data has been documented. But water is one of many solvents: a vast number of nonaqueous; nonaqueous-nonaqueous and aqueous-nonaqueous solvent mixtures exist, each of which is open to a range of measurements, probably, comparable in extent with the range of potentiometric measurements in aqueous solutions. The most serious limitation of electrochemical studies of nonaqueous solutions is the comparatively small range of solutes available<sup>81</sup>, since most nonaqueous solvents have dielectric constants appreciably lower than that of water and consequently show a markedly lower capacity to dissolve inorganic electrolyte.

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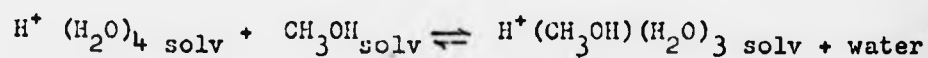
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There have been numerous accounts of potentiometric titration<sup>49</sup>, measurements of variation of standard emf values<sup>136</sup>, free energy of transfer of solute from one solvent to another<sup>114</sup>, the effect of changing dielectric constant and solvation energy on acidity of electrolytic dissociation in nonaqueous media<sup>81</sup>. The following review will only concern material which is directly relevant or which will serve to some extent to highlight the objective in view under the discussions in this thesis. Thus as much as possible, each electrode that has been used by the author will be considered one by one, in order to present a concise and still fairly thorough coverage of the previous work.

The effect of solvent on potentials of ion-selective electrode is well documented.<sup>113-123,170</sup> Wells,<sup>114</sup> in his studies of the free energy of transfer  $\Delta G_t^\circ(\text{H}^+)$  of the solvated proton from water to methanol + water proposed that this quantity ( $\Delta G_t^\circ(\text{H}^+)$ ) could be considered as a sum of two processes: the transfer of a tetrahedral aquo-proton from water onto the mixture, followed by the subsequent replacement of a water molecule in the tetrahedron by a methanol molecule as shown by the chemical equation below:



Furthermore, a plot of  $-\Delta G_t^\circ$  and hence  $\Delta E_t^\circ$ , the transfer potential, as a function of Wt% methanol in the range of (0-50) Wt% methanol using a constant concentration of hydrogen ion give a curve of systematic increase with increasing methanol concentration. In another study<sup>115</sup> of ionic solvation in water + cosolvent and the free energies of transfer of single ion from water into mixtures of water-acetone, -propanol and -methanol, Wells attributed the differences in free energies of transfer to solvent structure and ionic solvation. When investigating the influence of the solvent on the rates of  $S_N1$  - type solvolysis for metal complexes in water + co-solvent mixtures, he determined the free energies of transfer of halide ions from water into aquo-organic mixtures for ethanol-, dioxan-, methanol-, acetone-, and isopropanol-water<sup>124</sup>.

Selig and Salomon<sup>116</sup> recommended the use of ethanol or methanol in preference to dioxan for the potentiometric determination of sulphate ion with lead-selective electrode in order to avoid the problem associated with dioxan, which has a tendency to form peroxides poisonous to the lead electrode. Hansen and Ruzicka<sup>125</sup> described a lead (II) selectrode activated with lead sulphide / silver sulphide, which according to them exhibits a near - Nernstian response within

lead levels close to the theoretical limit imposed by the solubility product of lead sulphide. This electrode, they claimed afforded the EDTA titration of lead (II), as well as titration of  $\text{SO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  by lead nitrate. Stelting and Manahan<sup>117</sup> in their studies of allyl alcohol complexes of silver (I) using Orion silver sulphide and silver wire as indicator electrodes, fluoride and perchlorate ion-selective electrodes as reference electrodes, asserted that solvent effects at these electrodes were greater than liquid junction potential effect at a conventional calomel reference electrode. Furthermore, it was pointed out that solvent effect and liquid junction potential cannot be vigorously separated from each other.

Adhikari et al.<sup>118</sup> through a study of the free energy of transfer of electrolyte from water to aqueous methanol, associated with the membrane potential generated across a clay of resin from an aqueous-methanol solution of HCl obtained a result which deviated from those of the previous workers. Such a deviation, they argued, can be attributed to the differences in surface - solvent interaction at the membrane interface at various solvent composition. The free energy of transfer as a measure of cation and anion solvating

power of solvents was demonstrated by Parka et al<sup>119</sup>. Szczepaniak and coworkers<sup>126</sup> prepared a lead-selective membrane electrode containing lead diethyl dithiocarbamate chelate and reported on its suitability for Pb (II) with the concentration range of  $10^{-6}$  -  $10^{-2}$  M at pH 4.5 - 6. According to them, the electrode was used to determine the end point of  $\text{PO}_4^{3-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$  and  $\text{CrO}_4^{2-}$  in aqueous and and water-dioxan solution with lead nitrate standard solution.

Tanikawa et al<sup>120</sup> have reported that the sensitivity of a fluoride-selective electrode is improved by addition of methanol, ethanol, acetone or dioxan to aqueous fluoride containing sodium citrate, especially in 20 Vol % dioxan. And that the Nernstian relation holds for the fluoride concentration range greater than  $2 \times 10^{-6}$  M which according to them is an order of magnitude better than detection limit in aqueous solutions.

Parulekar and Mattoo<sup>127</sup>, though not studying the effect of solvent on potential, illustrated a rapid and reasonably precise graphical method of assaying ternary mixture of solvents of ethanol, methanol and water by the use of Zeiss dipping refractometry and measurement of relative density, and showed an evidence for the presence of hydrates of the alcohol in methanol-water and ethanol-water, which according to them were in agreement with those



of electrochemical measurement<sup>128,129</sup>.

Wells<sup>130</sup>, in a study of free energies of transfer of single ion from water into water + dioxan mixtures has shown that all the values for  $\Delta G_t^\circ(M^+)$  and  $\Delta G_t^\circ(M^{2+})$  are negative in water-rich conditions, and values for  $\Delta G_t^\circ(X^-)$  for most  $X^-$  are positive increasing with increasing dioxan concentration. Abraham et al.<sup>121</sup> from their study of free energies, entropies of transfer of ion from water to methanol, ethanol and n-propanol indicated that the free energies of simple cations and anions increase along the series,  $MeOH < EtOH < 1-ProH$ .

A study of solubility product<sup>131</sup> and complexation of silver halides and free energies of transfer of  $Ag^+$ ,  $Cl^-$  <sub>B<sub>r</sub></sub> - from water to a number of organic solvents has shown that  $Ag^+$  is generally more stable in aprotic solvents than in water while the reverse is true for  $Cl^-$ . From the formation constants and solubility product<sup>132</sup> study for silver halides in water-acetone mixtures Salmon showed that  $AgX_2^-$  and  $AgX_3^{2-}$  are the predominant species but the latter decreases rapidly with increasing water content.

Tables 9 and 10 below show weight percent acetone as a function of solubility product and the free energy of transfer for single ions from water to acetone, respectively, as obtained by Salomon<sup>131</sup>.

Table 9

Wt% acetone	0	9.6	19.8	42.1	54.2	80.0	91.2	98.5	100.0
$-\log K_{So}$	9.8	10.1	10.3	11.0	12.1	13.4	15.2	19.9	21.2

Table 10

Ion	$G_t^0(\text{ion}) \text{ Kcal mole}^{-1}$		
	a	b	c
$H^+$	-4.9	-4.9	-2.5
$Ag^+$	(-1.8)	3.3	5.7
Cl	17.5	12.3	9.9

Ben - Naim<sup>133</sup> discussed the standard free energy of transfer of a solute A between two solvents at both thermodynamic and statistical mechanical levels. Whereas thermodynamics alone cannot be used as the best standard quantity, statistical mechanics can. According to him, the standard free energy of transferring A, computed by the

number density (or molarity) is the simplest and least ambiguous quantity and also it is the quantity that directly probes the difference in solvation properties of two solvents with respect to the solute A.

The free energies of transfer of alkali metal fluoride from water to methanol + water were studied by Covington and Thain<sup>134</sup> and they reported that their results were in good agreement with the existing data. According to them, evaluation of free energy of transfer may be made either from emf measurement or by solubility methods, but the former is the more satisfactory. In the Tables 11 and 12 below values of  $\Delta E(t)/mV$  and  $\Delta G(t) / KJm^{-1}$  are given for sodium chloride and sodium fluoride from water to water + methanol<sup>134</sup>.

Table 11

Mole fraction MeOH	NaCl	
	$\Delta E(t)/mV$	$\Delta G(t)/KJm^{-1}$
0	0	0
0.197	47.9	4.72
0.401	89.1	8.82
0.590	125.0	12.29
0.800	155.2	15.2
1.00	178.8	18.0

Table 12

Mole fraction MeOH	$\Delta E(t)$	$\overset{\text{NaF}}{\Delta G(t)}/\text{KJm}^{-1}$
0	0	0
0.305	88.1	8.66
0.478	134.0	13.21
0.603	157.7	15.59
0.651	166.0	16.43
0.900	199.0	19.82
1.00	184.0	18.5

Feakins and Voice<sup>135</sup> measured the standard molar free energies of transfer,  $\Delta G_{(t)}^{\circ}$  of alkali metal-metal chloride MCl from water to 10-99% (w/w) methanol-water mixtures. The  $\Delta G_{(t)}^{\circ}$  behaviour for the associated cations were explained in terms of the acid-base theory of ionic solvation.

Table 13<sup>135</sup> show  $\Delta G$  and  $\Delta E$ , related to standard state for sodium chloride from water to water-methanol mixtures,  $m$  being the molarity.

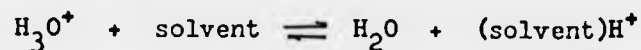
Table 13

Wt% MeOH	$\Delta E/mV$			$\Delta E$	$\Delta G_{(t)}^{\circ}$	$\Delta G_{(t)}^{\circ*}$
	0.20m	0.10m	0.04m			
0	0	0	0	0	0	0
10	16.76	17.06	17.36	18.06	437	428
20	3.64	34.46	35.07	36.57	883	867
30	50.46	-	52.57	55.00	1328	-
40	67.86	69.00	70.25	73.94	1784	1787
50	85.72	-	89.83	94.76	2291	-
60	104.64	106.58	108.65	115.21	2790	2830
70	-	-	-	-	-	-
80	146.50	149.18	152.53	163.38	4600	3910
90	167.03	171.18	174.70	189.1	4914	4830
95	177.32	181.10	185.83	201.8	5140	-
99	184.11	187.63	192.94	210.9	(5200)	-

\* From Akerlof's<sup>96</sup> results.

An extensive study of the solvent effect on standard electrode potential of silver-silver halide electrodes in methanol-water mixtures was made by Elsemongy<sup>136</sup>. The variation of standard potential with solvent composition as well as temperature was shown. According to him, the curves obtained from a plot of standard potential as a function of weight percent methanol showed a marked change in slope in the regions of higher methanol content, which according to Harned and Owen<sup>137</sup> is due to decreasing water content of the

mixture leading to the replacement of hydroxonium ion ( $\text{H}_3\text{O}^+$ ) by  $(\text{solvent})\text{H}^+$  molecule according to the reaction :



He proceeded that an evidence of the structural changes occurring in the solution as the percentage of methanol increases can be obtained from the thermodynamic functions of the cell. Thus effects can arise from the solvent properties and (or) from the solvation properties of the ions in different solvent mixture. It was shown that the free energy change increases positively with increasing methanol content in the mixture, i.e. with decreasing dielectric constant. This is expected, because as the dielectric constant decreases, more work is required to keep the ions apart and therefore less work is produced by the electrode reaction and more positive free energy changes result.

Abraham et al<sup>138</sup> measured the standard free energy of transfer of solute from methanol to other solvent on the mole fraction scale.

Table 14

Solute	$\text{H}_2\text{O}$	MeOH	EtOH	$\text{Pr}^n\text{OH}$	$\text{Pr}^i\text{OH}$
$\text{Et}_4\text{NCl}$	-1.8	0	1.6	1.9	2.6

The table 15<sup>163</sup> below gives a data of free energies of transfer from methanol to other solvents of the dissociated species ( $\text{Et}_4\text{N}^+ + \text{I}^-$ ) in  $\text{Kcal mol}^{-1}$  at  $293^\circ \text{K}$ .

Table 15

Solvent	$\Delta G^\circ$		
	$\text{Et}_4\text{N}^+ + \text{I}^-$	$\text{Et}_4\text{N}^+ + \text{Br}^-$	$\text{Et}_4\text{N}^+ + \text{Cl}^-$
Water	-1.8	-2.5	-4.2
Methanol	0	0	0
Ethanol	2.5	3.0	3.5
n-propanol	3.7	4.2	4.7
i-propanol	5.0	5.6	6.2
acetone	3.5	6.6	9.5

Rechnitz and Kenny<sup>140</sup> evaluated a lead electrode for performance in aqueous, non-aqueous and biological media, using a differential measuring technique to eliminate the aqueous-nonaqueous liquid junction. Linear plots of lead in pure, 20% and 50% methanol within about  $10^{-6}$ - $10^{-2}$   $\text{MPb}^{2+}$ , although there was no reference to the slope of the resulting graph, it was clear from their plots, that the slope increases with increasing methanol composition.

A considerable amount of investigations on the effect of solvent on potential has been carried out in this department. Thus Kakabadse et al.<sup>53,84,85,112,141</sup> have shown in

their study of aqueous-alcohol binary mixture that for a given concentration of indicator ion  $X$  ( $X = Ag^-, H^+, F^-, Cl^-, Br^-, I^-, OH^-$  and  $S^{2-}$ ) the systematic change of electrode potential with variation in alcohol (MeOH, EtOH, n-PrOH, i-PrOH and t-BuOH) concentration affords a new graphical method for the estimation of these alcohols in alcohol-water mixtures. Furthermore in the  $H^+/ROH$  system containing 99-99.9% m/m trace water can be determined accurately due to a potential anomaly. Also, application of electrochemical techniques to organic reactions, and extension of the lower limit of detection of an electrode as an aid to trace analysis have been vigorously pursued.

The Russian workers<sup>142,143</sup> have reported the behaviour of a fluoride-selective membrane electrode in organo-aqueous media. In one of their studies, it was pointed out that the solubility of lanthanum fluoride decreases with an increase in the concentration of organic component, and that the most suitable properties of the electrodes are obtained in solvent containing 80% acetone or dioxan. In another by Cava et al<sup>142</sup>, it was reported that the direct potentiometric determination of fluoride ion is possible in mixtures containing up to 90% methanol, 60% ethanol and acetone 30% n-propanol and only 10% Vol. dioxan.



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Below is a summary (Table 16) of the electrode slopes in mV per decade concentration of fluoride ion, as obtained by them for different concentrations of organic solvents expressed in Vol. percent.

Organic Solvent	10%	30%	90%
MeOH	58	56	62
EtOH	60	57	*
n-PrOH	57	58	*
Acetone	58	58	*
Dioxan	60	*	*

\* Non-linear plot of E Vs  $P^F$  obtained.

Various iodide salts ( $KI$ ,  $NH_4I$ ,  $LiI$ ,  $BaI_2 \cdot 2H_2O$ ,  $MgI \cdot 8H_2O$ ,  $Me_4NI$ ,  $Et_4NI$ ,  $But_4NI$ ) in water - ROH mixtures (ROH = MeOH, EtOH, n-PrOH, i-PrOH) were studied<sup>162</sup> by direct potentiometry using solid-state silver iodide electrode and SCE.

Wt% ROH varied from 10-100.

Electrode slopes in mV per decade varied as shown in table 17.

Table 17

Organic Solvent	10%	100%
MeOH	59	59
EtOH	59	58
n-PrOH	58	53
iso-PrOH	58	52

Iodide concentration:  $10^{-1}M$  -  $10^{-6}M$   $I^-$

The direct potentiometry of chloride in alcohols and alcohol-water mixtures was studied by Kreshkov et al<sup>161</sup>. Potential measurements were made by a cell consisting of silver chloride electrode (Radelkis), SCE (saturated  $(C_2H_5)_4NCl$  in corresponding solvents) and potassium nitrate salt bridge.

Electrode slopes obtained in pure alcohols and in alcohol-water mixtures were 35-50 and 40-59 mV/decade respectively (instead of the Nernstian slope of 59 mV).

According to them, while their calibration graphs do not always obey the Nernst equation ( $E_{N.} = 0.059/n \log a$ ) and cannot therefore be used for the calculation of activity coefficients in these media, the graphs are, however, linear and can be used for chloride determination by direct potentiometry.

Low level determinations of sulphide in water, using silver sulphide, and Orion double-junction reference electrodes were made by Baumann<sup>163</sup>. The observed potential and the sulphide concentration were assumed to obey the modified Nernst relationship.

$$E = E_0 - A \log C$$

where A is defined as the tangential slope to the calibration curve at concentration C.

The variation of electrodes slopes with sulphide concentration is shown in Table 18.

Table 18

Sulphide Concn PPb	Slope (A)
9.1	53
18.2	45
45.4	31
181.6	31

Various available commercial electrodes were assessed<sup>164</sup> with respect to their response slopes, in order to determine a suitable electrode for the determination of carbon dioxide in power station water. The results shown in table 19 indicate that variation in electrode slopes for different cell may vary from 30-59 mV per decade concentration. Although the radiometer type E 5036 was found to give the best response slope, it was admitted that its sensitivity could vary in the range of 50-58 mV per decade between assembly of the same electrode.

Table 19

Electrode	Response Slope* /mV per decade
Radiometer E 5036	55-59
E.I.L (19210)	36-46
E.I.L 8002- (modified)	42-46
E.I.L 8002-2 (Klingerflonmin)	30-33

Midgley et al<sup>168</sup> studied the stability of the standard potentials of various glass electrodes. According to them the observed changes in potential cannot be assigned exclusively to the behaviour of the glass electrodes since reference electrodes may not be truly constant.

Table 20 shows the average rate of change of standard potential per week over a period of 12 weeks as observed by them.

Table 20

Electrode type	Rate of change of potential/mV week <sup>-1</sup>
A1, A2	-0.2, -0.3
B1, B2	-0.6, 0.2
C1, C2	0.5, 0.3
D1, D2	0.2, 0.2
D1, E2	0.1, 0.1
F1, F2	0.2, 0.1

Bishop et al.<sup>165</sup> investigated the interaction of cations and electron transfer systems on the silver ion response of a glass electrode, of diverse halide ions on the halide response and of electron transfer systems on the silver and halide ion responses of metal halide and amalgam electrodes. According to them, supporting electrolytes improves response slopes, but shorten response ranges of the electrodes. They demonstrated that silver ion response slopes increased from about 40 to 56 mV per unit  $P_{Ag}$  for both membrane and metal electrodes.

In another article, the same authors<sup>166</sup> demonstrated the beneficial effect of supporting electrolyte on their prepared silver - and halide responsive electrodes. According to them, all the electrodes (silver - and halide responsive electrodes) respond to silver with efficiencies of 65 to 75 per cent in the absence of a supporting electrolyte.

Bishop et al.<sup>167</sup> investigated potential shift with solvent concentration in a binary water-organic solvent mixture using silver chloride electrode (see table 21). They pointed out that fouling or poisoning of electrodes by solvent adsorption is pronounced and difficult to remove, e.g. acetone is known to give rise to a remarkable potential response and severe electrode poisoning.

Electrode Potential Vs. N.H.E. in  $2 \times 10^{-2}M$   
chloride in 80 per cent V/V solvent-water  
media

Table 21

Solvent	Dielectric Constant	AgCl
Water	80.4	385
Ethanol	24.3	302.5
Dioxan	2.2	263.5
Acetone	20.7	278
Methanol	33.6	322

Ratkovics et al.<sup>144</sup> investigated solvent interactions in alcohol-hydrogen chloride systems in the temperature range 20-40°C. The standard potential of the alcoholic calomel electrode was determined in methanol, ethanol, n-propanol and n-butanol. From a study of the concentration dependence of the mean activity coefficient at concentrations beyond the range of validity of the Debye - Huckel theory, it was found that the deviation from this theory could be interpreted by assuming strong interaction between the ions and the solvent, which increase with an increase in the molecular weight of the solvent. This phenomenon, also provides an explanation for the finding that the solubility of gaseous hydrogen chloride in the alcohol increases considerably with an increase in the molecular weight of alcohol.

### 1.5 EFFECT OF TEMPERATURE

Some reference electrodes (see section 1.2) show temperature hysteresis, an effect which could give rise to an appreciable error under certain circumstances. In general it is essential to maintain a constant temperature, as much as possible, during a series of electrode measurements: since the linearity between logarithm of activity as a function of electrode potential is valid for given constant temperatures. To a varying, though to a much less extent, the diffusivity of ions across electrode membrane, and therefore the liquid junction potential, is temperature-dependent. Amongst other factors which though may be small, but have measurable effects are: change of solvent properties with temperature: concentration expressed on molarity basis is temperature dependent. Table 21a shows the mean value of Nernst factor  $(\frac{2.303RT}{F})$ , as given by Orion<sup>145</sup>, for different halide electrodes at different temperatures.



Table 21a.

Variation of Nernstian slope factor  
with temperature for Halide electrodes

$t^{\circ}\text{C}$	$2.303RT/F$
0	54.20
10	56.18
20	58.18
25	59.16
30	60.15
40	62.13
50	64.11
100	74.04

## 1.6

EFFECT OF pH

The pH requirement for different species determined by ion-selective electrodes, depend on both the nature of species as well as the ion-selective electrode used. For instance, hydroxide ions rarely, if at all, react with fluoride ions, yet determination of fluoride in sample solution of a high pH medium will suffer from appreciable interference arising from the hydroxide ions because of the interaction of the latter with the Lanthanum fluoride crystal membrane. On the other hand at low pH, interference in fluoride determination is basically a result of interaction

between hydrogen and fluoride ions.

In general, sodium electrodes require a high pH to free them from interference from protons, although different sodium electrodes by different manufacturers have different lower pH limits (see table 22).

Mattock<sup>146</sup>, Phan and Steel<sup>147</sup> have compared the effect of pH on sodium response and their results were in agreement with those of Wilson et al<sup>148</sup>. The impression gained from their results is that, samples containing sodium ions as the determinand should be buffered so that  $\text{pH} \gg \text{pNa} + 3$ .

Judging by the publications of electrode makers, virtually all the solid-state can be used over the entire pH range, provided sample pretreatments are carried out where necessary. However, in practice, it is good to work within the optimum range. For fluoride determination, an optimum pH range of 5-8, is recommended and for chloride determination, a pH range of 2-11. In the tables 22,23 below are some literature quoted values for various ions.

Table 22

Lower pH limit for sodium electrode

NaCl M	Beckman 39278	Electrode E.I.L. 1048200	Crion 94-11	Radiometer G500 Na
$10^{-1}$	5.5	4.5	4.5	4.0
$10^{-2}$	7.0	5.0	5.5	4.5
$10^{-3}$	8.0	6.0	7.0	5.5
$10^{-4}$	9.0	7.0	8.0	6.5

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$10^{-4}$	9.0	7.0	8.0	6.5

Table 23

The pH of Unbuffered Solution with  
respect to Determinand of Ion-  
Selective Electrode

Electrode	pH Range
F <sup>-</sup>	5-8
Cl <sup>-</sup>	2-11
Br <sup>-</sup>	2-12
I <sup>-</sup>	3-13
Ag <sup>+</sup>	2-9
Pb <sup>2+</sup>	3-7
Cd <sup>2+</sup>	3-7
Cu <sup>2+</sup>	3-7

Generally, for divalent cations, the actual pH range depend on cation type present since complexation with hydroxide ion is pH dependent.

#### 1.7 RESPONSE TIME AND REPRODUCIBILITY

The electrode response time, that is the time taken before stability is achieved varies from a few seconds to several minutes<sup>150-154</sup>, usually depending on type of electrode, medium and sample concentration.

Several people have reported on the response time of different ion-selective electrode. Toth et al.<sup>150-151</sup> using the heterogeneous silver halide electrode reported that a steady state potential proceeds exponentially with time.

According to Bailey<sup>18e</sup>, the response time seldom limits the application of electrode except in solutions of concentration very close to the limit of detection. And as would be expected, electrodes respond more quickly in strong or buffered solution of determinand and in solution with a high background concentration of inert electrolyte. Erdmann<sup>153</sup> found the response of the lanthanum fluoride electrode was sufficiently fast when a total ionic adjustment buffer (T.I.S.A.B.) was added to enable samples in the concentration range  $0.1-2 \text{ mg l}^{-1}$  to be analysed at the rate of 2 min per sample, while Sekerka and Lechner<sup>154</sup> analysed fluoride in the range  $10^{-5}-10^{-7} \text{ M}$  allowing 10 min for the electrodes to reach equilibrium.

The theoretical and practical problems of manufacturing highly selective sodium glass electrodes with a short response time were thoroughly discussed by Pungor et al.<sup>155</sup> Michael and his coworker<sup>156</sup> drew attention to the fact that only limited progress has been made in improving the performance of sodium ion-sensor and that much has yet to be attained in the performance of commercially available electrodes, especially from the point of view of response time and selectivity with respect to hydrogen ion. The shortcomings of different reference electrodes for analysis of low level sodium were highlighted. For instance, the ordinary

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silver-silver chloride electrode is unsuitable because of subsequent liberation of silver which interferes considerably, and the conventional cell with potassium chloride salt bridge poses some difficulty owing to leakage of potassium ion capable of giving rise to emf transients. However, the problem could be overcome by using a double junction reference electrode with 2M rubidium chloride as the filling solution for the outer compartment, since  $K_{Na Rb}$  is of the order of  $10^{-5}$ .

The preparation of lead (II)- selective electrode made of mixed silver sulphide-lead sulphide were discussed by Heijne et al<sup>157</sup>. A series of investigations with the new electrode showed that it behaves very closely to Orion commercial lead electrode. Time response of the ion-selective electrode after addition of trien or EDTA in the presence of  $10^{-6}M$  lead was of the order of 50 sec.

Buffle et al<sup>152</sup> have proposed a model to explain the response time of solid-state membrane electrodes in the range of several minutes. According to them in the range of millisecond to seconds diffusion seem to be the rate - determining factor, but for times exceeding about 10 sec., dissolution or crystallization and charge transfer at the membrane seem to be the predominant factors. A mathematical model which is applicable to any solid-state membrane

electrodes and takes into account the change in time response with change in the concentration or nature of the lost ion and surface electrochemical properties of the membrane is given.

Reproducibility may be limited by several factors: instrumental, electrode stability, instability of the ambient environment, irreproducible execution of a given repeat procedure by an analyst and so on. However, despite all these uncontrollable conditions, which an analyst often faces, virtually all workers in this field have reported reasonable electrode reproducibility. According to Orion, their silver halide electrodes, with frequent calibration are reproducible to  $\pm 1\%$  of the halide activity in the sample. Various work in this department has shown reasonable potential reproducibility, though there seem to be a gradual loss of reproducibility at low-level indicator ion concentration and at high solvent concentration for organo-aqueous systems.

#### 1.8 DETECTION LIMIT

The detection limit of an ion-selective electrode has been defined in many ways. It is, however admitted that the lower limit of Nernstian response or simply Nernstain limit is less ambiguous and undoubtedly the most useful criterion



of assessing electrode performance. It is defined as the lower activity of the determinand at which the Nernstian plot of electrode potential against logarithm of activity begins to depart from linearity.

According to IUPAC<sup>159</sup> recommendation, the detection limit should be defined as the concentration of the determinand at which the electrode potential deviates by  $18/n$  mV from the extrapolation of the linear portion of the calibration graph,  $n$  being the charge number carried by the determinand ion. Bailey<sup>18e</sup> remarks that although this definition appears to be satisfactory in general, examples of its use are rare to find. According to him, it is sufficient in practice to realise that both the detection limit and the Nernstian limit depend on the individual electrode and conditions of measurement.

In a very recent paper, the detection limit in analysis with ion-selective electrode was discussed by Midgley<sup>160</sup>. He advanced a forceful argument that definitions of limit of detections based only on the deviation of an electrode calibration from the theoretical without taking account of the associated random errors of measurement are inadequate.

He derived equations, which take into account reagents blank, solubility product of membrane and interferences, all

of which, according to him, are crucial factors in determining the deviation of the electrodes response from the Nernstian values. The equations, he claims, enable one to predict (a) the degree of precision to which emf has to be measured in order to achieve a desired limit and (b) whether changing the conditions of measurements might bring the desired limit of detection within reach of a given precision of measurement. Finally he demonstrated that his proposed statistical treatment of the limit of detection is justified from a practical point of view and that the errors for electrodes operating in the non-Nernstian region are usually normally distributed.

## RESULTS

2.1      FLUORIDE ION

2.1.1      Direct Measurements

2.1.2      Indirect Measurements

2.1.3      Comparison of Direct and Indirect Measurements.

### 2.1.1 DIRECT MEASUREMENTS

Table 24

Comparison of changes in potential,  $\Delta E$ , for a given cell system (lanthanum fluoride/silver-silver chloride d/i.  $10^{-3}$  M potassium fluoride) and various solvent concentrations in different solvent-water mixtures.

Solvent % m/m	$\Delta E/mV$						
	MeOH	EtOH	HOAc	n-PrOH	1-PrOH	acetone	1,4-dioxan
0	0 (-40.7)	0 (-37.4)	0 (-37.1)	0 (-39.6)	0 (-39.2)	0 (-7.4)	0 (-42.0)
10	-10.9	-14.3	53.9	-15.2	-15.8	-10.2	8.1
20	-23.4	-29.6	63.4	-28.9	-32.4	-19.7	5.1
30	-36.0	-46.6	70.8	-44.8	-49.5	-32.7	-1.8
40	-48.4	-64.2	75.9	-58.7	-66.5	-45.7	-11.8
50	-63.5	-86.6	81.0	-77.5	-90.8	-59.4	-28.5
60	-77.5	-106.1	89.4	-95.5	-114.7	-82.8	-55.0
70	-90.6	-128.1	98.3	-121.5	-142.8	-105.0	-80.2
80	-101.8	-150.7	108.9	-151.5	-177.6	-130.9	-114.1
90	-110.9	-175.1	113.7	-186.3	-224.5	-207.7	-154.0
95	-114.5	-187.5	106.3	-210.7	-251.9	-257.0	-152.0
99	-116.3	-195.0	94.6	-222.9	-278.2	-330.4	-

\*SCE(LiCl) was used as reference electrode.

Table 25

Comparison of changes in potential,  $\Delta E$ , for a given cell system (lanthanum fluoride/  
silver-silver chloride d/i,  $10^{-3}$  M potassium fluoride) and various solvent concentrations  
in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$					
	EtOH	HOAc	n-PrOH	1-PrOH	acetone	1,4-dioxan
0	0*	* 0(-106.9)	0(-154.9)	0(-153.6)	0(-55.4)	0(-157.7)
10	-5	147.4	-6.1	-9.7	-12.1	11.4
20	-11	175.0	-12.5	-18.3	-20.2	12.1
30	-16	195.3	-19.0	-27.7	-30.5	8.0
40	-23	212.5	-26.7	-38.0	-42.3	0.2
50	-30	227.2	-35.2	-51.4	-56.2	-11.8
60	-39	240.6	-44.3	-67.4	-74.2	-27.6
70	-47	252.3	-55.8	-85.8	-99.3	-39.6
80	-57	257.6	-69.2	-108.5	-129.6	-54.6
90	-69	253.3	-86.4	-135.4	-192.4	-74.8
95	-74	250.6	-95.8	-151.4	-240.8	-80.3
99	-80	246.2	-103.3	-166.1	-254.1	-

(1).  $10^{-4}$  M KF was used.

(2). \*Absolute potential not available.

$$\Delta E_{\text{max}}/\text{mV} = 116$$

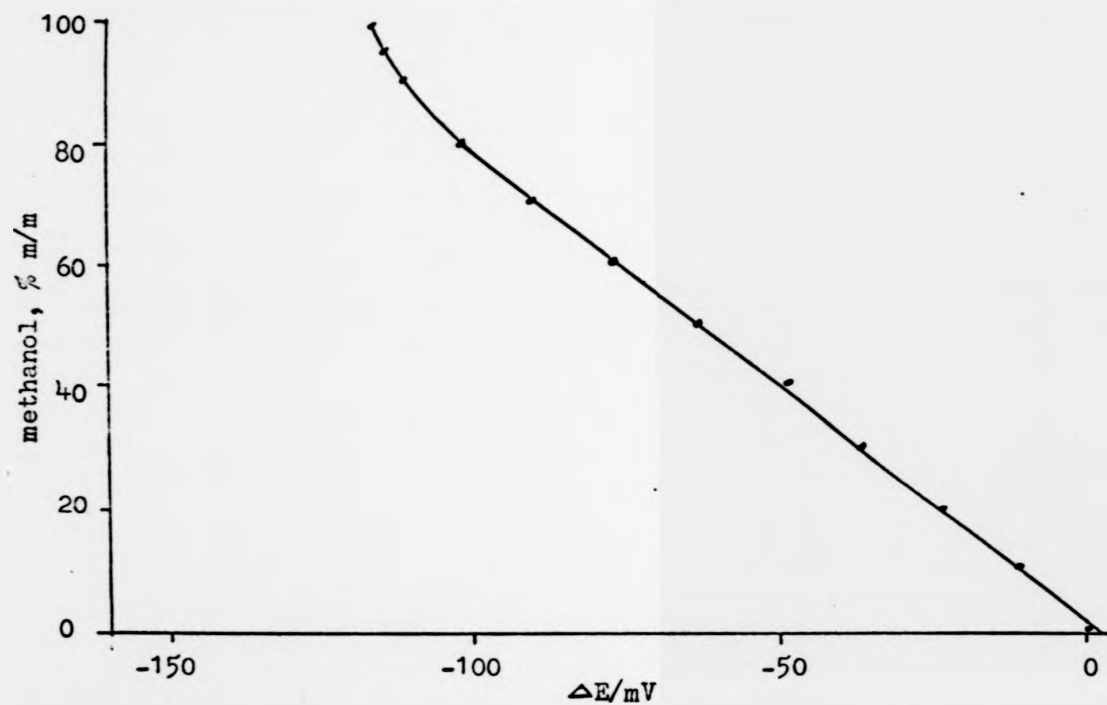


Fig. 1 Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{MeOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M potassium fluoride and various methanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

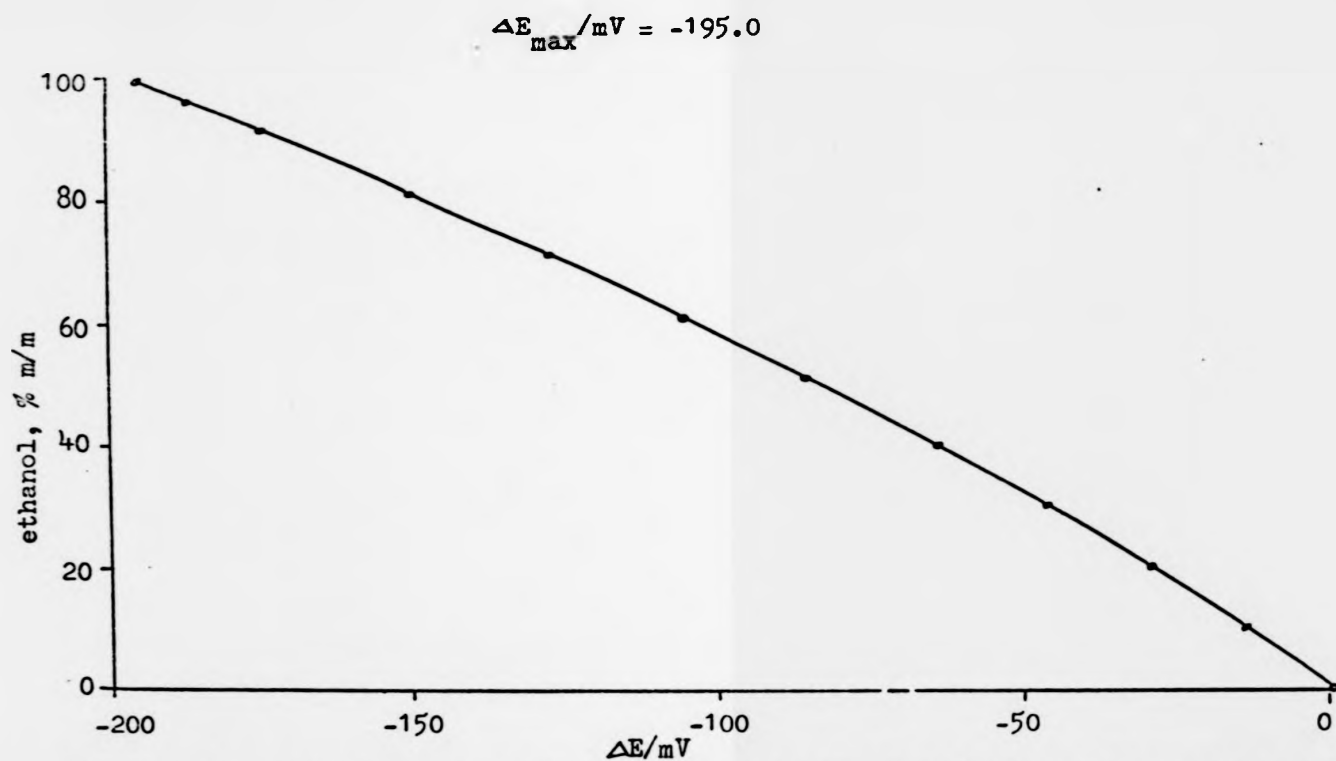


Fig. 2a Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M potassium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



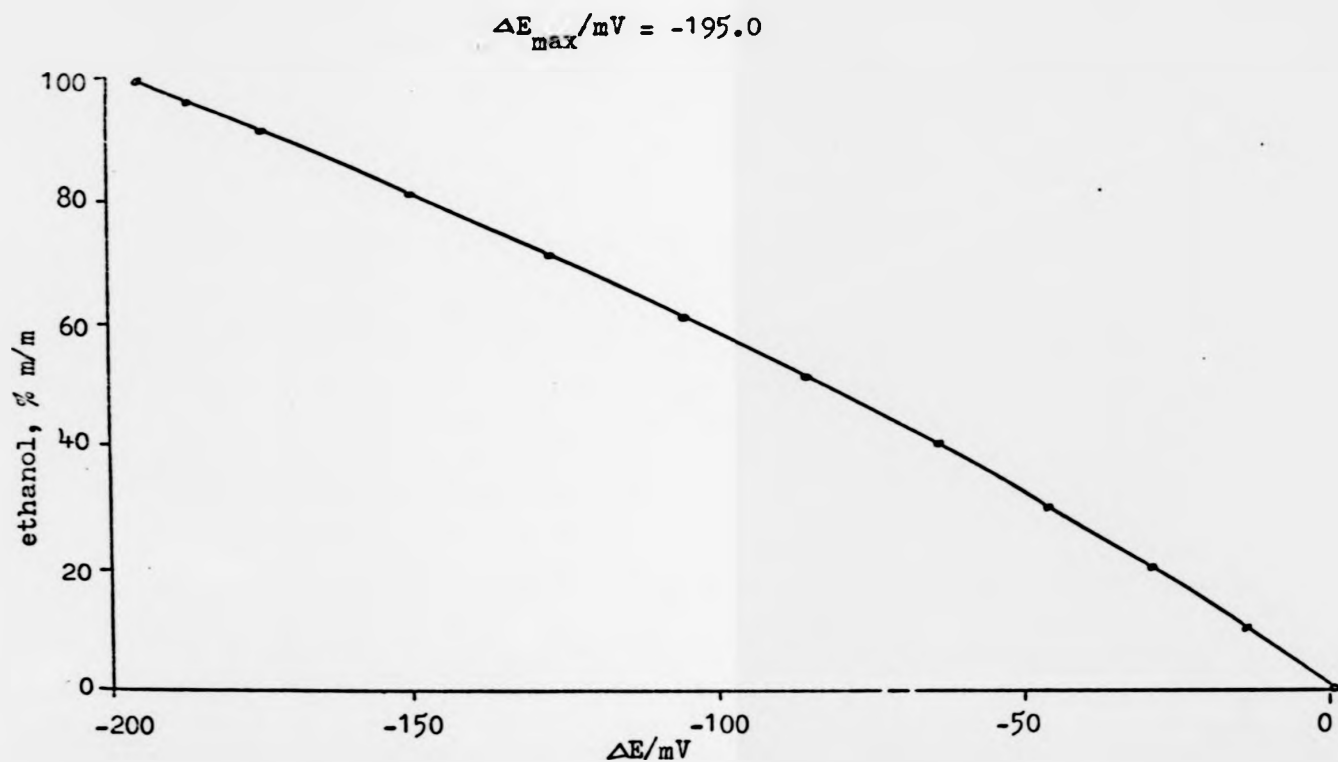


Fig.2a Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M potassium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

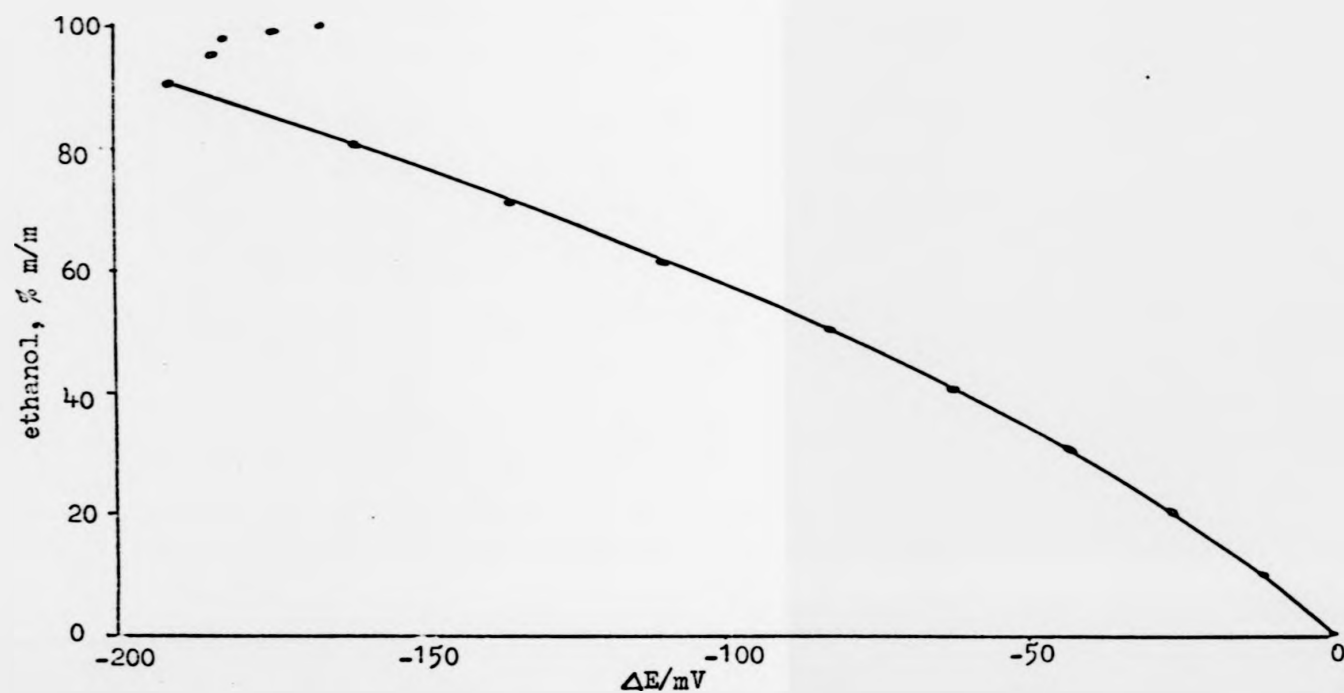


Fig. 2b Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and SCE electrodes.

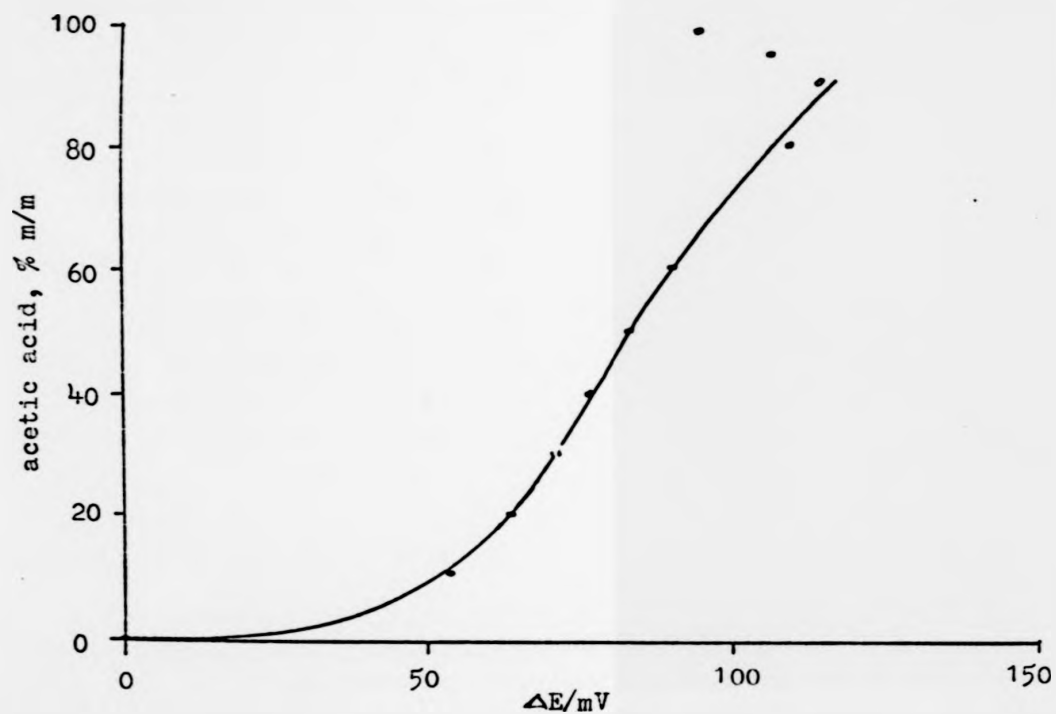


Fig. 3 Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M potassium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/mV = -230$$

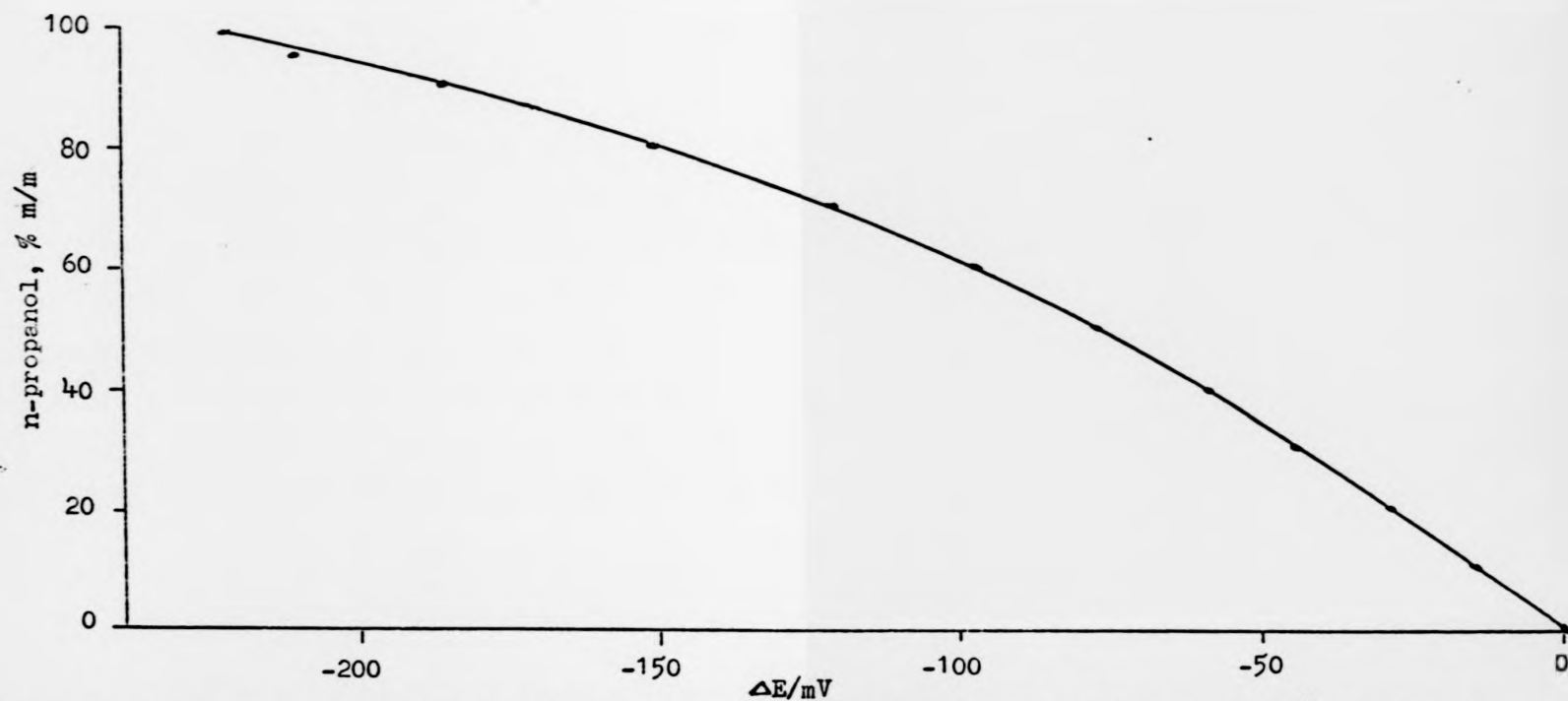


Fig. 4a Change in potential,  $\Delta E$ , for the system,  $KF-n-PrOH(H_2O)$ , in solutions of  $10^{-3}M$  potassium fluoride and various n-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

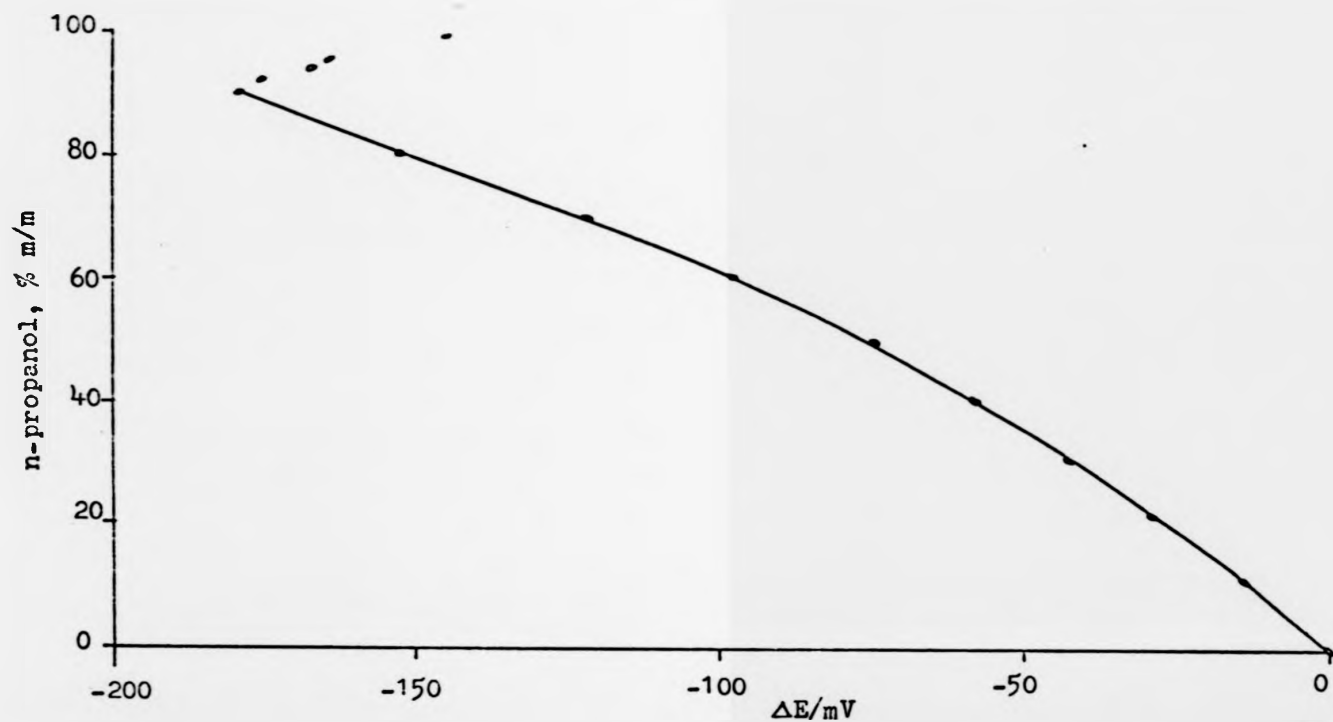


Fig. 4b Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{n-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}\text{M}$  sodium fluoride and various n-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = -278$$

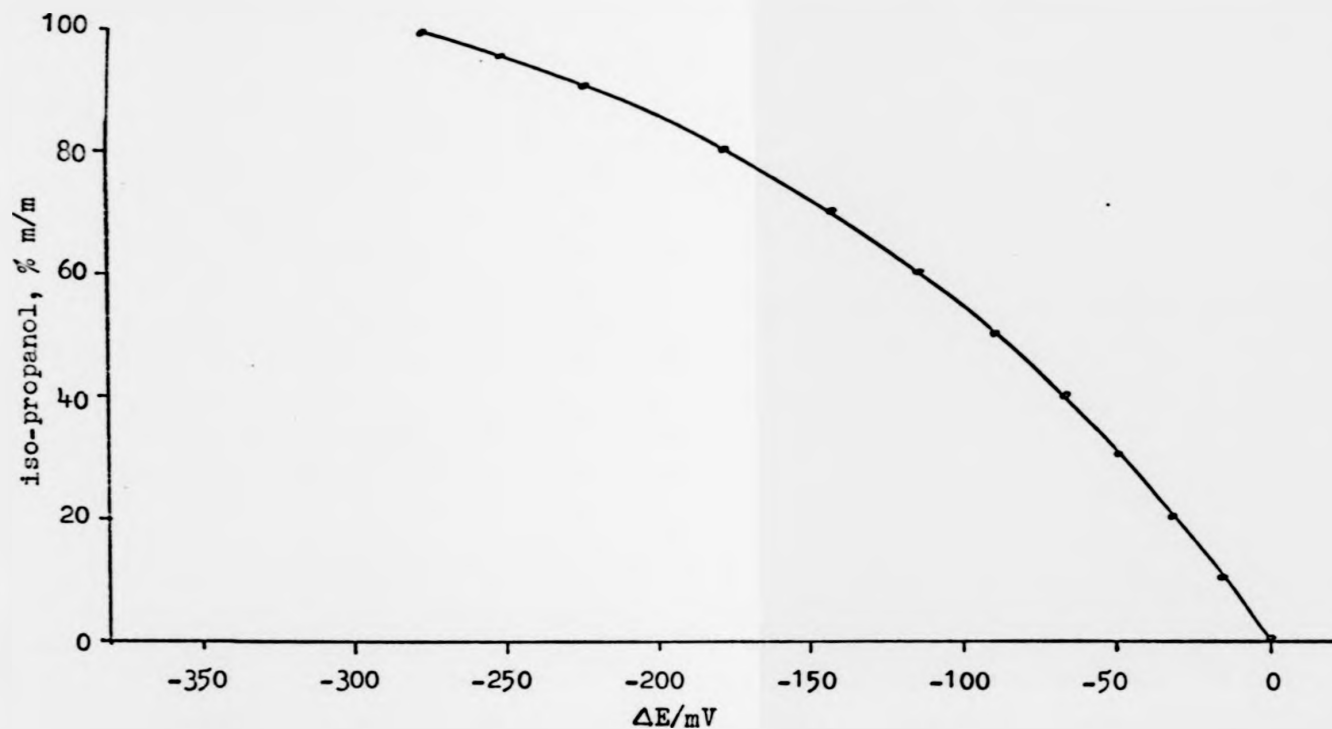


Fig. 5a Change in potential,  $\Delta E$ , for the system,  $\text{KF}-1\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M potassium fluoride and various iso-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

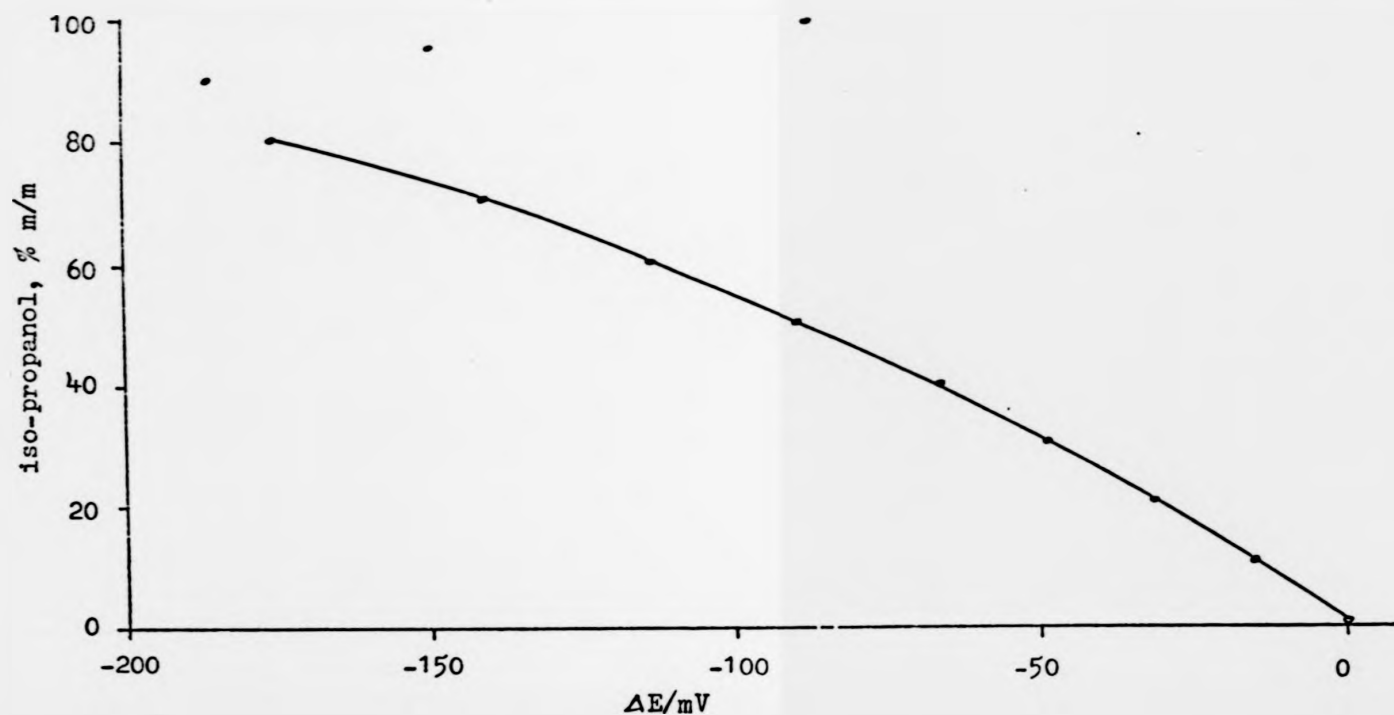


Fig. 5b Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-1\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various iso-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = -330$$

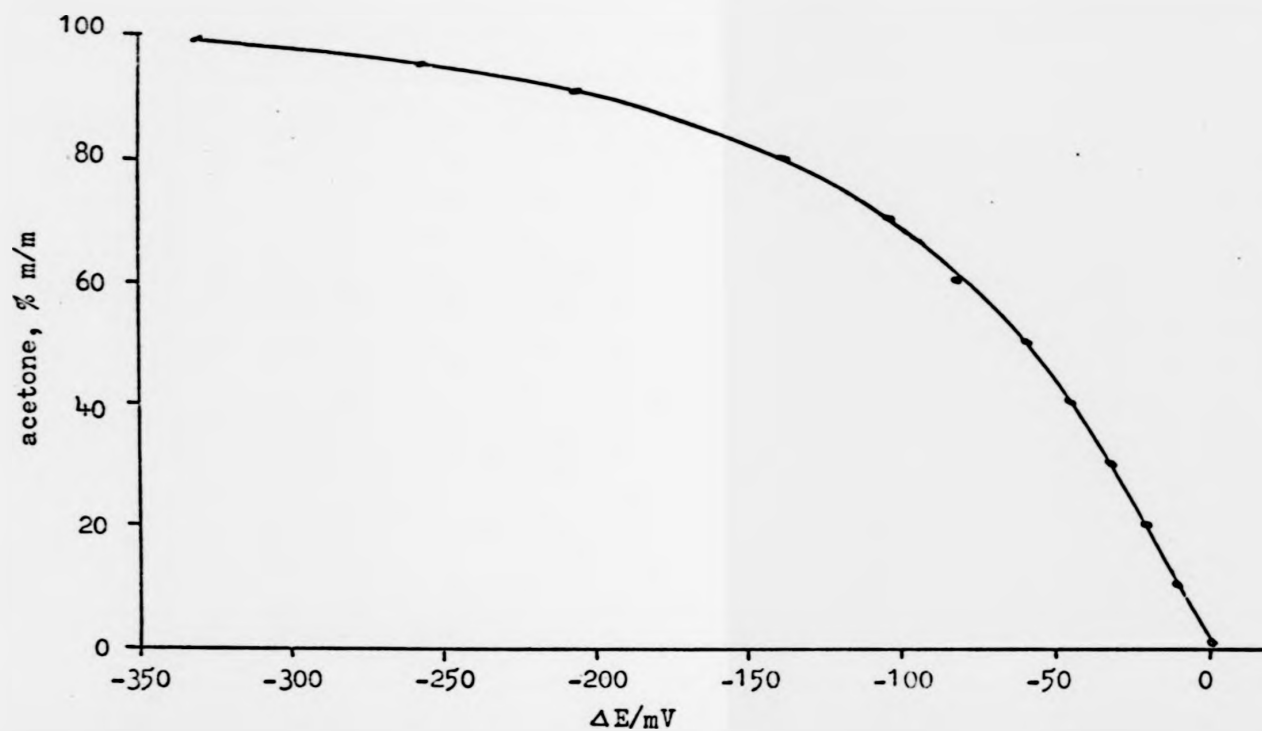


Fig. 6a Change in potential,  $\Delta E$ , for the system, KF-acetone( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M potassium fluoride and various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes.



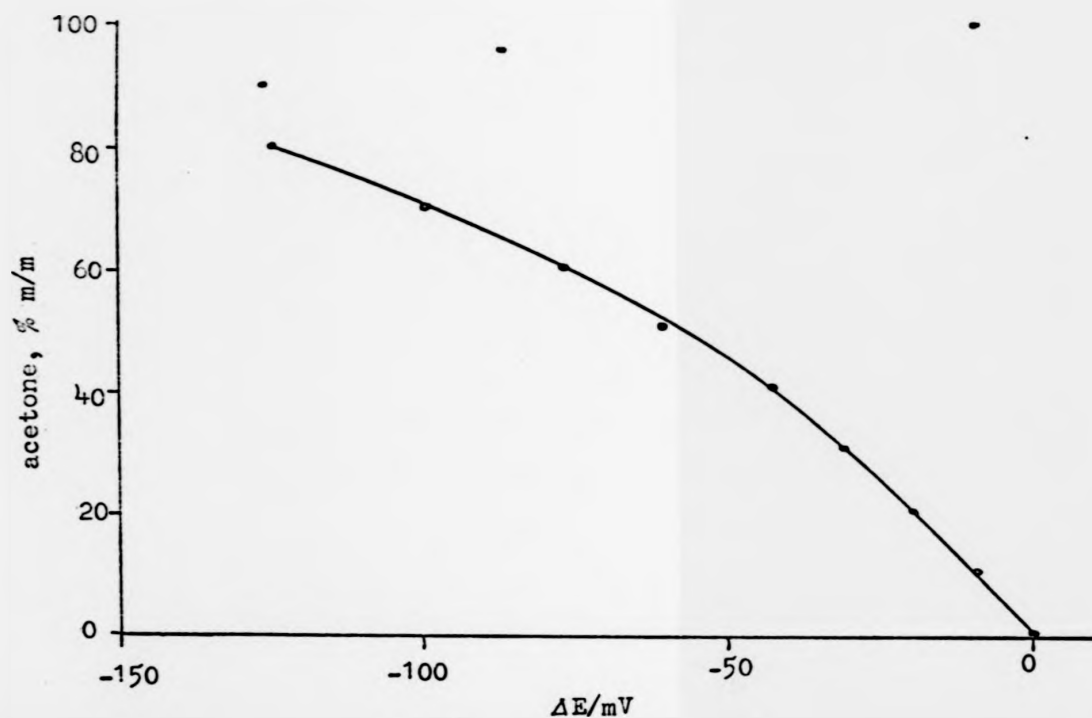


Fig. 6b Change in potential,  $\Delta E$ , for the system,  $\text{NaF-acetone(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M sodium fluoride and various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes.

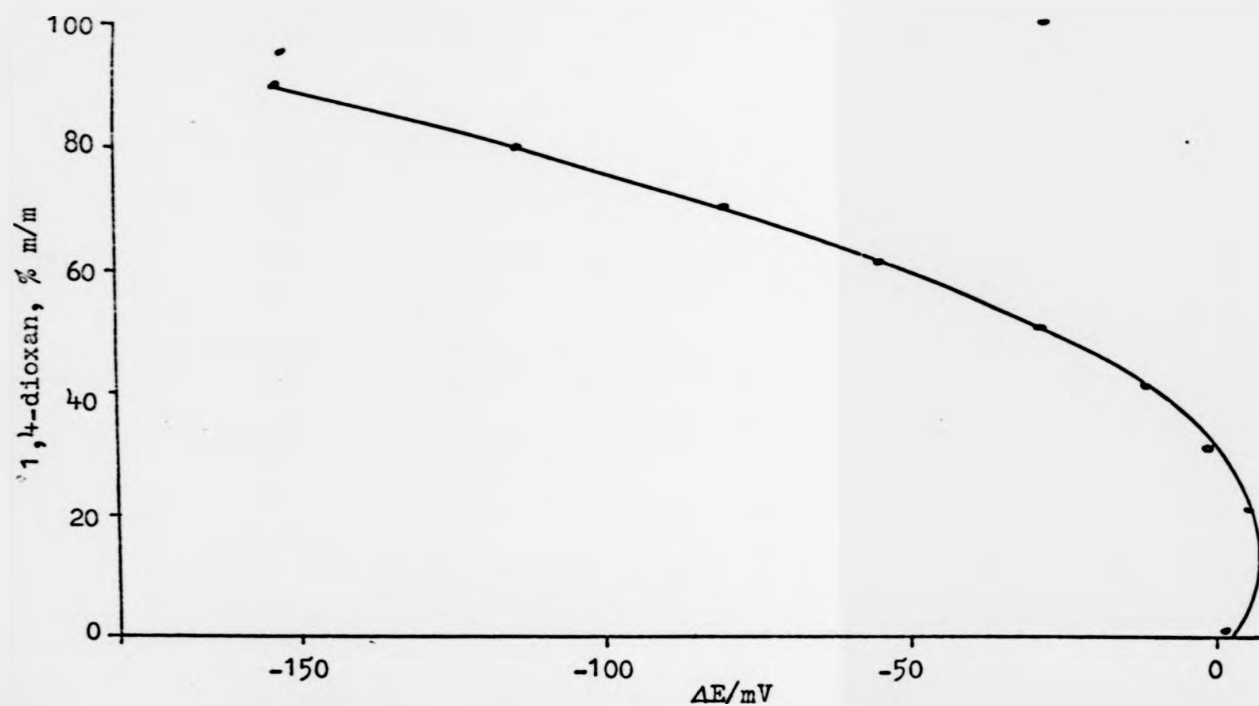


Fig. 7 Change in potential,  $\Delta E$ , for the system, NaF-1,4-dioxan( $H_2O$ ), in solutions of  $10^{-3}$  M sodium fluoride and various 1,4-dioxan concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = -80$$

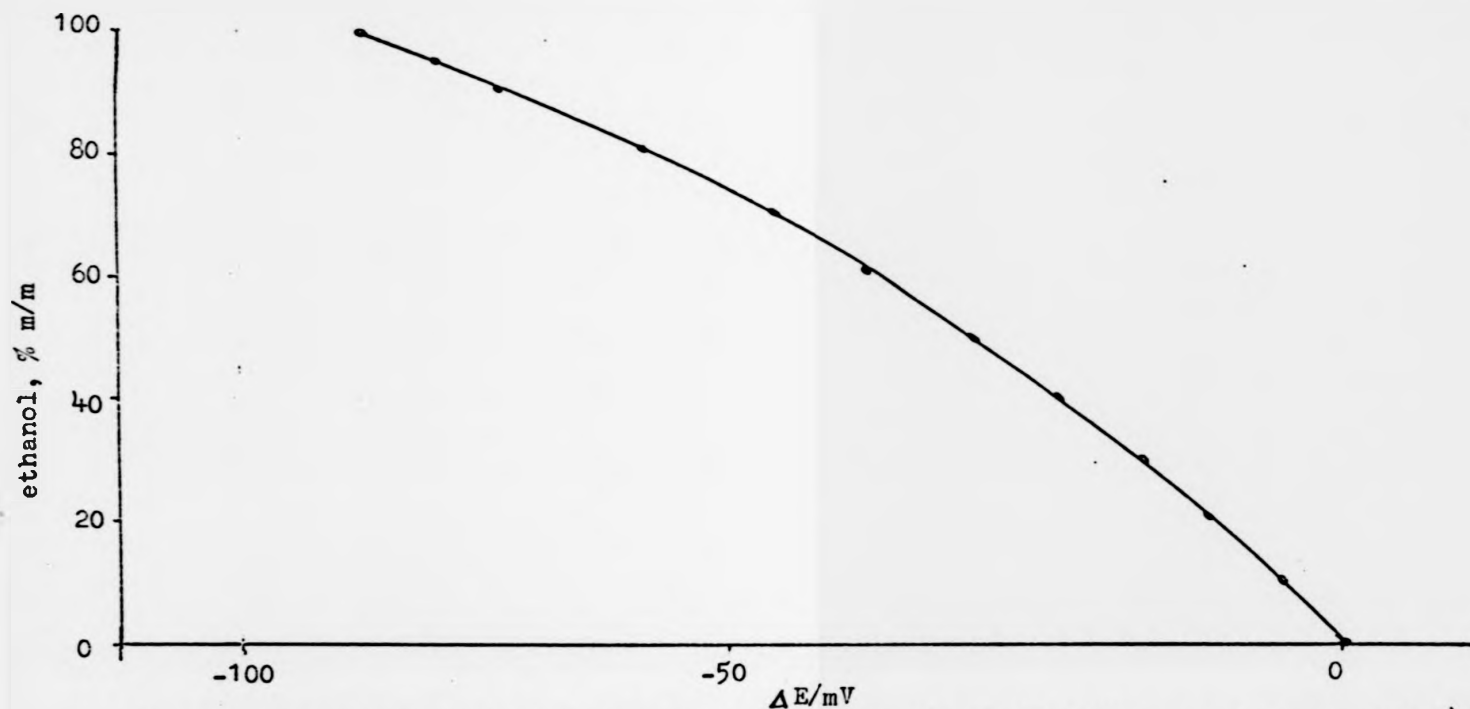


Fig. 8 Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{EtOH}(\text{MeOH})$ , in solutions of  $10^{-4}$  M potassium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

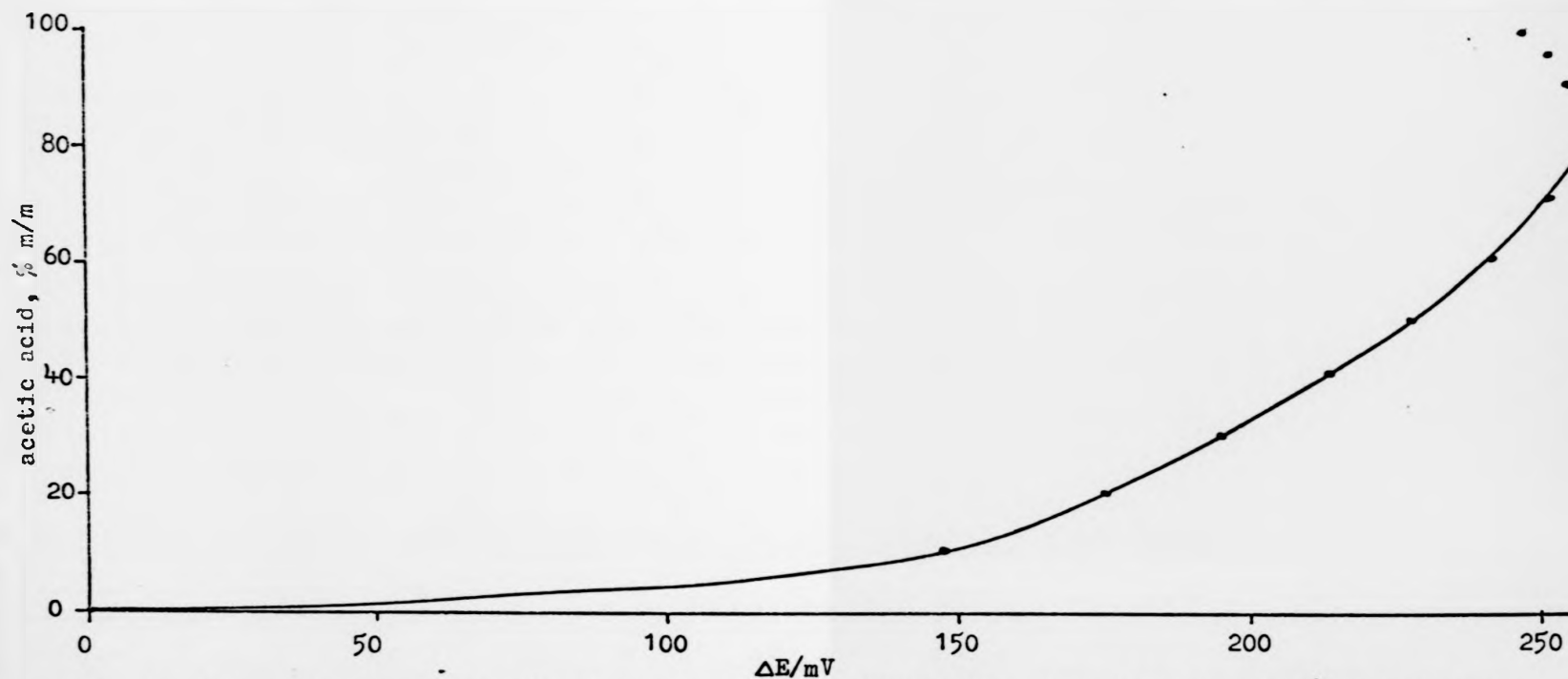


Fig. 9 Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{HOAc}(\text{MeOH})$ , in solutions of  $10^{-4}$  M potassium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

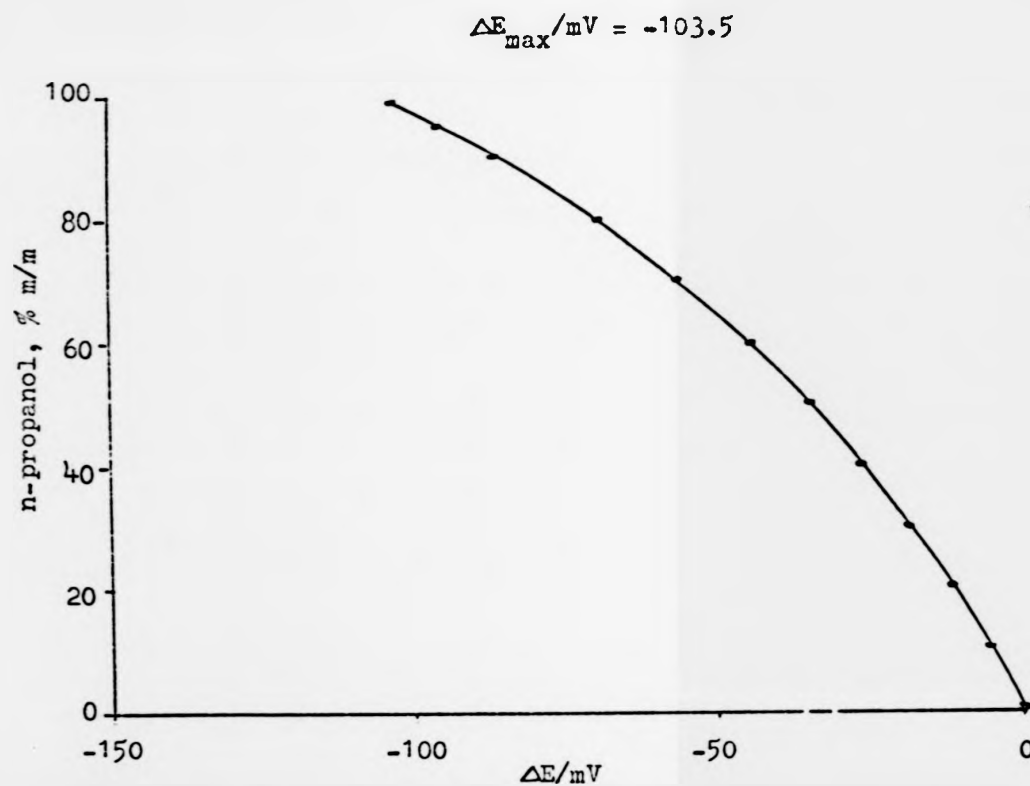


Fig. 10 Change in potential,  $\Delta E$ , for the system,  $\text{KF}-\text{n-PrOH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M potassium fluoride and various n-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

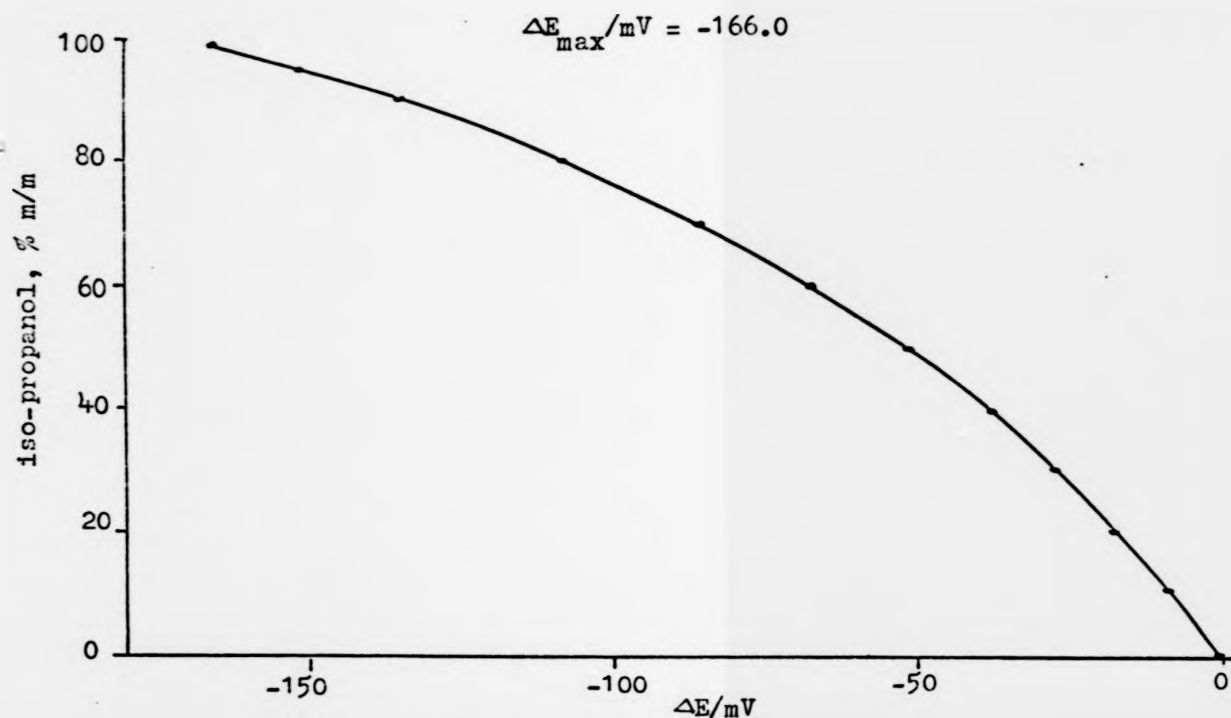


Fig. 11 Change in potential,  $\Delta E$ , for the system,  $KF-i\text{-}PrOH(MeOH)$ , in solutions of  $10^{-3}$  M potassium fluoride and various iso-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

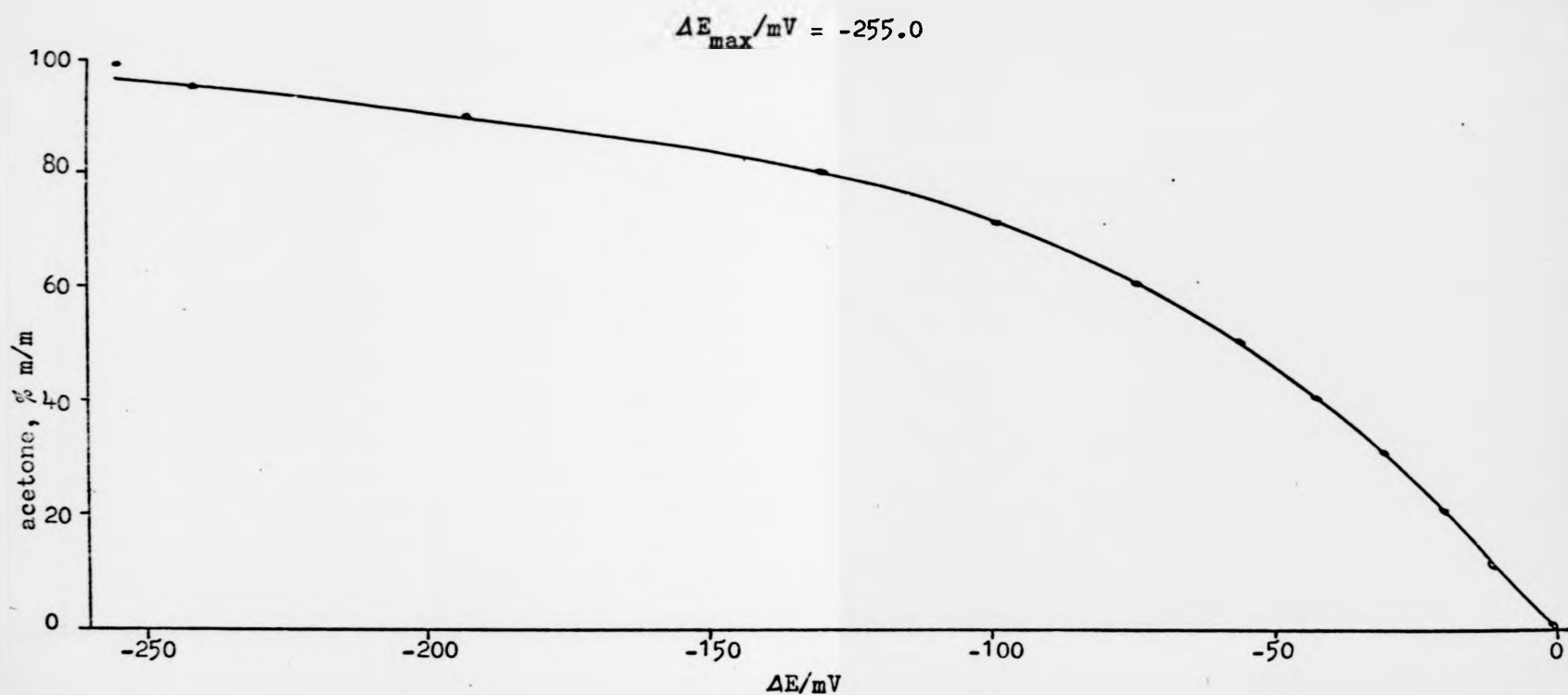


Fig. 12 Change in potential,  $\Delta E$ , for the system, KF-acetone(MeOH), in solutions of  $10^{-3}$  M potassium fluoride and various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes.

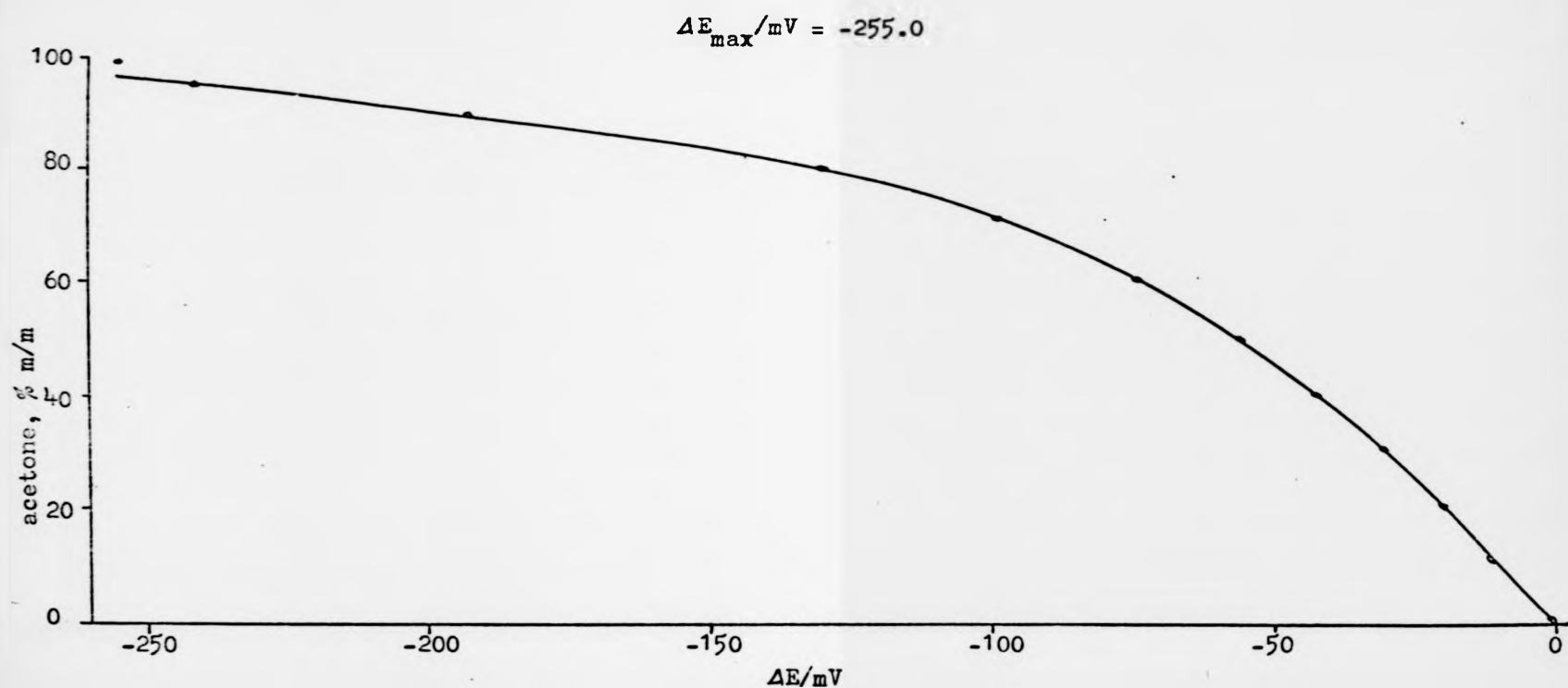


Fig. 12 Change in potential,  $\Delta E$ , for the system, KF-acetone(MeOH), in solutions of  $10^{-3}$  M potassium fluoride and various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes.



$$\Delta E_{\max}/\text{mV} = 80.3$$

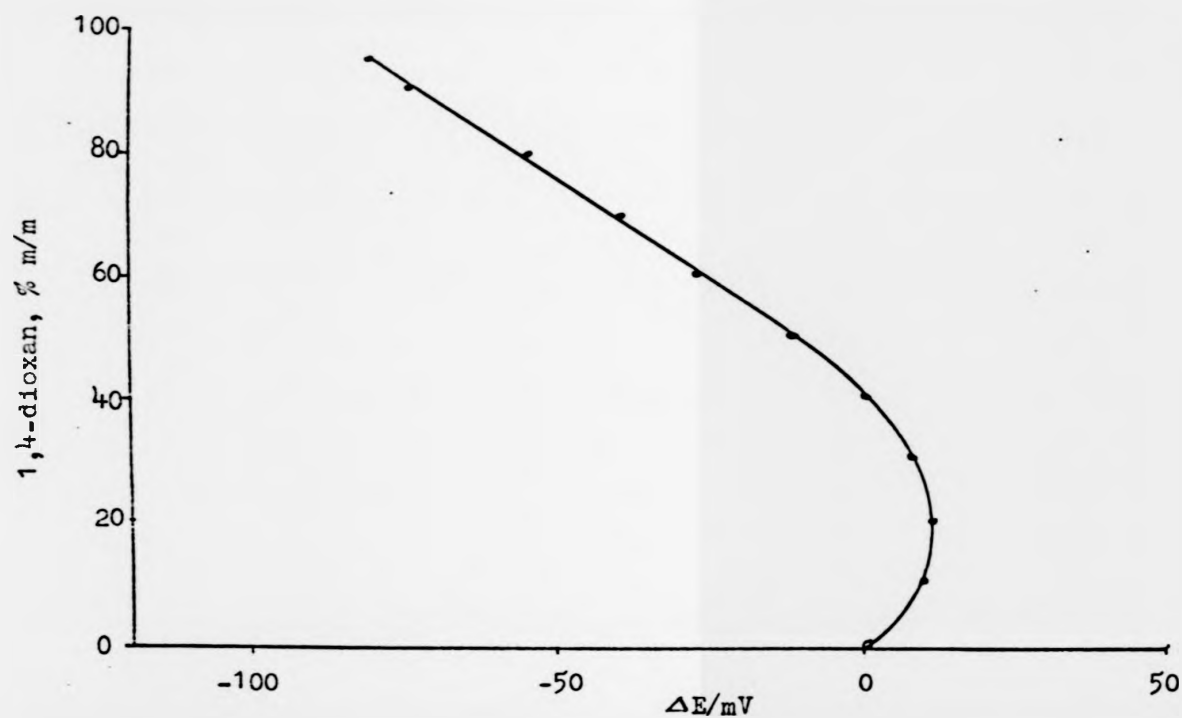


Fig.13 Change in potential,  $\Delta E$ , for the system, KF-1,4-dioxan(MeOH), in solutions of  $10^{-3}$  M potassium fluoride and various 1,4-dioxan concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

2.1.2 INDIRECT MEASUREMENTS

Table 26

Change in potential (obtained by the 'indirect method') for the system,  $\text{KF--MeOH(H}_2\text{O)}$ , in solutions  $10^{-3}\text{M}$ ,  $10^{-4}\text{M}$  and  $10^{-5}\text{M}$  in potassium fluoride and of various methanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m methanol	Potential/mV			Electrode slope/- mV per decade	LLPR	$E^\circ/\text{mV}$
	$10^{-3}\text{ MF}^-$	$10^{-4}\text{ MF}^-$	$10^{-5}\text{ MF}^-$			
0	-28.0	23.4	77.0	52.5	$2 \times 10^{-6}$	-185.5
20	-50.6	2.2	58.0	54.3	$2 \times 10^{-6}$	-213.5
40	-73.0	-19.3	34.8	53.9	$2 \times 10^{-6}$	-234.7
60	-98.3	-46.9	7.8	53.1	$2 \times 10^{-6}$	-257.6
80	-124.1	-72.3	-16.5	53.8	$2 \times 10^{-6}$	-285.5
90	-134.9	-83.3	-29.4	52.8	$2 \times 10^{-6}$	-293.3
99	-141.0	-89.5	-35.8	52.6	$2 \times 10^{-6}$	-298.8
$\Delta E_{\text{max}}/\text{mV}$	-113.0	-112.9	-112.8			

Table 22

Change in potential (obtained by the 'indirect method') for the system, NaF--EtOH(H<sub>2</sub>O), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium fluoride and of various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes

% m/m ethanol	Potential/mV			Electrode slope/-mV per decade	LLRR (LR)
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>		
0	60	120	182	60.5	$2 \times 10^{-6}$
10	48	108	168	60.0	$3 \times 10^{-6}$
20	31	91	152	60.5	$3 \times 10^{-6}$
30	4	73	134	60.0	$3 \times 10^{-6}$
40	-7	53	112	59.5	$3 \times 10^{-6}$
50	-29	29	87	58.5	$3 \times 10^{-6}$
60	-51	5	60	55.5	$3 \times 10^{-6}$
70	-84	-29	28	55.0	$2 \times 10^{-6}$
80	-112	-60	-6	54.0	$1 \times 10^{-6}$
90	-149	-94	-38	56.0	$1 \times 10^{-6}$
95 *	-147(-210.4)	-108(-161.0)	-56(-105.7)	55. (55.0)	$5 \times 10^{-6}$ - $5 \times 10^{-4}$ ( $5 \times 10^{-6}$ )
99 *	-140(-219.7)	-118(-170.3)	-54(-114.9)	62 (55.0)	$5 \times 10^{-6}$ - $10^{-4}$ ( $1 \times 10^{-5}$ )
$\Delta E/mV$ (90% m/m)	209	214	220		

( \*) \*Measured separately and KF used instead of NaF

Table 28

Change in potential (obtained by the 'indirect method') for the system, NaF--HOAc(H<sub>2</sub>O), in solutions 10<sup>-3</sup> M, 10<sup>-4</sup> M and 10<sup>-5</sup> M in sodium fluoride and of various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes

% m/m HOAc	Potential/mV			Electrode slope /-mV per decade	LLRR
	10 <sup>-3</sup> MF <sup>-</sup>	10 <sup>-4</sup> MF <sup>-</sup>	10 <sup>-5</sup> MF <sup>-</sup>		
0	-27	30	90	60.0	1 X 10 <sup>-6</sup>
10	27	87	146	59.5	1 X 10 <sup>-6</sup>
20	37	96	154	59.0	1 X 10 <sup>-6</sup>
30	43	104	163	59.5	1 X 10 <sup>-6</sup>
40	49	110	170	60.0	1 X 10 <sup>-6</sup>
50	54	114	174	59.5	2 X 10 <sup>-6</sup>
60	59	119	180	61.0	2 X 10 <sup>-6</sup>
70	69	130	189	59.5	2 X 10 <sup>-6</sup>
80	74	137	197	60.0	6 X 10 <sup>-6</sup>
90	78	148	209	61.0	6 X 10 <sup>-6</sup> -10 <sup>-4</sup>
95	73	153	213	60.0	6 X 10 <sup>-6</sup> -10 <sup>-4</sup>
99	69	145	129	55.0	2 X 10 <sup>-6</sup> -2 X 10 <sup>-5</sup>
ΔE/mV (80% m/m)	101	107	107		

Table 28

Change in potential (obtained by the 'indirect method') for the system, NaF--HOAc(H<sub>2</sub>O), in solutions 10<sup>-3</sup> M, 10<sup>-4</sup> M and 10<sup>-5</sup> M in sodium fluoride and of various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes

% m/m HOAc	Potential/mV			Electrode slope /-mV per decade	LLRR
	10 <sup>-3</sup> MF <sup>-</sup>	10 <sup>-4</sup> MF <sup>-</sup>	10 <sup>-5</sup> MF <sup>-</sup>		
0	-27	30	90	60.0	1 X 10 <sup>-6</sup>
10	27	87	146	59.5	1 X 10 <sup>-6</sup>
20	37	96	154	59.0	1 X 10 <sup>-6</sup>
30	43	104	163	59.5	1 X 10 <sup>-6</sup>
40	49	110	170	60.0	1 X 10 <sup>-6</sup>
50	54	114	174	59.5	2 X 10 <sup>-6</sup>
60	59	119	180	61.0	2 X 10 <sup>-6</sup>
70	69	130	189	59.5	2 X 10 <sup>-6</sup>
80	74	137	197	60.0	6 X 10 <sup>-6</sup>
90	78	148	209	61.0	6 X 10 <sup>-6</sup> -10 <sup>-4</sup>
95	73	153	213	60.0	6 X 10 <sup>-6</sup> -10 <sup>-4</sup>
99	69	145	129	55.0	2 X 10 <sup>-6</sup> -2 X 10 <sup>-5</sup>
ΔE/mV (80% m/m)	101	107	107		

Table 29

Change in potential (obtained by the 'indirect method') for the system,  $\text{KF-n-PrOH(H}_2\text{O)}$ , in solutions  $10^{-3} \text{ M}$ ,  $10^{-4} \text{ M}$  and  $10^{-5} \text{ M}$  in potassium fluoride and silver-silver chloride (double-junction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope /-mV per decade	LLLR	$E^0$ /mV
	$10^{-3} \text{ MF}^-$	$10^{-4} \text{ MF}^-$	$10^{-5} \text{ MF}^-$			
0	-34.0	17.2	68.8	51.4	$2 \times 10^{-6}$	-188.2
10	-49.9	1.4	55.3	52.6	$2 \times 10^{-6}$	-207.7
40	-92.4	-41.4	11.4	52.0	$2 \times 10^{-6}$	-248.4
60	-128.9	-80.6	-28.2	50.4	$2 \times 10^{-6}$	-280.1
80	-179.0	-133.0	-79.2	50.0	$2 \times 10^{-6}$	-329.0
90	-211.2	-166.0	-115.1	48.1	$2 \times 10^{-6}$	-355.5
99	-244.0	-198.3	-143.3	54.0	$2 \times 10^{-6} - 2 \times 10^{-4}$	-414.3
$\Delta E_{\text{max/mV}}$	-210.0	-215.5	-212.1			

Table 30

Change in potential (obtained by the 'indirect method') for the system,  $\text{KF--i-PrOH(H}_2\text{O)}$ , in solutions  $10^{-3} \text{ M}$ ,  $10^{-4} \text{ M}$  and  $10^{-5} \text{ M}$  in potassium fluoride and of various isopropanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /-mV per decade	LLLRR	$E^0$ /mV
	$10^{-3} \text{ MF}^-$	$10^{-4} \text{ MF}^-$	$10^{-5} \text{ MF}^-$			
0	-34.0	17.2	68.8	51.4	$2 \times 10^{-6}$	-188.2
10	-51.0	1.1	55.5	53.3	$2 \times 10^{-6}$	-210.9
40	-102.8	-50.4	4.7	53.8	$2 \times 10^{-6}$	-264.2
60	-147.8	-97.6	-43.8	53.8	$2 \times 10^{-6}$	-309.2
80	-206.9	-159.7	-159.7	55.4	$2 \times 10^{-6}$	-373.1
90	-246.3	-203.2	-150.0	53.2	$6 \times 10^{-6}$	-405.9
99	-278.8 (-20)	-251.8 (-40)	-198.3 (-76)	NL	-	
$\Delta E_{\text{max/mV}}$	-244.8	-269.0	-267.1			

NL = Non-linear

Table 31

Change in potential (obtained by the 'indirect method') for the system, KF--acetone( $H_2O$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope /-mV per decade	LLRR (LR)	$E^0$ /mV **
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-3.7	38.4	89.6	51.2	2 X 10	-157.3 (-172.3)
10	-9.7	33.0	79.8	46.8	2 X 10	-150.7 (-174.9)
40	-47.3	-0.8	48.0	47.7	2 X 10	-190.4 (-248.0)
60	-82.1	-34.0	18.6	50.4	2 X 10	-233.3 (-323.5)
80	-130.1	-80.6	-27.6	51.3	6 X 10	-284.0 (-413.0)
90	-182.3	-139.5	-90.4	49.1	$6 \times 10^{-6}$ - $2 \times 10^{-4}$	-335.9 (-494.8)
99	-263.7 (12)	-279.4 (0)	(-15.1) (92)	NL	-	
$\Delta E$ /mV(90% m/m)	-178.6	-177.9	180.0			

NL: Non-linear

( )\*: Tangential slope

( )\*\*:  $E^0$  normalised w.r.t. silver-silver chloride (d/j) electrode



Table 32

Change in potential (obtained by the 'indirect method') for the system, KF--1,4-dioxan( $H_2O$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M, and  $10^{-5}$  M in potassium fluoride and of various 1,4-dioxan concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m 1,4-dioxan	Potential/mV			Electrode slope /-mV per decade	LLLR (LR)*	$E^\circ$ /mV
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-35.6	16.9	72.6	54.1	$2 \times 10^{-6}$	-197.9
10	-50.7	0.9	54.0	52.6	$2 \times 10^{-6}$	-207.9
20	-69.2	-16.7	36.0	52.6	$2 \times 10^{-6}$	-227.0
40	-113.6	-62.6	-10.3	52.7	$2 \times 10^{-6}$	-271.7
60	-176.7	-127.0	-71.6	52.6	$2 \times 10^{-6}$	-334.5
80	-256.5 (-30)**	-218.2 (-46)**	-163.2 (-62)**	NL	$2 \times 10^{-6}$ - $2 \times 10^{-5}$	
90	-304.1 (-28)**	-269.5 (-49)**	-210.4 (-70)**	NL	-	
$\Delta E_{\max}/mV$	-268.5	-286.4	-283.0			

\*LR: linear region

( ) \*\*: tangential slope at the given concentration point.

Table 33

Change in potential (obtained by the 'indirect method') for the system, KF--EtOH(MeOH), in solutions of  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m ethanol	Potential/mV			Electrode slope /-mV per decade	LLRR
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>		
0	15	65	120	55	$2 \times 10^{-6}$
10	10	60	113	53	$5 \times 10^{-6}$
20	5	55	108	53	$5 \times 10^{-6}$
30	1	49	99	50	$6 \times 10^{-6}$
40	-7	44	94	50	$6 \times 10^{-6}$
50	-15	35	83	49	$6 \times 10^{-6}$
60	-22	26	71	48	$2 \times 10^{-5}$
70	-30	19	64	49	$2 \times 10^{-5}$
80	-40	9	51	49	$2 \times 10^{-5}$
90	-50	-2	42	48	$2 \times 10^{-5}$
95	-56	-8	33	48	$2 \times 10^{-5}$
99	-59	-12	30	47	$2 \times 10^{-5}$
$\Delta E_{\text{max/mV}}$	74	77	90		

Table 34

Change in potential (obtained by the 'indirect method') for the system, KF--HOAc(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m acetic acid	Potential/mV			Electrode slope/-mV per decade	-LLLRR	$E^0$ /mV
	$10^{-3}$ MF	$10^{-4}$ MF	$10^{-5}$ MF			
0	-151.2	-95.0	-37.2	58.5	$4 \times 10^{-6}$	-326.7
10	-52.3	46.5	118.6	96.0	$5 \times 10^{-5}$	-340.3
20	-24.6	72.4	141.3	96.0	$5 \times 10^{-5}$	-312.6
30	-5.1	90.0	155.3	96.0	$5 \times 10^{-5}$	-293.1
40	12.0	105.7	170.2	94.0	$5 \times 10^{-5}$	-270.0
50	26.9	119.2	180.9	94.0	$5 \times 10^{-5}$	-255.1
60	41.5	133.4	195.4	93.0	$5 \times 10^{-5}$	-237.5
70	52.4	146.0	209.7	94.0	$5 \times 10^{-5}$	-229.6
$\Delta E_{\max}/\text{mV}$	203.6	201.0	246.9			

Table 35

Change in potential (obtained by the 'indirect method') for the system, KF--n-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various n-propanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope/-mV per decade	LLRR (LR)*	$E^0$ /mV
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-163.6	-109.7	-57.5	53.1	$2 \times 10^{-6}$	-322.9
10	-168.1	-117.9	-72.0	50.2	$1 \times 10^{-5}$	-318.7
40	-187.6	-136.3	-85.7	51.3	$1 \times 10^{-5}$	-341.5
60	-205.3	-155.5	-112.5	50.0	$1 \times 10^{-5}$	-355.3
80	-228.3	-178.3	-124.2	52.1	$2 \times 10^{-6}$	-384.6
90	-245.0	-196.5	-147.8	49.0	$6 \times 10^{-6}$	-392.0
99	-261.3	-212.2	-158.5	52.0	$2 \times 10^{-6}$ - $2 \times 10^{-4}$	-420.2
$\Delta E_{\max}/mV$	-97.7	-102.5	-101.0			

\*LR: linear region

Table 36

Change in potential (obtained by the 'indirect method') for the system, KF--i-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various isopropanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope/mV per decade	LLLR	$E^0$ /mV
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-163.6	-109.7	-57.5	53.1	$2 \times 10^{-6}$	-322.9
10	-168.8	-117.1	-65.1	52.0	$2 \times 10^{-6}$	-324.8
40	-197.8	-145.8	-93.4	52.2	$2 \times 10^{-6}$	-354.4
60	-222.2	-170.8	-117.8	52.2	$2 \times 10^{-6}$	-378.8
80	-261.4	-212.8	-162.9	49.5	$2 \times 10^{-6}$	-409.9
90	-280.9	-236.9	-190.5	46.5	$2 \times 10^{-6}$	-420.4
99	-303.8	-263.2	-213.4	50.0	$2 \times 10^{-6}$ - $6 \times 10^{-4}$	-463.2
$\Delta E_{\text{max/mV}}$	-140.2	-153.5	-144.9			

Table 32

Change in potential (obtained by the 'indirect method') for the system, KF--acetone(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various acetone concentrations, measured by using lanthanum fluoride and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope/-mV per decade	LLRR	$E^0/\text{mV}$ **
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-65.1	-13.3	45.0	55.1	$2 \times 10^{-6}$	-230.4 (-311.3)
10	-73.3	-22.2	33.2	53.3	$2 \times 10^{-6}$	-233.2 (-321.1)
40	-100.8	-49.4	5.5	53.2	$2 \times 10^{-6}$	-260.4 (-368.8)
60	-133.1	-81.5	-24.4	54.4	$2 \times 10^{-6}$	-296.3 (-421.8)
80	-187.0	-135.2	-79.2	55.0	$2 \times 10^{-6}$	-352.0 (-509.1)
90	-240.8	-193.5	((-15.6))	47.3	$7 \times 10^{-5}$	-382.7 (-550.3)
99	-315.9(+10) <sup>†</sup>	-320.2(-10) <sup>†</sup>	((-28)) ( $\infty$ )	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	-250.8	-306.9	-73			

NL: Non-linear

( )\*: tangential slope

( )\*\*:  $E^0$  normalised w.r.t. silver-silver chloride, (double-junction) electrode)

(( )): unstable

Table 38

Change in potential (obtained by the 'indirect method') for the system, KF--1,4-dioxan(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in potassium fluoride and of various 1,4-dioxan concentrations, measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

% m/z Dioxan	Potential/mV			Electrode slope -mV / decade	LLRR (LR)	E°/mV
	$10^{-3}$ MF <sup>-</sup>	$10^{-4}$ MF <sup>-</sup>	$10^{-5}$ MF <sup>-</sup>			
0	-207.2	-155.2	-99.2	54.0	$2 \times 10^{-6}$	-369.2
20	-189.9	-141.2	-89.2	50.4	$5 \times 10^{-6}$	-341.1
40	-221.5	-176.9	-130.	45.5	$4 \times 10^{-6}$	-358.0
60	-264.6	-225.1	-175.0	50.1	$2 \times 10^{-6}$ - $2 \times 10^{-4}$	-425.5
80	-320.3	-290.8	-252.3	43.6	$2 \times 10^{-6}$ - $2 \times 10^{-5}$	-470.3
85	-309.6	-282.5	-245.3	27.1	$5 \times 10^{-5}$	
90	-363.8 (-20)*	-328.6 (-70)*	-206.1 (+10)*	NL		
$\Delta E_{\max}/mV$	-156.6	-173.4	-106.9			

LR: linear region

( )\* tangential slope

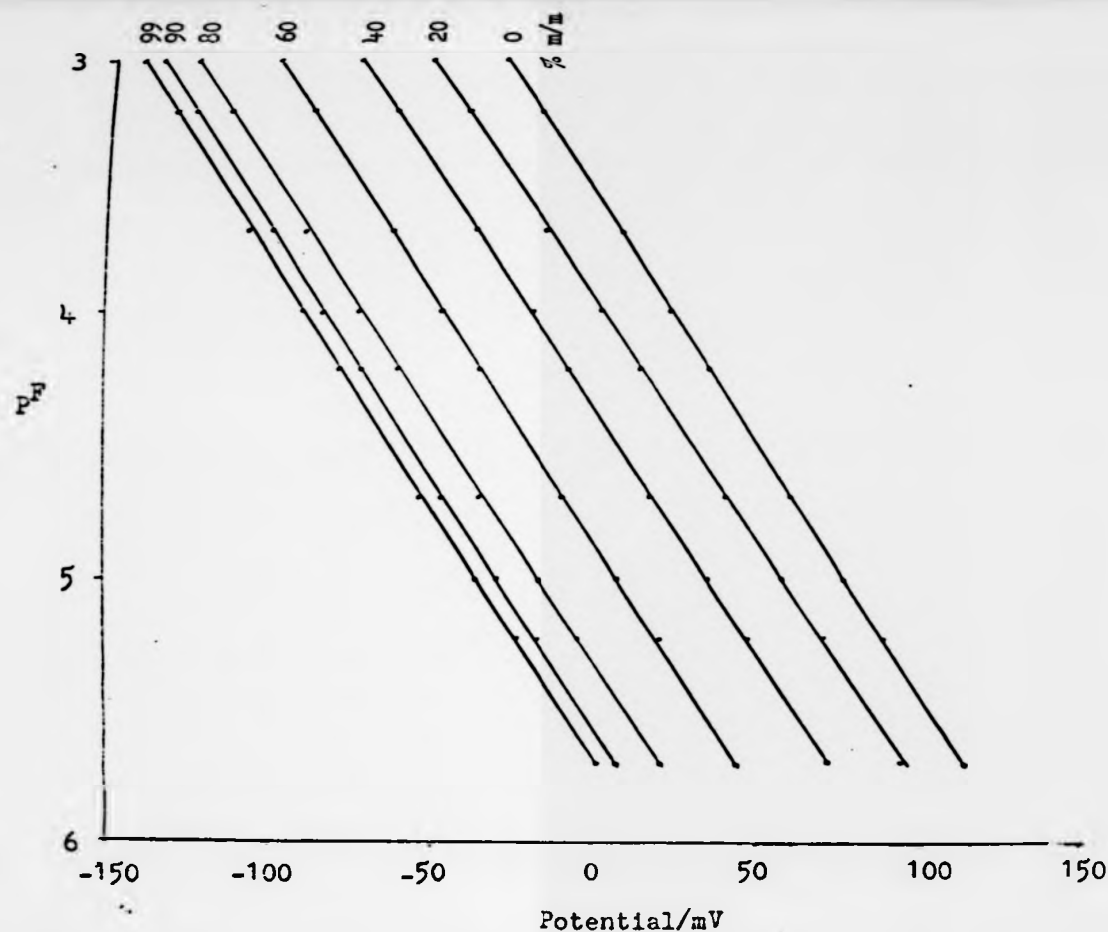


Fig. 14 Electrode calibration graphs for the system,  $\text{KF—MeOH(H}_2\text{O)}$ , in solutions of constant methanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



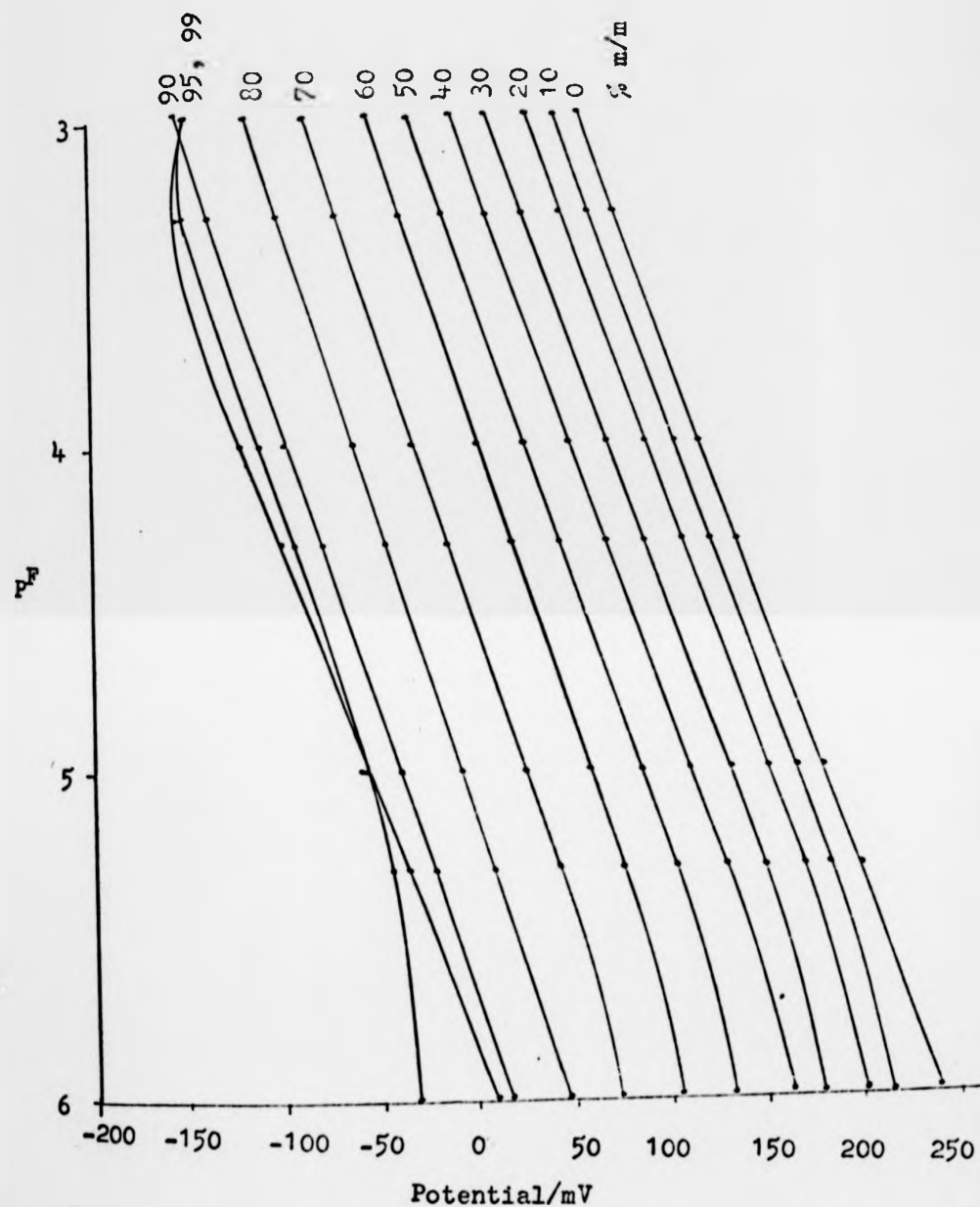


Fig. 15 Electrode calibration graphs for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of constant ethanol concentration and various sodium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

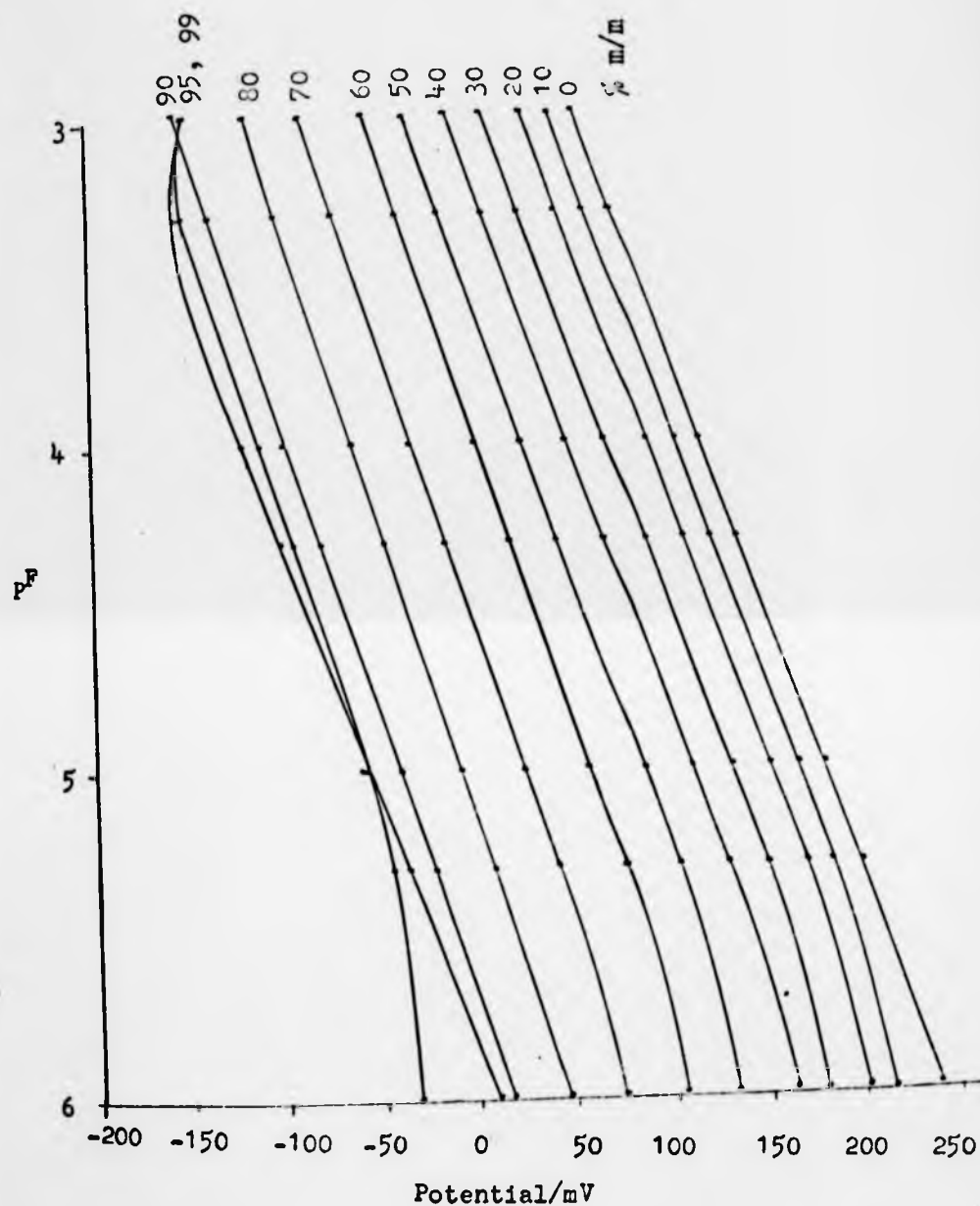


Fig. 15 Electrode calibration graphs for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of constant ethanol concentration and various sodium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

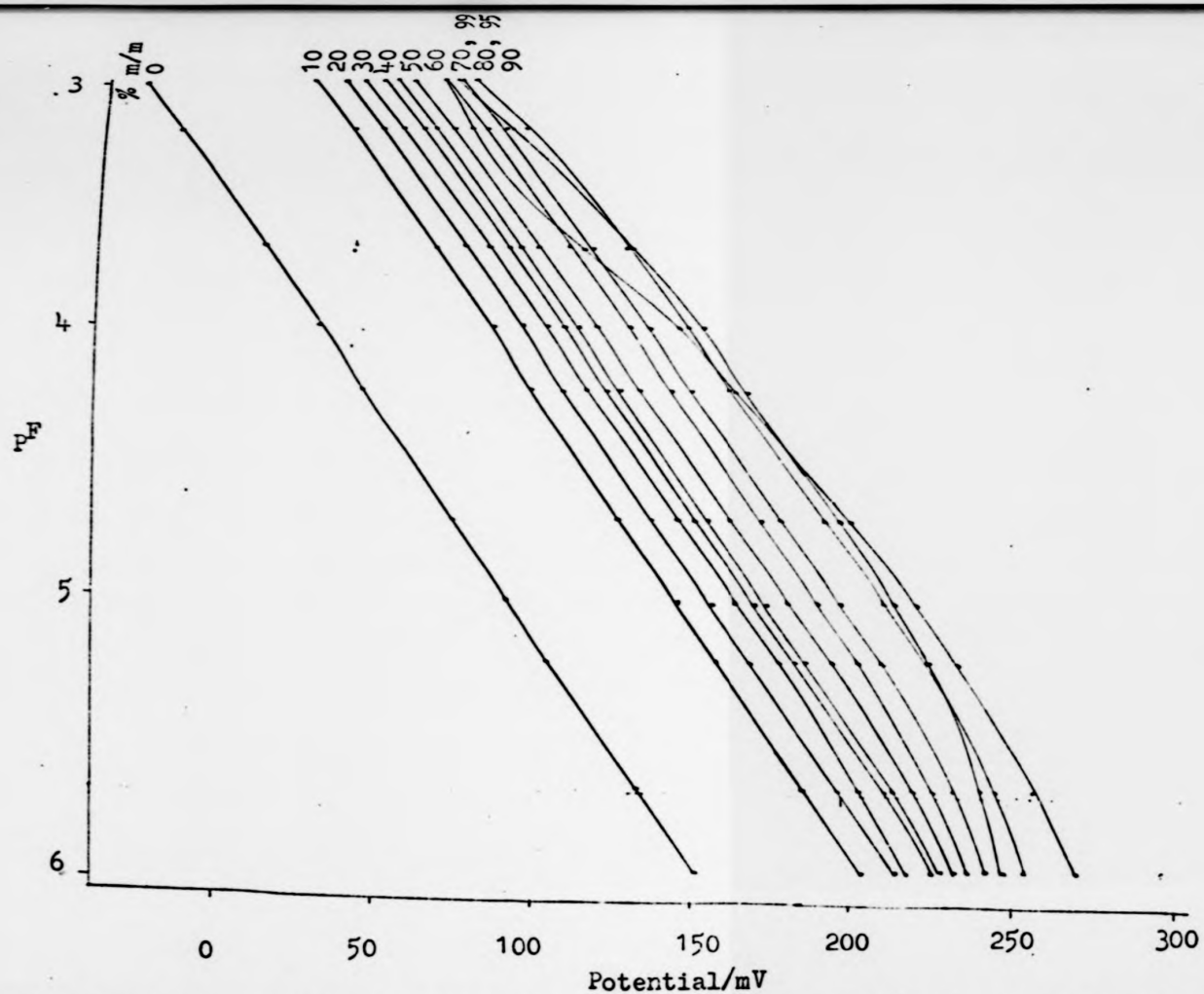


Fig.16 Electrode calibration graphs for the system,  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of constant acetic acid concentration and various sodium chloride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

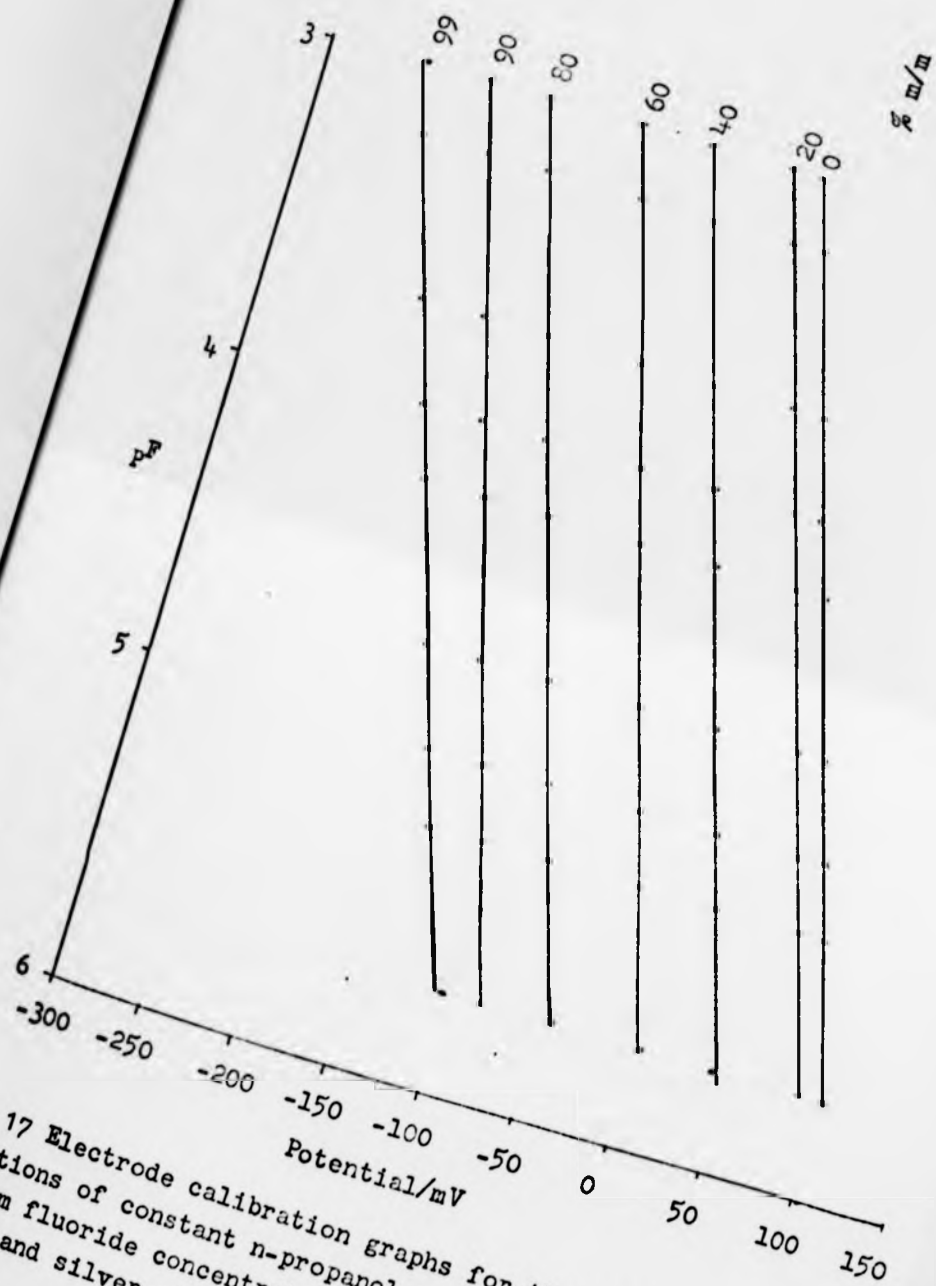


Fig. 17 Electrode calibration graphs for the system, KF-n-ProH(H<sub>2</sub>O), in solutions of constant n-propanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

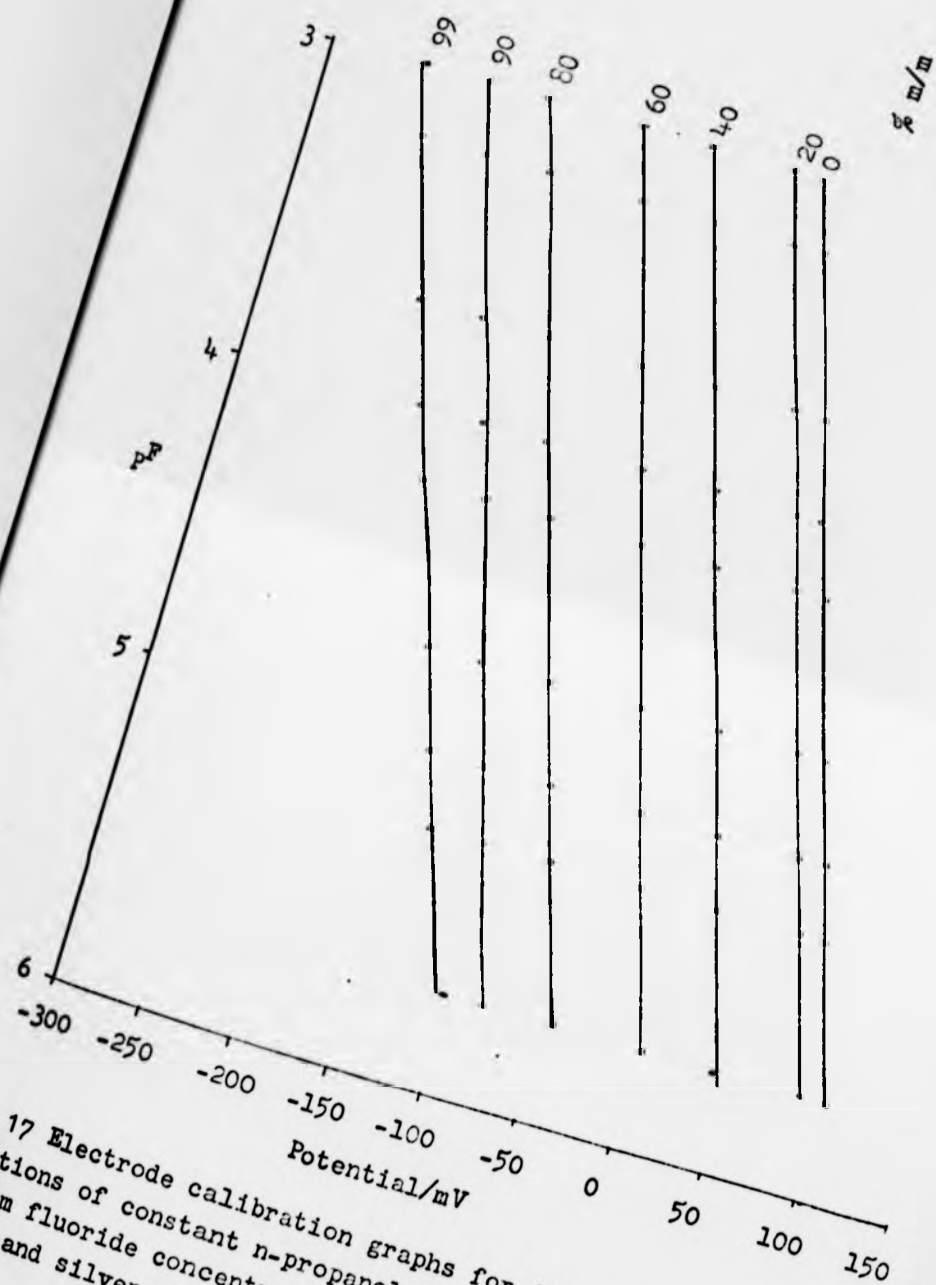


Fig. 17 Electrode calibration graphs for the system,  $\text{KF-n-PrOH(H}_2\text{O)}$ , in solutions of constant n-propanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

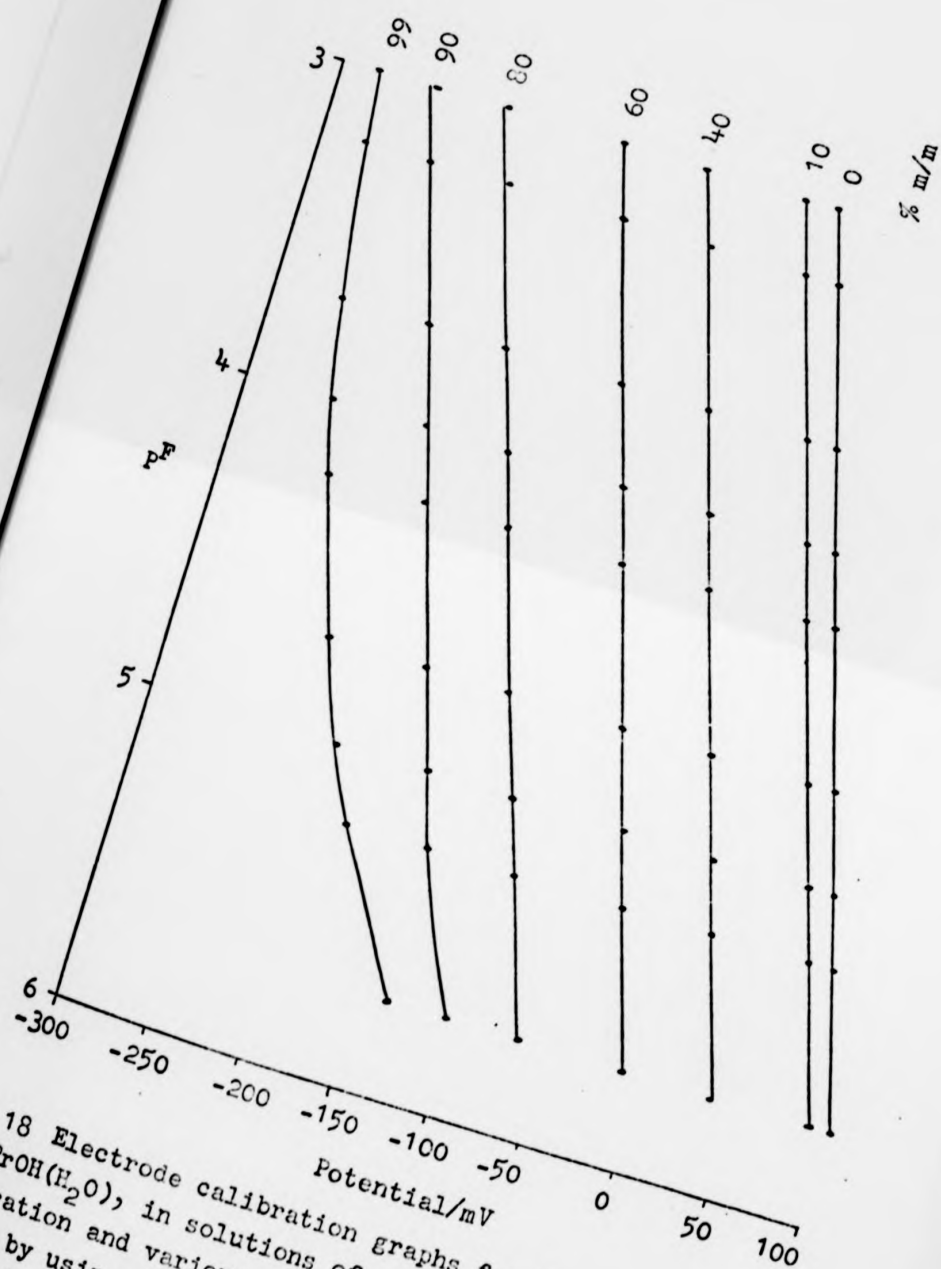


Fig. 18 Electrode calibration graphs for the system, KF-i-PrOH( $H_2O$ ), in solutions of constant iso-propanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



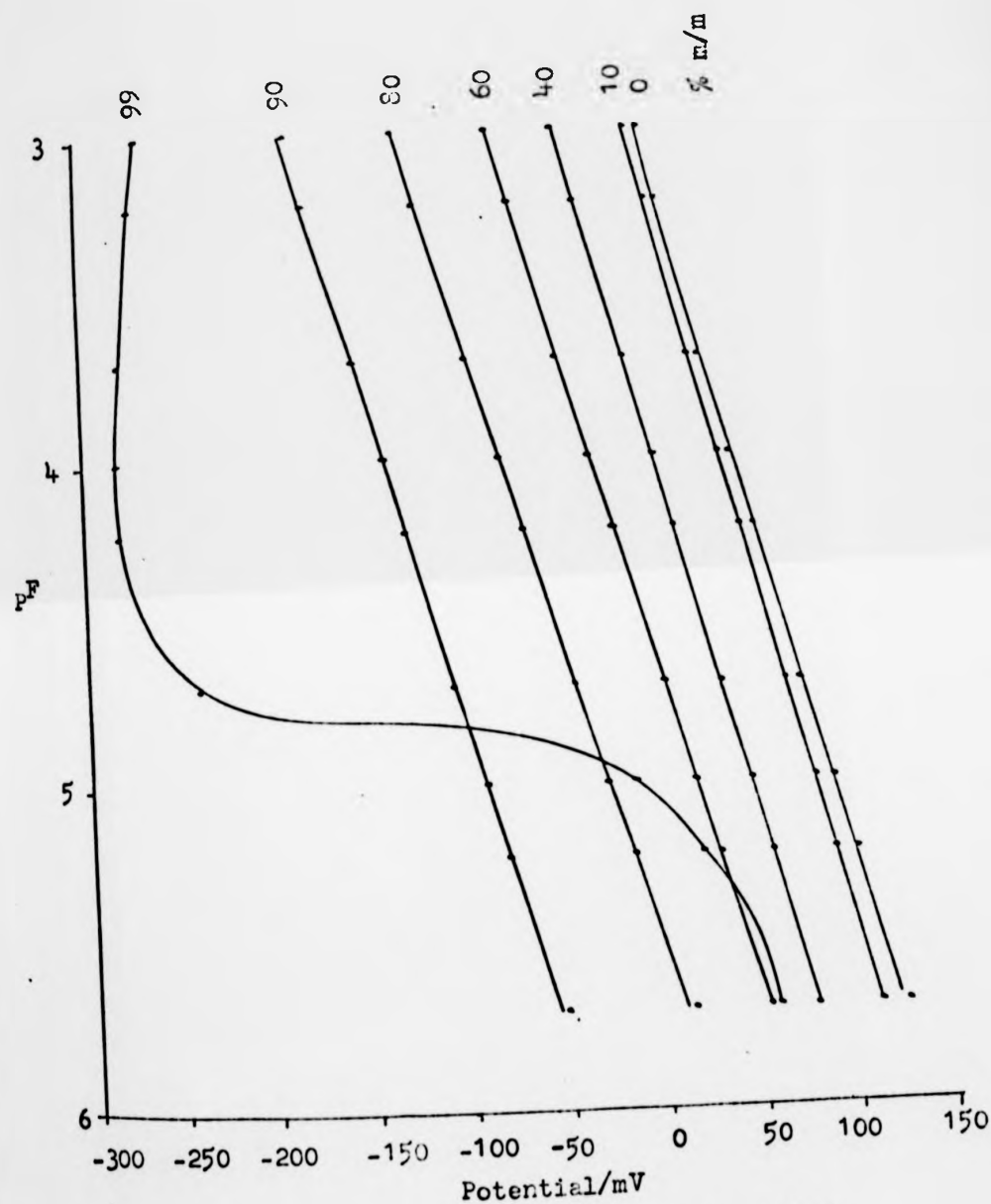


Fig. 19 Electrode calibration graphs for the system, KF-acetone(H<sub>2</sub>O), in solutions of constant acetone concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and SCE(LiCl) electrodes.

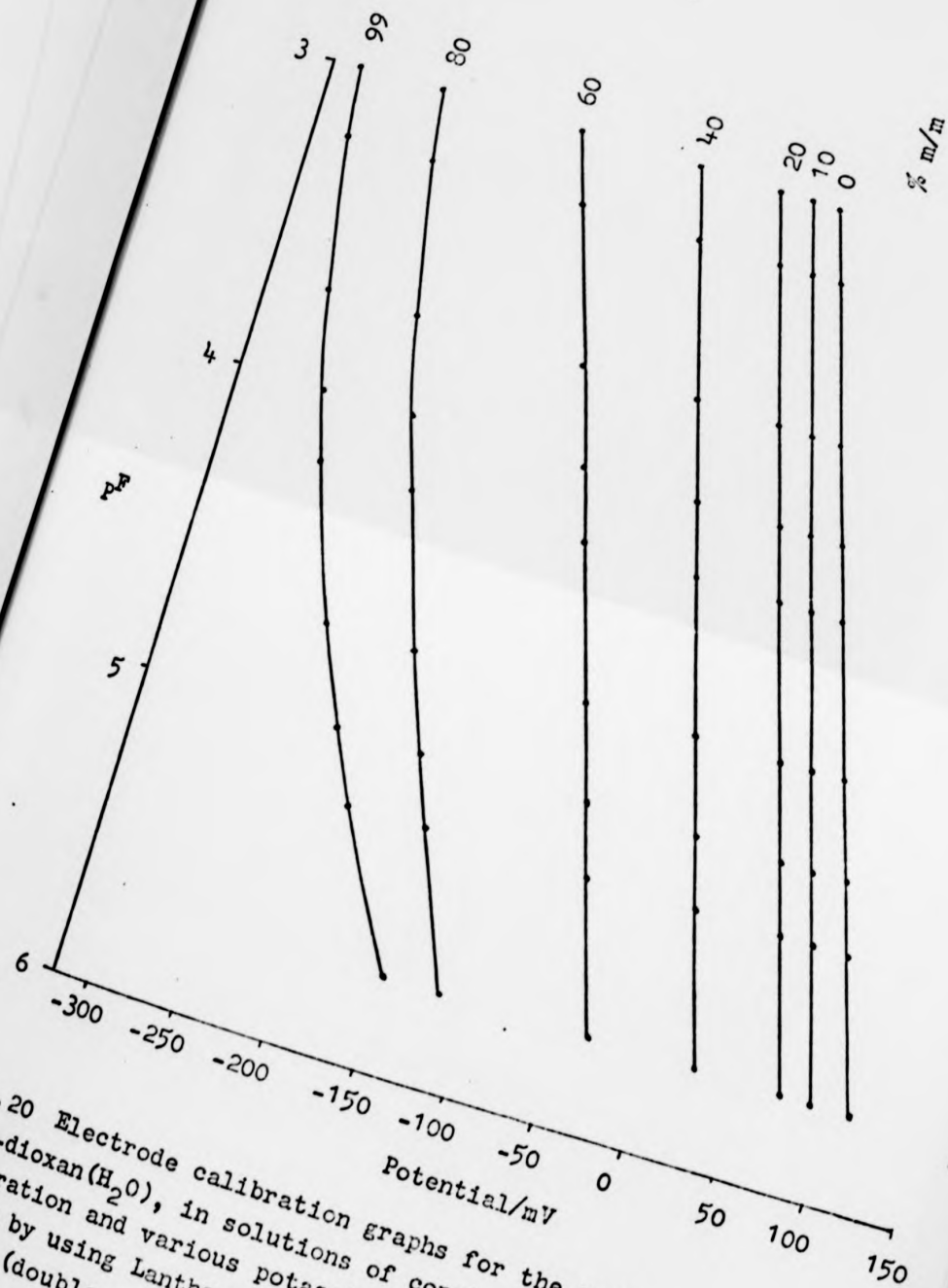


Fig. 20 Electrode calibration graphs for the system, KF-1,4-dioxan( $H_2O$ ), in solutions of constant 1,4-dioxan concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



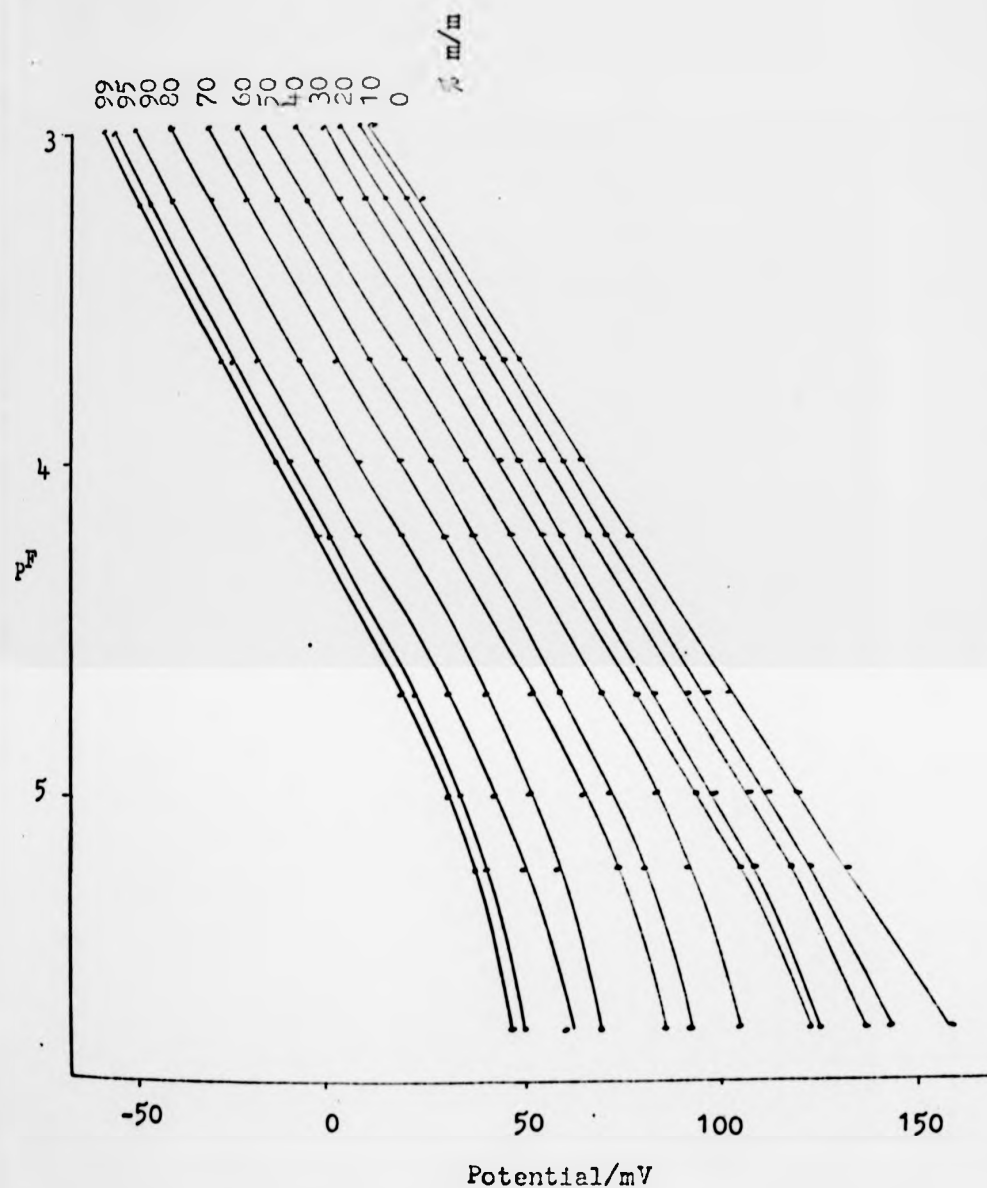


Fig.21 Electrode calibration graphs for the system, KF-EtOH(MeOH), in solutions of constant ethanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

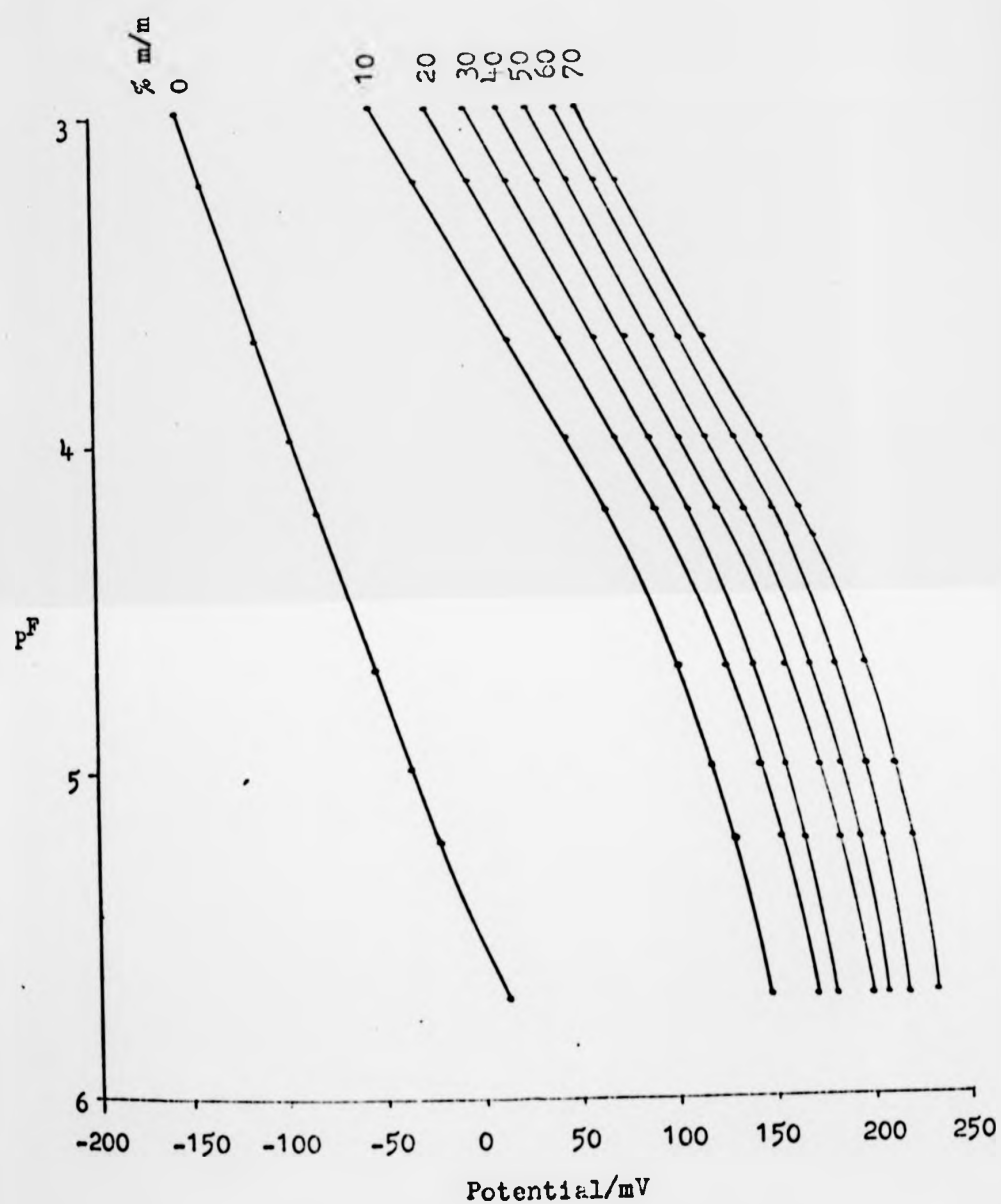


Fig. 22 Electrode calibration graphs for the system, KF-HOAc (MeOH), in solutions of constant acetic acid concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



Fig. 23 Electrode calibration graphs for the system, KF-n-PrOH (MeOH), in solutions of constant n-propanol and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



Fig. 24 Electrode calibration graphs for the system, KF-1-PrOH(MeOH), in solutions of constant iso-propanol concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

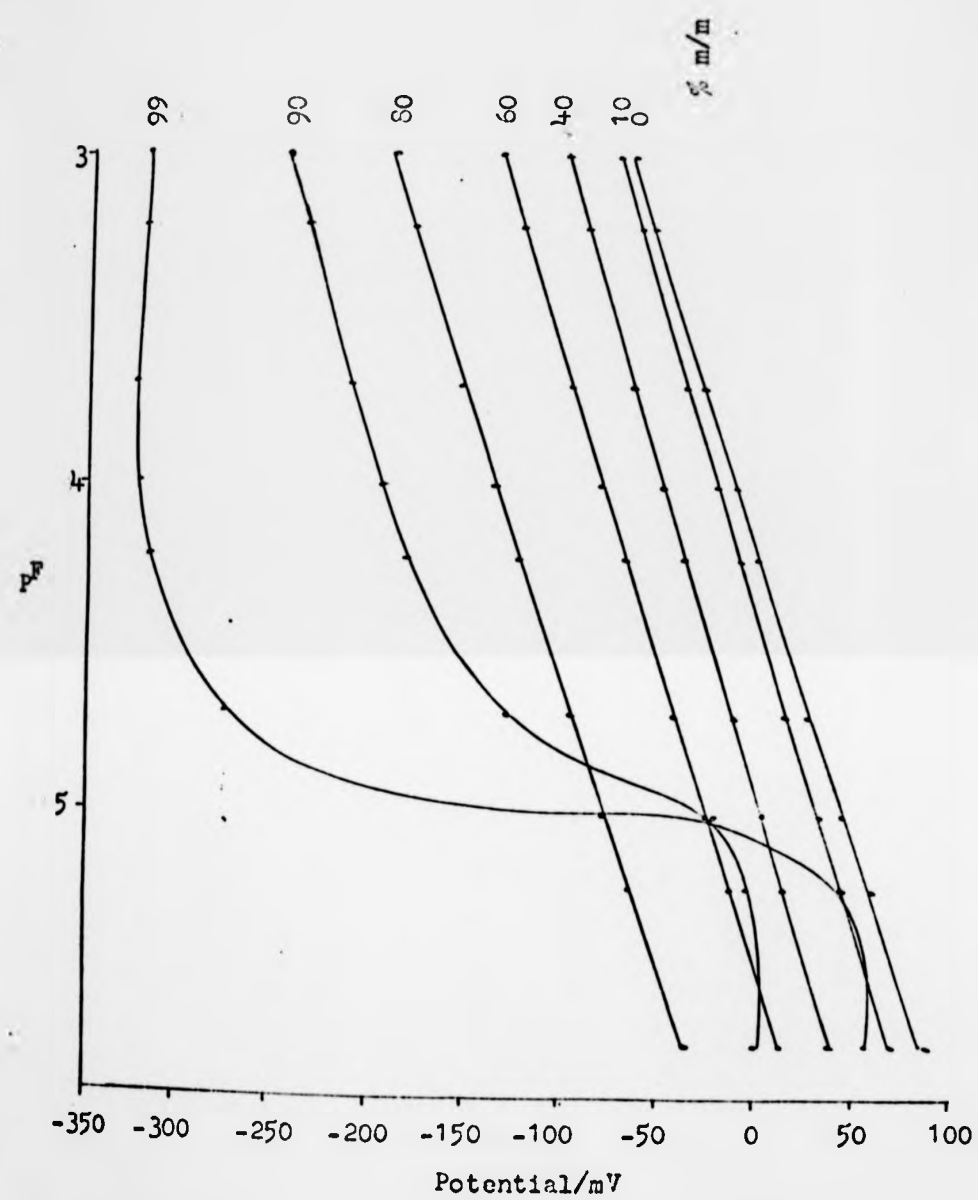


Fig. 25 Electrode calibration graphs for the system, KF-acetone (MeOH), in solutions of constant acetone concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and SCE (LiCl) electrodes.

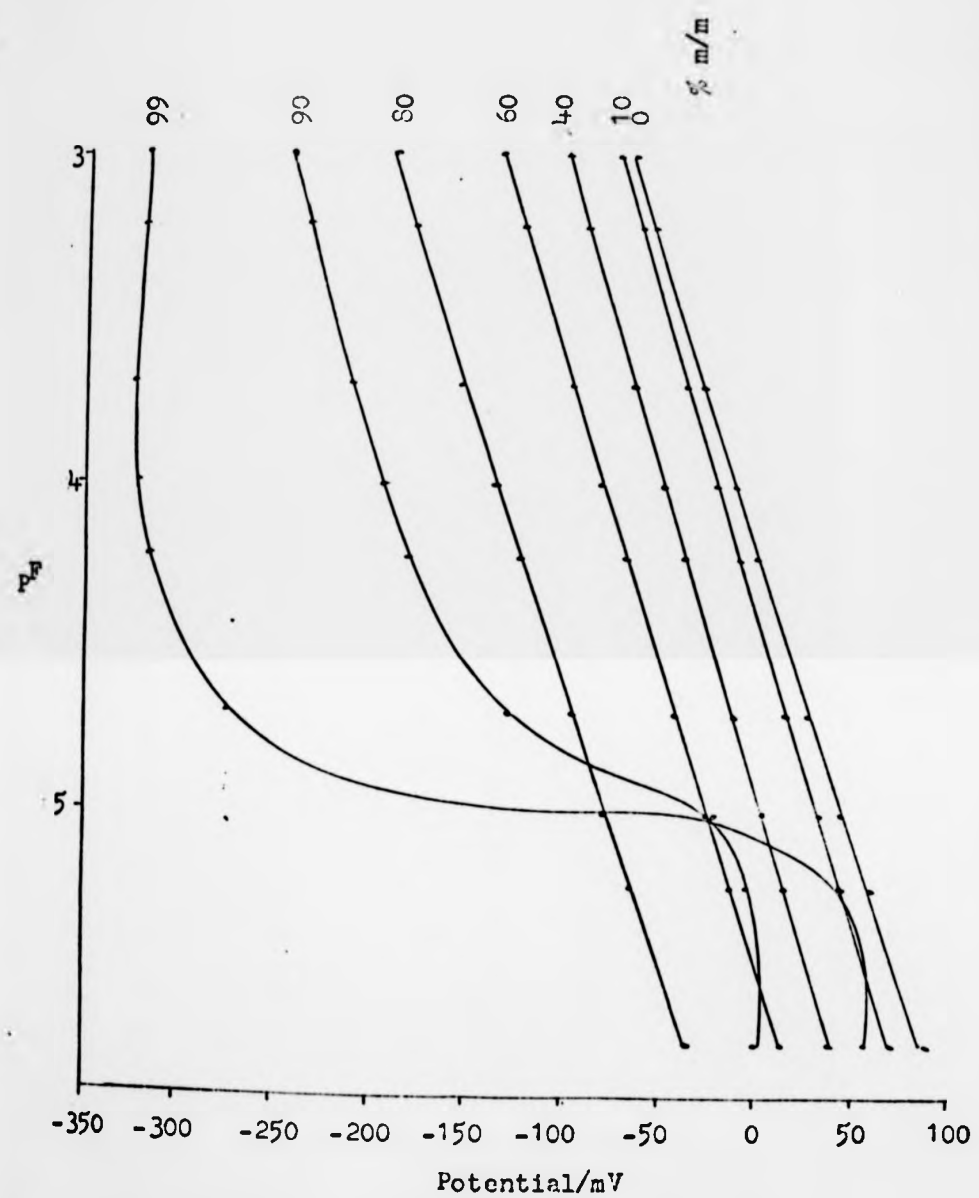


Fig. 25 Electrode calibration graphs for the system, KF-acetone (MeOH), in solutions of constant acetone concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and SCE (LiCl) electrodes.

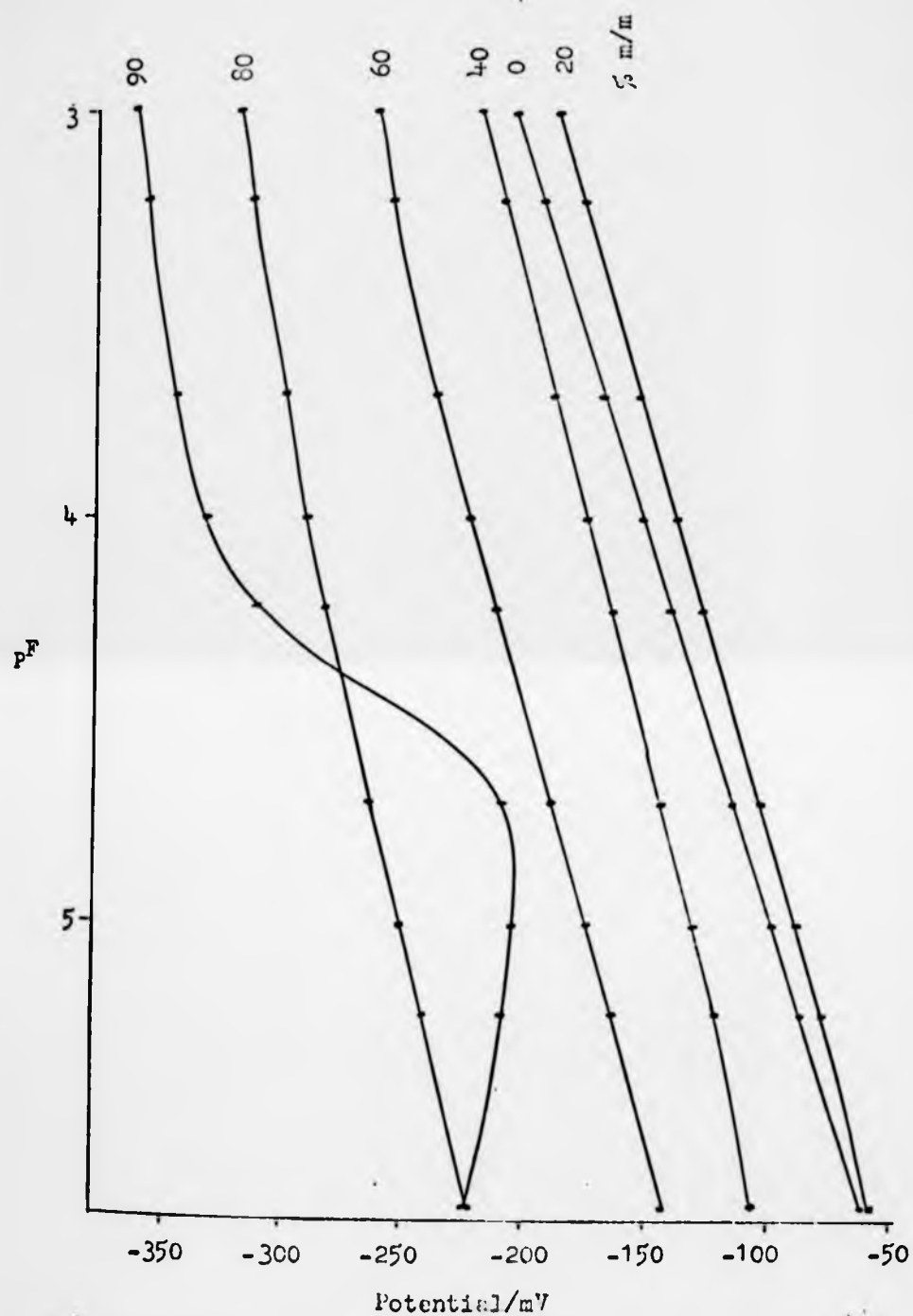


Fig. 26 Electrode calibration graphs for the system, KF-1,4-dioxan(MeCH), in solutions of constant 1,4-dioxan concentration and various potassium fluoride concentrations, measured by using Lanthanum fluoride and silver-silver chloride (double-junction) electrodes.



### 2.1.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 39

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{KF}-\text{EtOH}(\text{H}_2\text{O})$  and  $\text{KF}-\text{EtOH}(\text{MeOH})$ , in  $10^{-3}$  M solutions of potassium fluoride for various ethanol concentrations measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

ethanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect*		Direct	Indirect	
0	0	0	0	0	0	0
10	-14.3	-12	-2	-5	-5	0
20	-29.6	-29	-1	-11	-10	-1
30	-46.6	-56	9	-16	-16	0
40	-64.2	-67	3	-23	-21	-2
50	-86.6	-89	2	-30	-30	0
60	-106.1	-111	4	-39	-39	0
70	-128.1	-144	16	-47	-46	-1
80	-150.7	-172	21	-57	-56	-1
90	-175.1	-209	24	-69	-67	-2
95	-187.5	-207	20	-74	-73	-1
99	-195.0	-200	5	-80	-77	-3

(1). \* Silver-silver chloride (single-junction) reference electrode was used.

(2). NaF was used instead of KF.



Table 40

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{KF}-\text{HOAc}(\text{H}_2\text{O})$  and  $\text{KF}-\text{HOAc}(\text{MeOH})$ , in  $10^{-3}$  M solutions of potassium fluoride for various acetic acid concentrations measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

acetic acid % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV}(\text{MeOH})$		$\Delta\Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect*		Direct	Indirect	
0	0	0	0	0	0	0
10	53.9	54	0	147.4	141.5	5.9
20	63.4	64	-1	175.0	167.4	7.6
30	70.8	70	-1	195.3	185.0	10.3
40	75.9	76	0	212.5	200.7	11.8
50	81.0	81	0	227.2	214.2	13.0
60	89.4	86	3	240.6	228.4	12.2
70	98.3	96	2	252.3	241.0	11.3
80	108.9	101	8	254.6		#
90	113.7	105	9	253.3	#	#
95	106.3	100	6	250.6	#	#
99	94.6	96	-1	246.2		

(1). \*  $\text{NaF}$  was used for indirect measurement.

(2)\* No measurement made.

Table 41

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system, KF- n-PrOH(H<sub>2</sub>O) and KF- n-PrOH(MeOH), in 10<sup>-3</sup> M solutions of potassium fluoride for various n-propanol concentrations measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta\Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta\Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
10	-15.3	-15.9	0.6	-6.1	-4.5	-1.6
40	-58.7	-58.4	-0.3	-26.7	-24.0	-2.7
60	-95.5	-94.9	-0.6	-44.3	-41.7	-2.6
80	-151.5	-145.0	-6.5	-69.2	-64.7	-4.5
90	-186.3	-177.2	-9.1	-86.4	-81.4	-5.0
99	-222.9	-210.0	-12.9	-103.3	-97.7	-5.6

Table 42

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system, KF-1-PrOH(H<sub>2</sub>O) and KF-1-PrOH(MeOH) in 10<sup>-3</sup> M solutions of potassium fluoride for various iso-propanol concentrations measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes

iso-propanol % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta \Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
10	-15.8	-17.0	1.2	-9.7	-5.2	-4.5
40	-66.5	-68.8	2.3	-38.0	-34.2	-3.8
60	-114.7	-113.8	-0.9	-67.4	-58.6	-8.8
80	-177.6	-172.9	-4.7	-108.5	-97.8	-10.7
90	-224.5	-212.3	-12.2	-135.4	-117.3	-18.1
99	-278.2	-244.8	-33.4	-166.1	-140.2	-25.9

Table 43

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system, KF-acetone(H<sub>2</sub>O) and KF-acetone(MeOH), in 10<sup>-3</sup> M solutions of potassium fluoride for various acetone concentrations measured by using lanthanum fluoride and SCE(LiCl) electrodes.

acetone % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta \Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
10	-10.2	-6.0	-4.2	-12.1	-8.2	-3.9
40	-45.7	-43.6	-2.1	-42.3	-35.7	-6.6
60	-82.8	-78.4	-4.4	-74.2	-68.0	-6.2
80	-138.9	-126.4	-12.5	-129.3	-121.9	-7.4
90	-207.7	-178.6	-29.1	-192.4	-175.7	-16.7
99	-330.4	-260.0	-70.4	-254.1	-250.8	-3.3

Table 43

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system, KF-acetone(H<sub>2</sub>O) and KF-acetone(MeOH), in 10<sup>-3</sup> M solutions of potassium fluoride for various acetone concentrations measured by using lanthanum fluoride and SCE(LiCl) electrodes.

acetone % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta \Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
10	-10.2	-6.0	-4.2	-12.1	-8.2	-3.9
40	-45.7	-43.6	-2.1	-42.3	-35.7	-6.6
60	-82.8	-78.4	-4.4	-74.2	-68.0	-6.2
80	-138.9	-126.4	-12.5	-129.3	-121.9	-7.4
90	-207.7	-178.6	-29.1	-192.4	-175.7	-16.7
99	-330.4	-260.0	-70.4	-254.1	-250.8	-3.3

Table 44

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system, KF-1,4-dioxan(H<sub>2</sub>O) and KF-1,4-dioxan(MeOH), in 10<sup>-3</sup> M solutions of potassium fluoride for various 1,4-dioxan concentrations measured by using lanthanum fluoride and silver-silver chloride (double-junction) electrodes.

1,4-dioxan % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta\Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta\Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	5.1	-33.6	38.7	12.1	17.3	-5.2
40	-11.8	-78.0	66.2	0.2	-14.2	14.0
60	-55.0	-141.1	86.1	-27.6	-57.4	29.9
80	-114.1	-220.9	106.8	-54.6	-113.1	58.5
90	-154.0	-268.5	114.5	-74.8	-156.6	81.8

\* Analar grade of 1,4-dioxan was used for indirect measurements, whereas ordinary laboratory grade was used for direct measurement.

2.2      CHLORIDE ION

2.2.1    Direct Measurements

2.2.2    Indirect Measurements

2.2.3    Comparison of Direct and Indirect Measurements.

# 2.2.1 DIRECT MEASUREMENTS

Table 45

Comparison of changes in potential,  $\Delta E$ , for a given cell system (silver chloride/silver-silver chloride d/i.  $10^{-3}$  M tetraethylammonium chloride) and various solvent concentrations in different solvent-water mixtures.

Solvent % m/m	$\Delta E/mV$						
	MeOH	EtOH	HOAc	n-PrOH	i-PrOH	acetone**	1,4-dioxan
0	0(121.4)	0*	0*	0(116.9)	0(90.5)	0(-216.4)	0(112.5)
10	-4.4	-14	-7	-8.2	-4.8	3.2	-2.1
20	-10.4	-27	-13	-16.0	-11.7	0.5	-9.6
30	-17.0	-38	-19	-27.2	-20.8	-3.9	-20.0
40	-24.8	-51	-27	-38.8	-30.2	-11.7	-31.5
50	-35.6	-70	-39	-52.8	-47.7	-22.5	-46.1
60	-46.6	-86	-51	-70.6	-65.5	-42.5	-69.0
70	-60.5	-99	-64	-87.0	-85.6	-66.0	-93.2
80	-71.3	-108	-81	-105.3	-109.7	-100.6	-123.9
90	-79.3	-130	-112	-126.0	-126.0	-162.6	-165.1
95	-84.9	-146	-139	-137.9	-157.8	-213.4	-200.5
99	-83.6	-160	-149	-146.5	-174.5	-250.0	-282.5

(1).\*\* SCE(LiCl) reference electrode was used. (2) \* Absolute potential not available.



Table 46

Comparison of changes in potential,  $\Delta E$ , for a given cell system (silver chloride/silver-silver chloride d/i.  $10^{-3}$  M tetraethylammonium chloride) and various solvent concentrations in different solvent-methanol mixtures

Solvent % m/m	$\Delta E/mV$				
	EtCH	HOAc	n-PrOH	i-PrOH	acetone
0	0*	*0(88.1)	0(17.3)	0(25.6)	0(-272.6)
10	-2	3.5	-5.4	-6.6	-5.6
20	-7	-0.1	-11.0	-13.3	-12.4
30	-12	-2.9	-16.7	-20.1	-19.7
40	-18	-6.5	-23.3	-28.0	-27.2
50	-24	-9.1	-30.2	-38.4	-37.9
60	-29	-14.7	-35.5	-49.8	-55.1
70	-35	-22.6	-43.9	-62.6	-72.6
80	-41	-33.4	-54.1	-77.3	-98.1
90	-48	-57.1	-66.2	-95.8	-143.0
95	-48	-76.2	-74.5	-107.5	-173.0
99	-51	-94.3	-78.6	-117.0	-217.6

\*Absolute potential not available.

\* Lead acetate used.

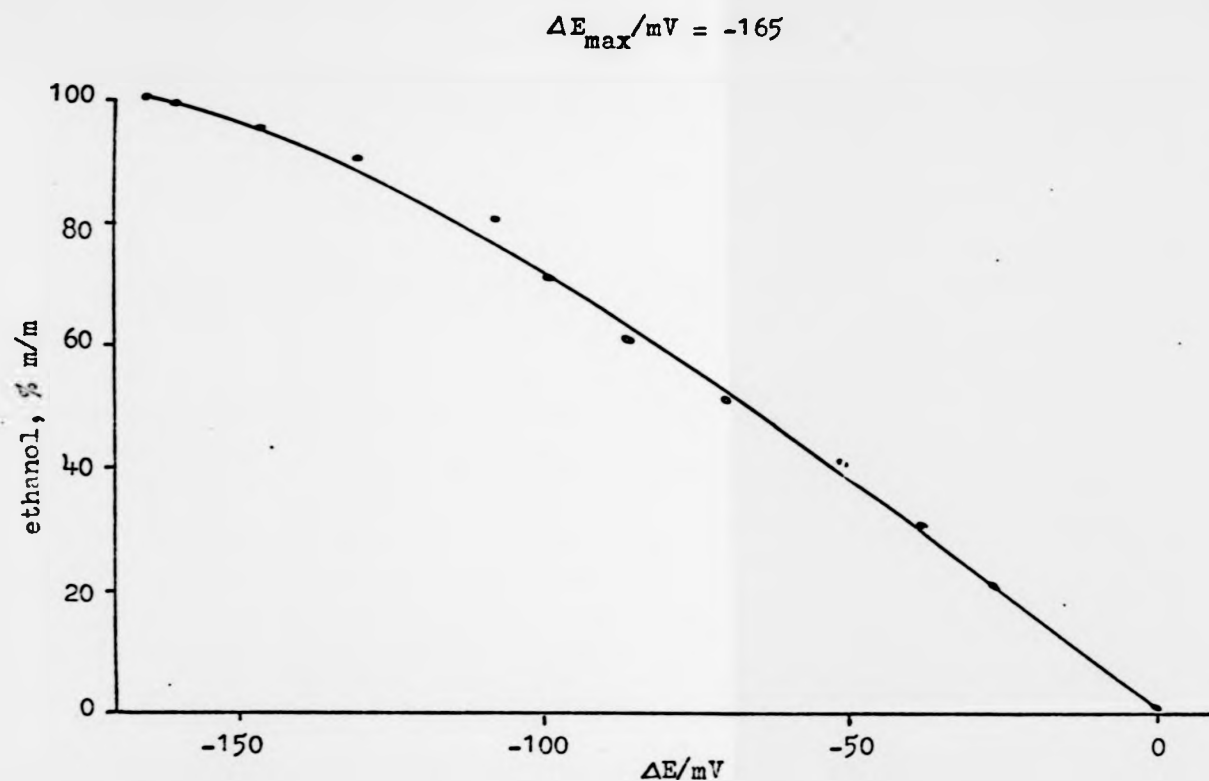


Fig. 27 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various ethanol concentrations, measured by using silver chloride and silver-silver chloride (single-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = -149$$

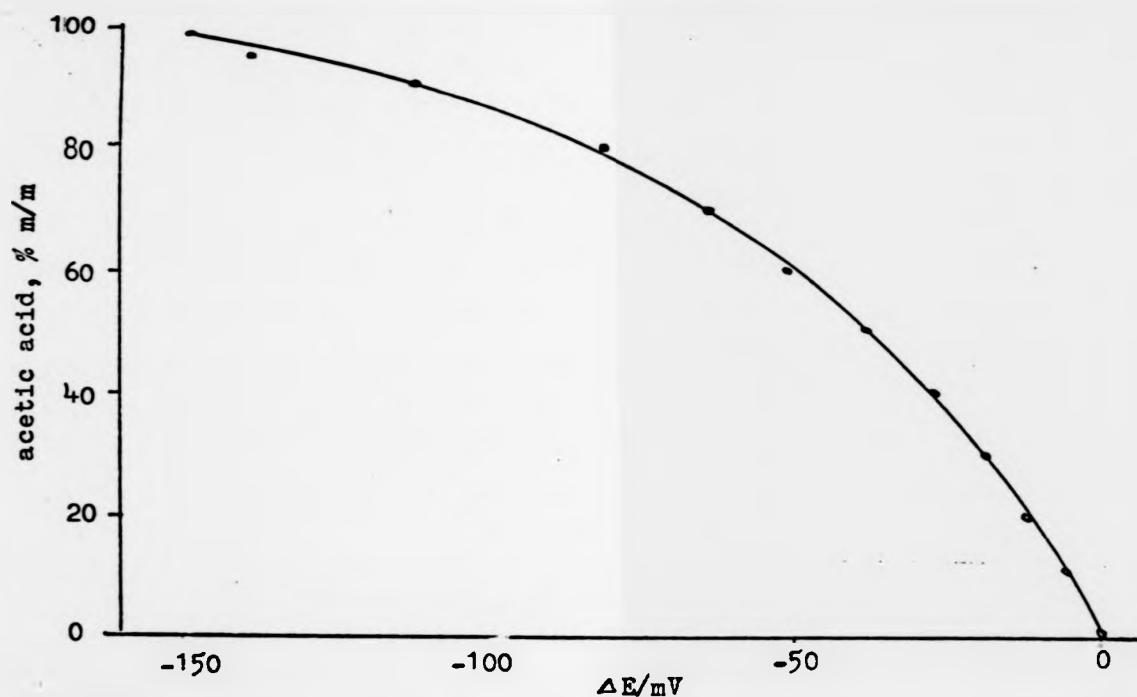


Fig. 28 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (single-junction) electrodes.

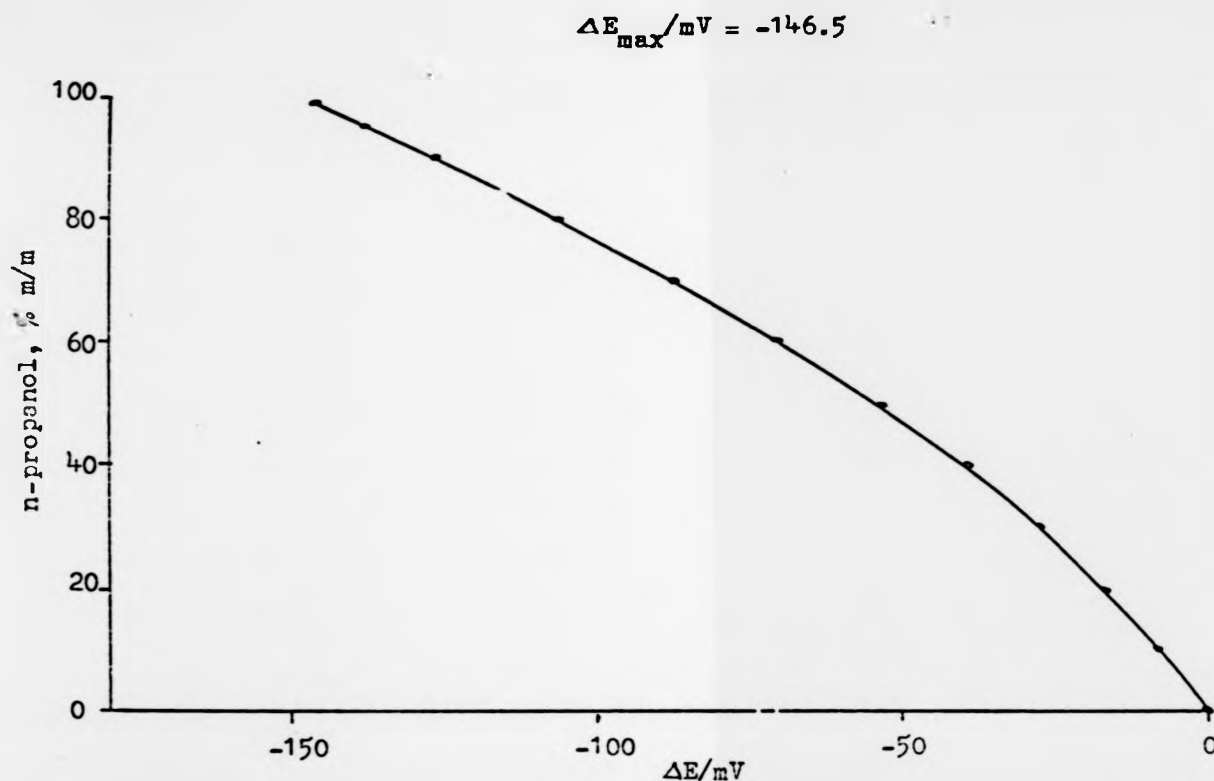


Fig. 29 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-n\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M tetraethylammonium chloride and various n-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

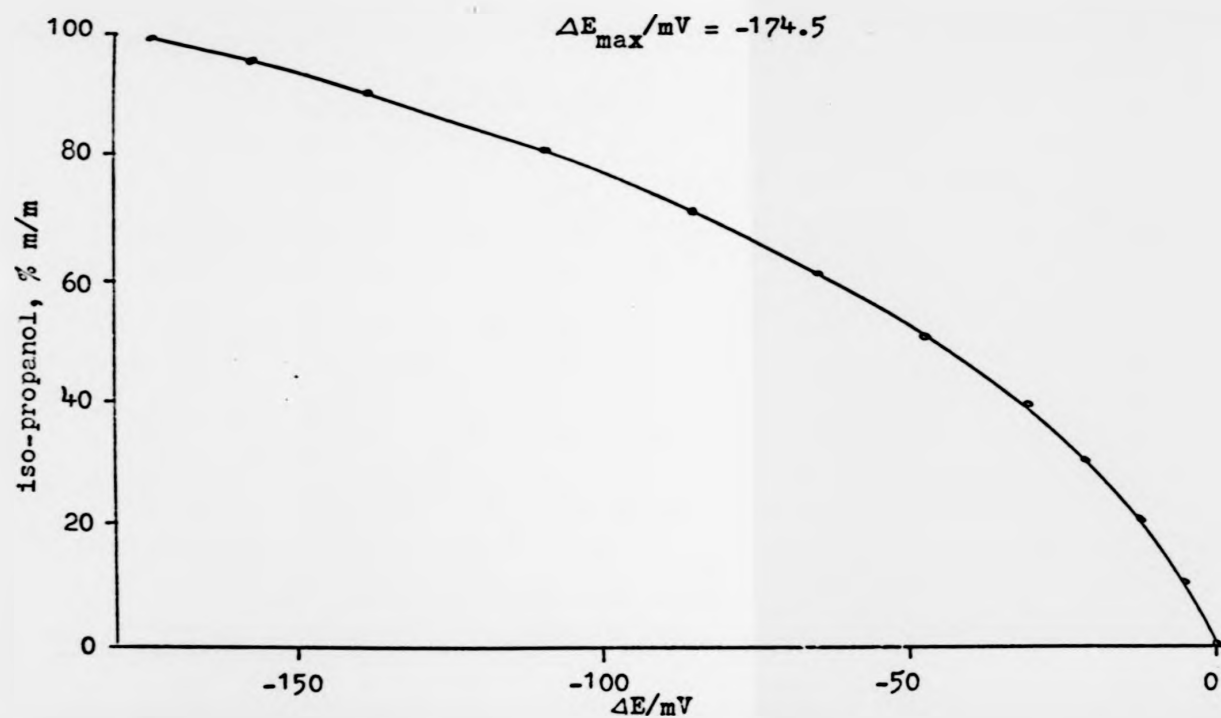


Fig. 30 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-i\text{-PrOH}(\text{H}_2\text{O})_m$  in solutions of  $10^{-3}$  M tetraethylammonium chloride and various iso-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

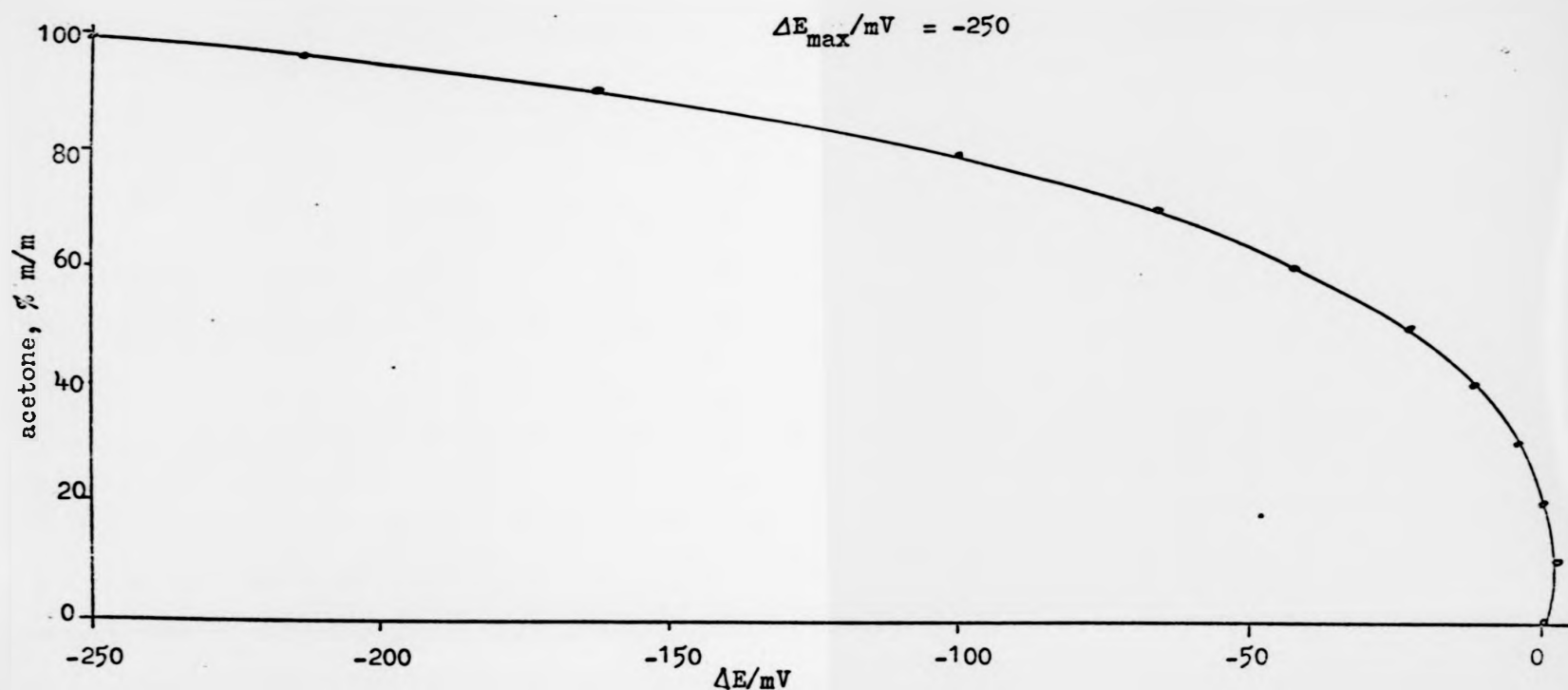


Fig. 31a Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}$ -acetone( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M tetraethylammonium chloride and various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

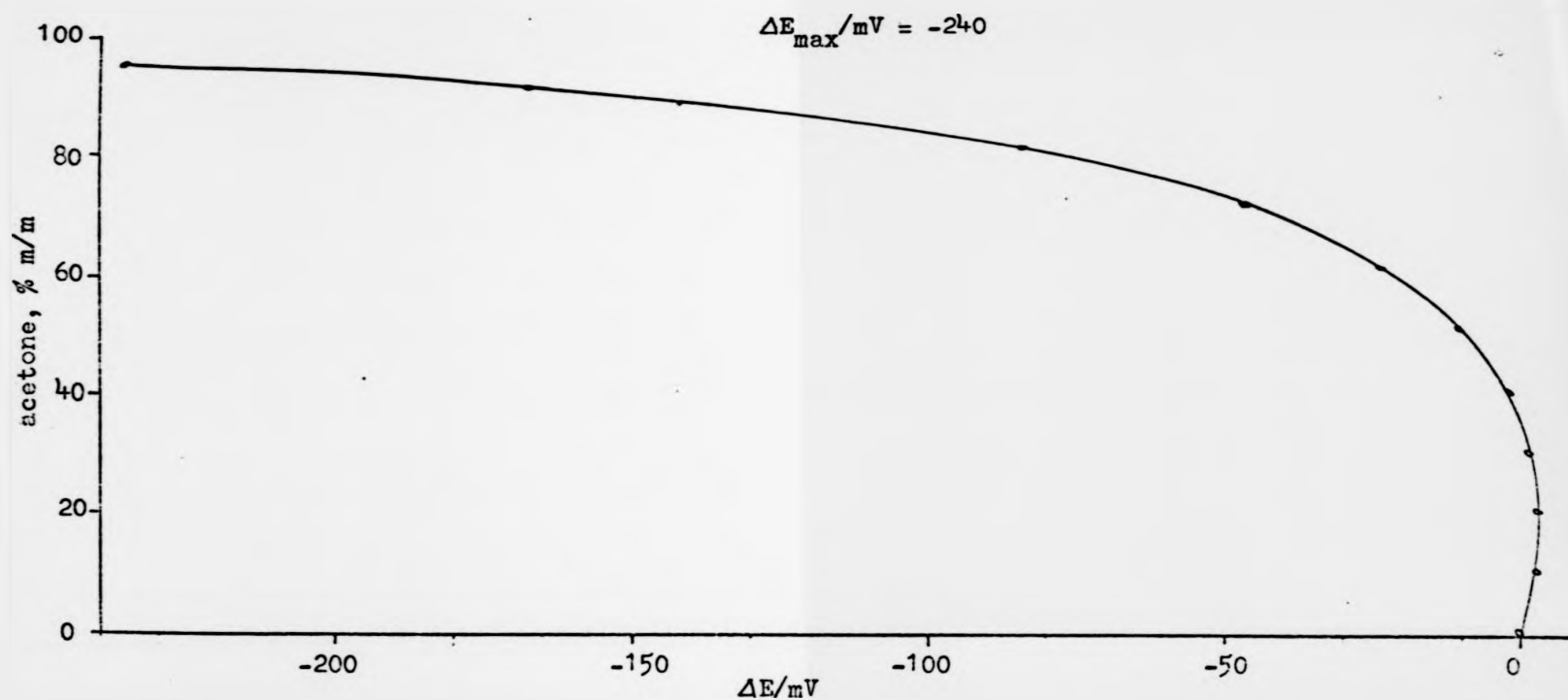


Fig. 31b Change in potential,  $\Delta E$ , for the system, NaCl-acetone( $\text{H}_2\text{O}$ ), in solutions, of  $10^{-3}$  M sodium chloride and various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

$$\Delta E_{\max}/\text{mV} = -51$$

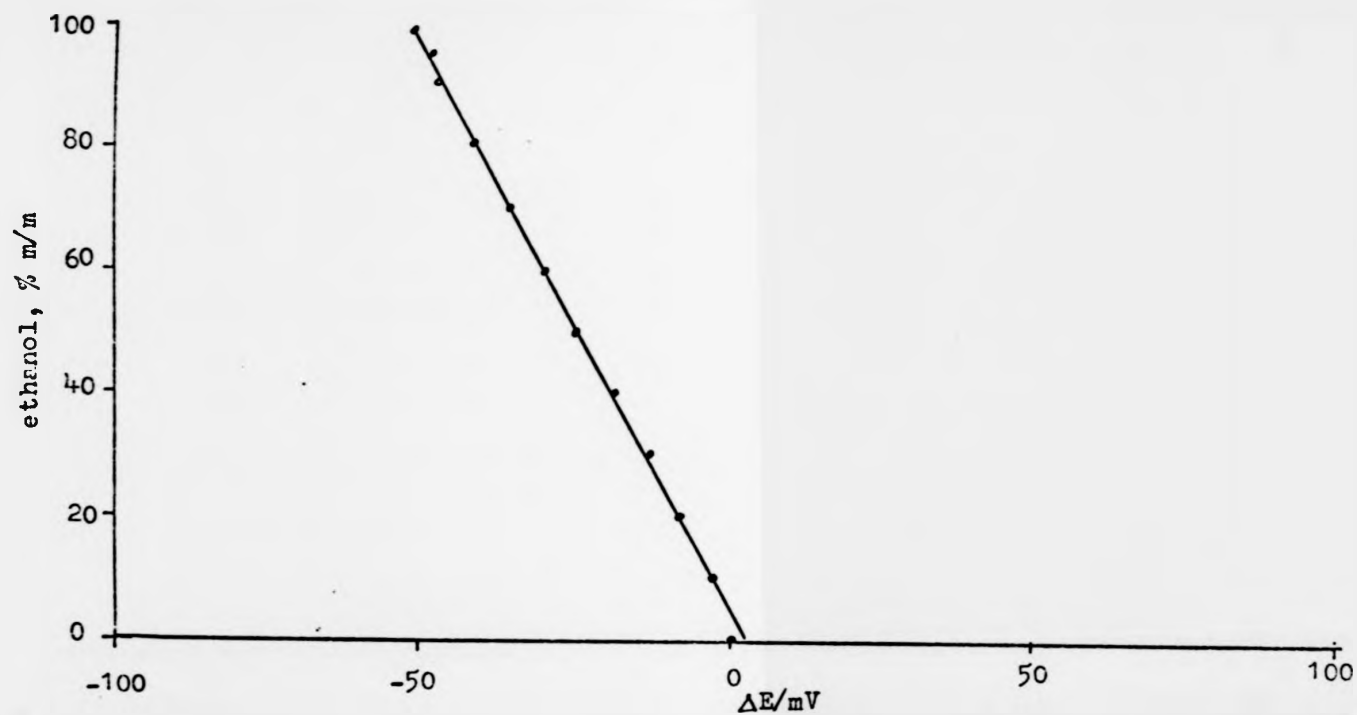


Fig. 32 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-\text{EtCH}(\text{MeOH})$ , in solutions of  $10^{-5}$  M tetraethylammonium chloride and various ethanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.



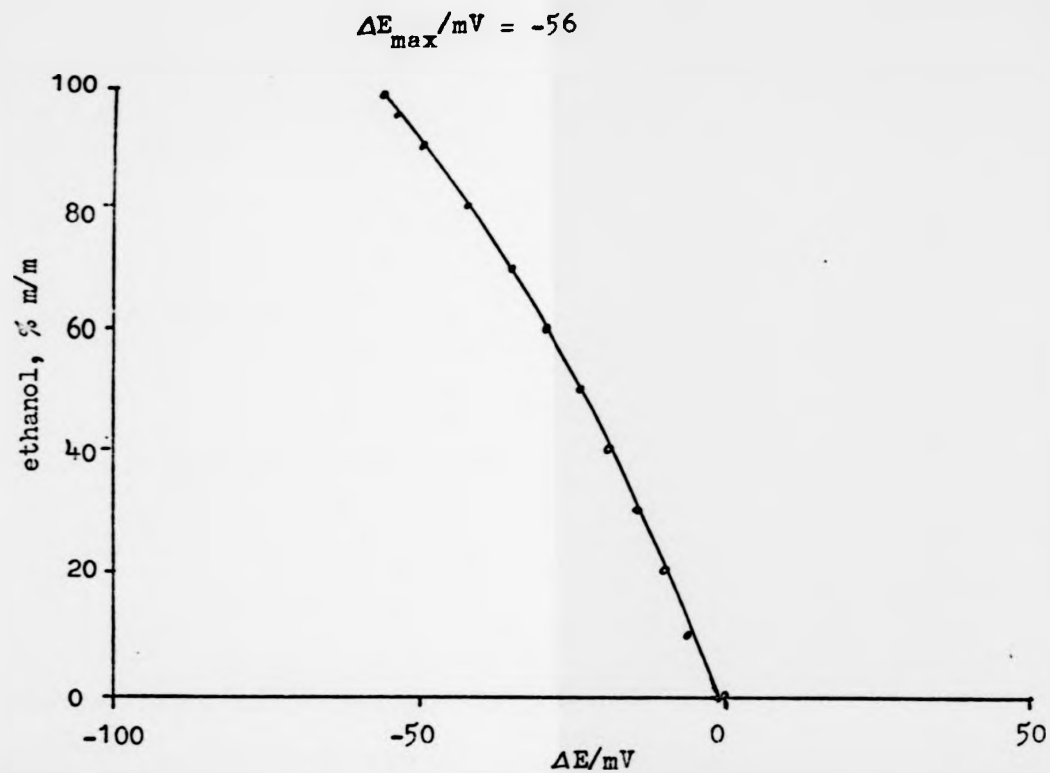


Fig. 33 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-\text{EtOH}(\text{MeOH})$ , in solutions of  $10^{-4}$  M tetraethylammonium chloride and various ethanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

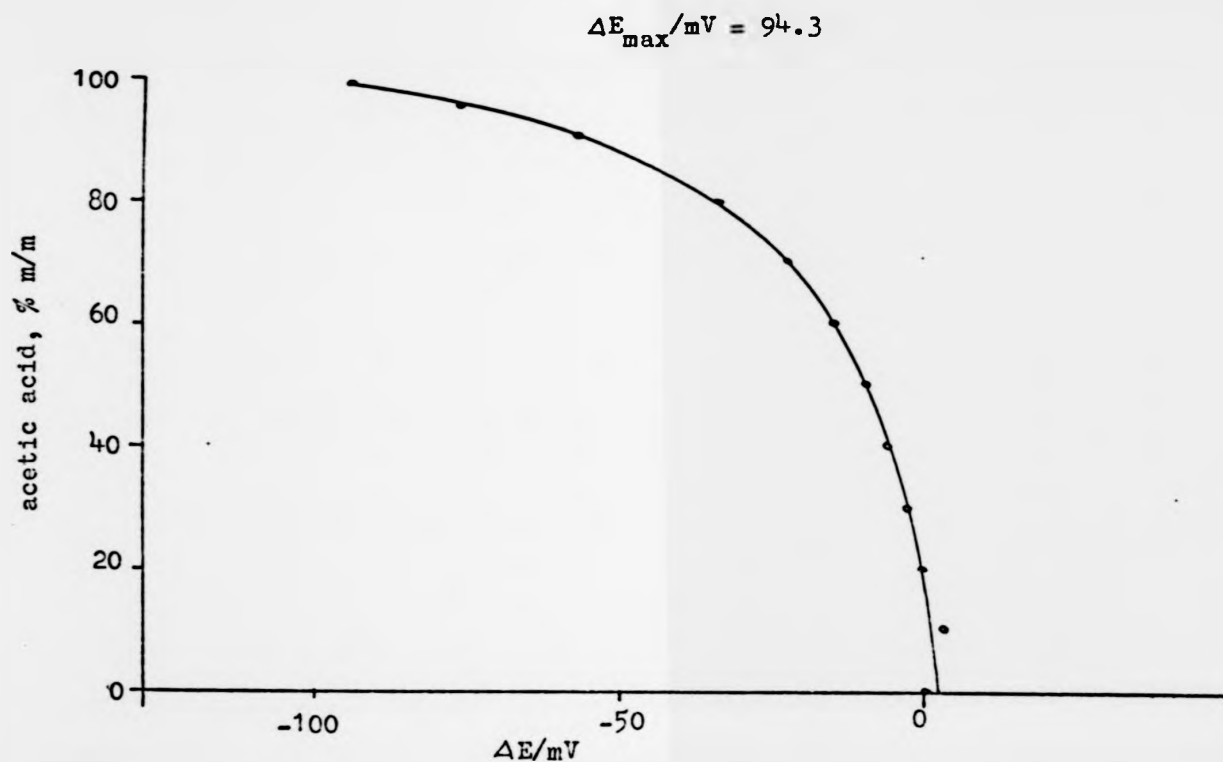


Fig. 34 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-\text{HOAc}(\text{MeOH})$ , in solutions of  $10^{-3}$  M tetraethylammonium chloride and various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

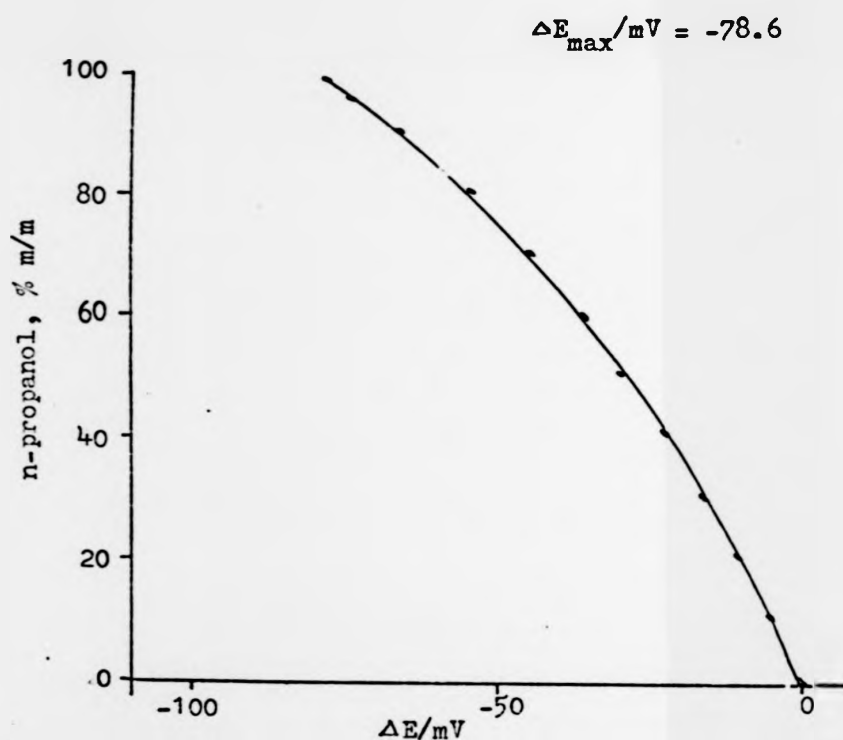


Fig.35 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}-\text{n-PrOH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M tetraethylammonium chloride and various n-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

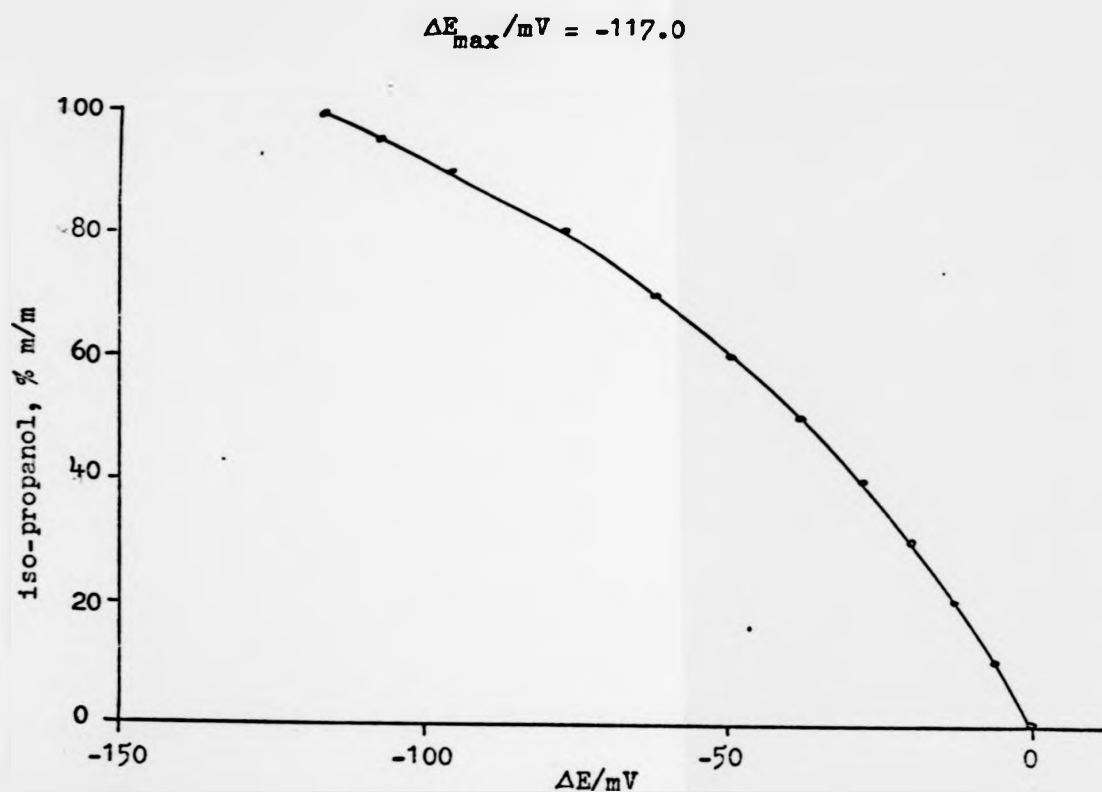


Fig. 36 Change in potential,  $\Delta E$ , for the system  $\text{Et}_4\text{NCl}-1\text{-PrOH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M tetraethylammonium chloride and various iso-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

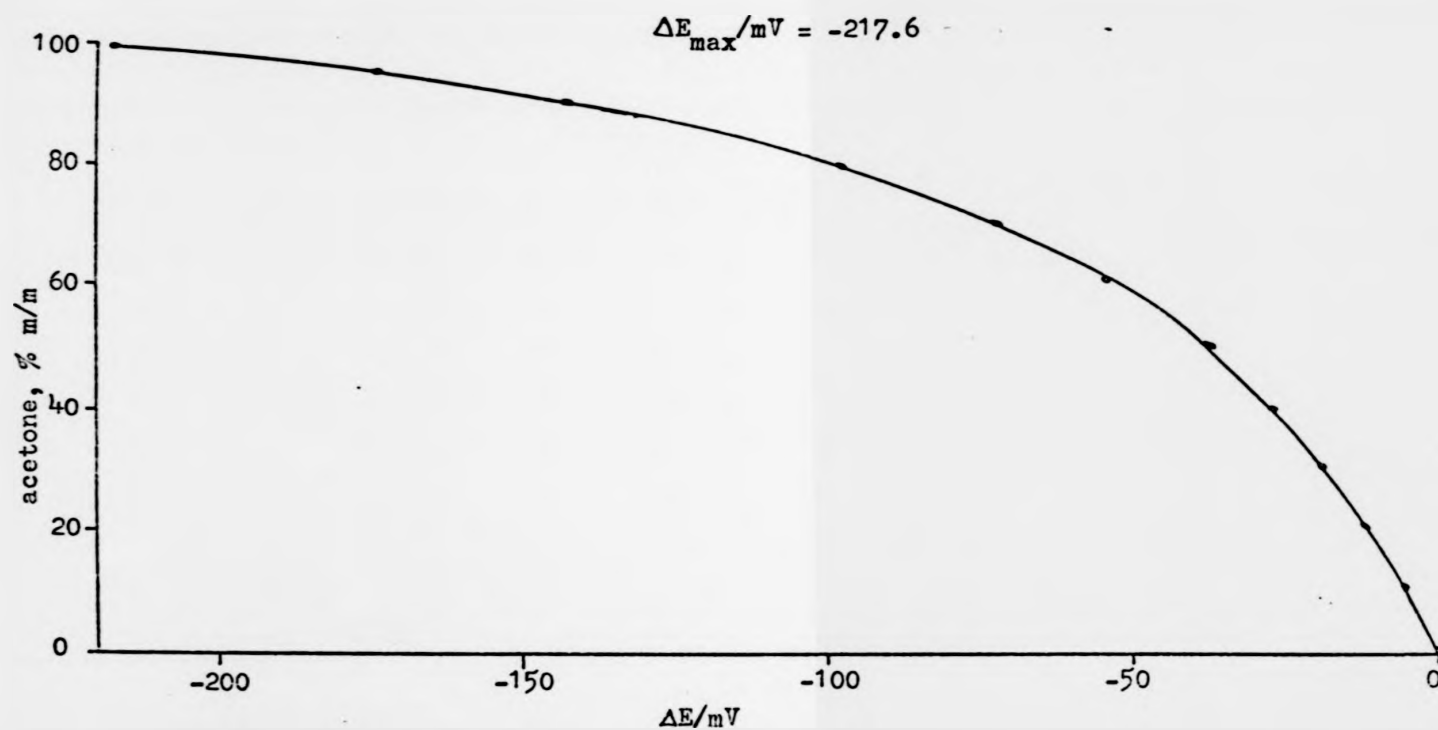


Fig. 37 Change in potential,  $\Delta E$ , for the system,  $\text{Et}_4\text{NCl}$ —acetone( $\text{MeOH}$ ), in solutions of  $10^{-3}$  M tetraethylammonium chloride and various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

### 2.2.2 INDIRECT MEASUREMENTS

Table 42

Change in potential (obtained by the 'indirect method') for the system, NaCl--EtOH(H<sub>2</sub>O), in solutions 10<sup>-2</sup> M, 10<sup>-3</sup> M, and 10<sup>-4</sup> M in sodium chloride and of various ethanol concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m ethanol	Potential/mV			Electrode slope /-mV per decade	LLLR
	10 <sup>-2</sup> MCl <sup>-</sup>	10 <sup>-3</sup> MCl <sup>-</sup>	10 <sup>-4</sup> MCl <sup>-</sup>		
0	91	153	208	62.0	2 X 10 <sup>-4</sup>
10	88	151	208	62.0	2 X 10 <sup>-4</sup>
20	88	150	212	62.0	2 X 10 <sup>-4</sup>
30	84	149	207	63.5	2 X 10 <sup>-4</sup>
40	81	146	208	63.5	2 X 10 <sup>-4</sup>
50	72	137	200	65.5	2 X 10 <sup>-4</sup>
60	62	132	195	66.5	1 X 10 <sup>-4</sup>
70	52	122	190	69.0	1 X 10 <sup>-4</sup>
80	28	114	186	86.0	1 X 10 <sup>-4</sup>
90	-6	89	182	95.5	1 X 10 <sup>-4</sup>
95	-16	78	171	92.5	2 X 10 <sup>-5</sup>
99	8	83	160	76.0	6 X 10 <sup>-5</sup>
$\Delta E/mV(90\% \text{ m/m})$	-107	-75	-37		

Table 48

Change in potential (obtained by 'indirect method') for the system,  $\text{NaCl--HOAc(H}_2\text{O)}$ , in solutions  $10^{-2}$  M,  $10^{-3}$  M and  $10^{-4}$  M in sodium chloride and of various acetic acid concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m acetic acid	Potential/mV			Electrode slope /-mV per decade	LLRR
	$10^{-2}$ MCl <sup>-</sup>	$10^{-3}$ MCl <sup>-</sup>	$10^{-4}$ MCl <sup>-</sup>		
0	61	123	182	59.5	$6 \times 10^{-5}$
10	50	106	160	54.0	$6 \times 10^{-5}$
20	44	100	154	55.0	$6 \times 10^{-5}$
30	35	93	147	56.0	$6 \times 10^{-5}$
40	30	84	139	55.5	$3 \times 10^{-5}$
50	22	76	130	54.0	$3 \times 10^{-5}$
60	10	63	119	54.5	$1 \times 10^{-5}$
70	-3	51	104	53.5	$1 \times 10^{-5}$
80	-18	29	57	50.0	$2 \times 10^{-4}$
90	-39	0	24	41.0	$6 \times 10^{-4}$
95	-54	-22	-4	31.0	$6 \times 10^{-4}$
99	-61	-34	-23	21.0	$6 \times 10^{-4}$
$\Delta E_{\text{max/mV}}$	-122	-158	-205		

Table 49

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ -- $n\text{-PrOH}(\text{H}_2\text{O})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various  $n$ -propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m $n$ -propanol	Potential/mV			Electrode slope /-mV per decade	LLLR	$E^0/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	116.9	169.0	203.7	52.1	$5 \times 10^{-5}$	-39.4
20	102.5	154.6	193.9	52.1	$4 \times 10^{-5}$	-53.8
40	80.1	131.1	172.0	51.1	$3 \times 10^{-5}$	-73.2
60	49.0	95.8	136.2	47.0	$2 \times 10^{-5}$	-92.0
80	11.0	56.0	96.0	45.0	$5 \times 10^{-5}$	-124.0
90	-10.2	35.4	76.8	45.6	$2 \times 10^{-5}$	147.0
99	-29.5	18.4	67.0	48.3	$1 \times 10^{-5}$	-174.4
$\Delta E_{\text{max}}/\text{mV}$	-146.4	-150.6	-136.7			



Table 5Q

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ -- $\text{i-PrOH}(\text{H}_2\text{O})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various isopropanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /-mV per decade	LLLR	$E^0/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	116.9	169.0	203.7	52.1	$5 \times 10^{-5}$	-39.4
20	101.7	154.6	193.8	52.3	$5 \times 10^{-5}$	-55.2
40	77.9	127.7	166.2	50.0	$5 \times 10^{-5}$	-72.1
60	42.4	89.0	123.8	46.6	$5 \times 10^{-5}$	-97.4
80	-1.0	44.6	75.1	45.6	$5 \times 10^{-5}$	-137.8
90	-30.2	16.0	49.6	46.2	$5 \times 10^{-5}$	-168.8
99	-58.2	-11.8	22.5	46.4	$5 \times 10^{-5}$	-197.4
$\Delta E_{\text{max}}/\text{mV}$	-175.1	-180.8	226.2			

Table 51

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ --acetone( $\text{H}_2\text{O}$ ), in solutions  $10^{-3} \text{ M}$ ,  $10^{-4} \text{ M}$  and  $10^{-5} \text{ M}$  in tetraethylammonium chloride and of various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m acetone	Potential/mV			Electrode slope /-mV per decade	LLRR	$E^\circ/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	-228.6	-166.6	-119.9	62.0	$6 \times 10^{-5}$	-414.6 (-375.8)*
20	-227.0	-165.8	-119.8	61.2	$6 \times 10^{-5}$	-410.6 (-388.1)
40	-231.9	-170.0	-123.0	61.9	$6 \times 10^{-5}$	-417.6 (-404.5)
60	-249.5	-183.7	-133.1	65.0	$6 \times 10^{-5}$	-444.5 (-442.7)
80	-284.5	-221.0	-170.6	62.5	$6 \times 10^{-5}$	-472.0 (-470.4)
90	-332.4	-275.4	-222.8	57.0	$2 \times 10^{-5}$	-503.4 (-513.8)
99	-420.5	-388.0	-337.5	58.0	$2 \times 10^{-5}$ - $2 \times 10^{-4}$	-594.5 (-609.1)
$\Delta E_{\text{max}}/\text{mV}$	-191.9	-221.4	-217.4			

( ) \*  $E^\circ$  normalised w.r.t. silver-silver chloride (double-junction) electrode.

Table 52

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ --1,4-dioxan( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various 1,4-dioxan concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m 1,4-dioxan	Potential/mV			Electrode slope /-mV per decade	LLLRR	$E^0$ /mV
	$10^{-3}$ $\text{MCl}^-$	$10^{-4}$ $\text{MCl}^-$	$10^{-5}$ $\text{MCl}^-$			
0	115.2	164.1	198.7	48.9	$5 \times 10^{-5}$	-31.5
20	107.7	153.6	189.8	45.9	$5 \times 10^{-5}$	-30.0
40	86.0	133.0	177.2	47.0	$2 \times 10^{-5}$	-55.0
60	46.6	92.6	139.4	46.4	$5 \times 10^{-6}$	-92.6
80	-16.2	24.8	72.0	45.5	$2 \times 10^{-6}$ - $2 \times 10^{-4}$	-157.2
90	-58.8 (25)*	-20.0 (46)*	30.0 (58)*	NL	-	
95	-90.1 (20)	-57.4 (42)	2.0 (119)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	-205.3	-221.5	-196.7			

( )\*: tangential slope

NL: Non-linear

Table 53

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ -- $\text{EtOH}(\text{MeOH})$ , in solutions  
 $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various ethanol concentrations,  
measured by using silver chloride and silver-silver chloride (double-junction)  
electrodes

% m/m ethanol	Potential/mV			Electrode slope /-mV per decade	LLLPR
	$10^{-3}$ $\text{MCl}^-$	$10^{-4}$ $\text{MCl}^-$	$10^{-5}$ $\text{MCl}^-$		
0	130	179	224	50.0	$2 \times 10^{-5}$
10	121	170	204	49.0	$6 \times 10^{-5}$
20	114	165	203	51.0	$6 \times 10^{-5}$
30	112	162	200	50.0	$6 \times 10^{-5}$
40	108	157	196	49.0	$6 \times 10^{-5}$
50	106	155	187	50.0	$6 \times 10^{-5}$
60	93	144	184	49.0	$6 \times 10^{-5}$
70	93	143	180	47.0	$6 \times 10^{-5}$
80	85	137	180	49.0	$6 \times 10^{-5}$
90	79	130	173	47.0	$6 \times 10^{-5}$
95	74	122	162	51.0	$6 \times 10^{-5}$
99	72	120	160	51.0	$6 \times 10^{-5}$
$\Delta E_{\text{max/mV}}$	58	59	64		

Table 54

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ -- $\text{HOAc}(\text{MeOH})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m acetic acid	Potential/mV			Electrode slope /-mV per decade	LLRR	$E^0/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	40.0	97.6	138.9	55.0	$6 \times 10^{-5}$	-125.0
10	36.9	92.4	137.0	54.6	$6 \times 10^{-5}$	-126.9
20	34.0	87.1	126.9	53.1	$6 \times 10^{-5}$	-125.3
30	29.9	83.2	122.8	53.0	$6 \times 10^{-5}$	-129.1
40	27.2	80.7	119.6	53.5	$6 \times 10^{-5}$	-133.3
50	23.0	76.3	111.6	53.3	$6 \times 10^{-5}$	-136.9
60	17.6	69.4	107.4	51.8	$6 \times 10^{-5}$	-137.8
70	10.0	61.4	99.4	61.4	$6 \times 10^{-5}$	-144.2
$\Delta E_{\text{max}}/\text{mV}$	-30	-36.2	-39.5			

Table 55

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ -- $n$ - $\text{PrOH}$  ( $\text{MeOH}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various  $n$ -propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m $n$ -propanol	Potential /mV			Electrode slope /-mV per decad	LLLRR	$E^0$ /mV
	$10^{-3}$ $\text{MCl}^-$	$10^{-4}$ $\text{MCl}^-$	$10^{-5}$ $\text{MCl}^-$			
0	37.9	86.0	125.3	48.1	$2 \times 10^{-5}$	-106.4
20	28.2	76.5	118.6	48.3	$2 \times 10^{-5}$	-116.7
40	17.4	62.9	105.1	45.5	$2 \times 10^{-5}$	-119.1
60	4.1	50.5	90.2	45.3	$2 \times 10^{-5}$	-131.8
80	-13.6	32.3	76.1	45.9	$2 \times 10^{-5}$	-151.3
90	-24.2	22.8	69.8	47.0	$2 \times 10^{-5}$	-165.2
99	-36.5	9.5	51.8	46.0	$2 \times 10^{-5}$	-174.5
$\Delta E_{\text{max}}/\text{mV}$	-74.4	-76.5	-73.5			

Table 56

Change in potential (obtained 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ --1-PrOH(MeCH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in tetraethylammonium chloride and of various isopropanol concentrations, measured by using silver chloride and silver-silver chloride (double junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /-mV per decade	LLRR	$E^0/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	37.9	86.0	125.3	48.1	$2 \times 10^{-5}$	-106.4
20	25.9	73.9	117.9	48.0	$2 \times 10^{-5}$	-118.1
40	11.4	59.7	104.0	48.3	$2 \times 10^{-5}$	-133.5
60	-6.8	41.2	88.0	48.0	$2 \times 10^{-5}$	-150.8
80	-32.9	14.8	59.2	47.7	$2 \times 10^{-5}$	-176.0
90	-49.8	-3.2	41.7	46.6	$2 \times 10^{-5}$	-189.6
99	-69.0	-24.6	17.4	44.4	$2 \times 10^{-5}$	-202.2
$\Delta E_{\text{max}}/\text{mV}$	-106.9	-110.6	-107.9			

Table 52

Change in potential (obtained by 'indirect method') for the system,  $\text{Et}_4\text{NCl}$ --acetone( $\text{MeOH}$ ), in solutions  $10^{-3} \text{ M}$ ,  $10^{-4} \text{ M}$  and  $10^{-5} \text{ M}$  in tetraethylammonium chloride and of various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m acetone	Potential/mV			Electrode slope /-mV per decade	LLPR	$E^0/\text{mV}$
	$10^{-3} \text{ MCl}^-$	$10^{-4} \text{ MCl}^-$	$10^{-5} \text{ MCl}^-$			
0	-351.1	-300.6	-253.8	46.8	$1 \times 10^{-5}$	-491.5 (-438.3)*
20	-353.5	-308.6	-271.3	44.0	$2 \times 10^{-5}$	-485.5 (-443.5)
40	-358.1	-311.8	-272.0	46.3	$2 \times 10^{-5}$	-497.0 (-462.0)
60	-375.4	-326.1	-285.0	47.3	$2 \times 10^{-5}$	-517.3 (-492.2)
80	-403.4	-363.5	-319.8	41.8	$1 \times 10^{-5}$	-528.8 (-514.7)
90	-424.7	-380.5	-327.6	52.9	$1 \times 10^{-5}$ - $5 \times 10^{-4}$	-592.1 (-589.0)
99	-462.3	-412.0	-358.2	58.0	$2 \times 10^{-5}$ - $2 \times 10^{-4}$	-644.0 (-649.8)
$\Delta E_{\text{max}}/\text{mV}$	-111.2	-111.4	-104.4			

(\*)  $E^0$  normalised w.r.t. silver-silver chloride (double-junction) electrode.



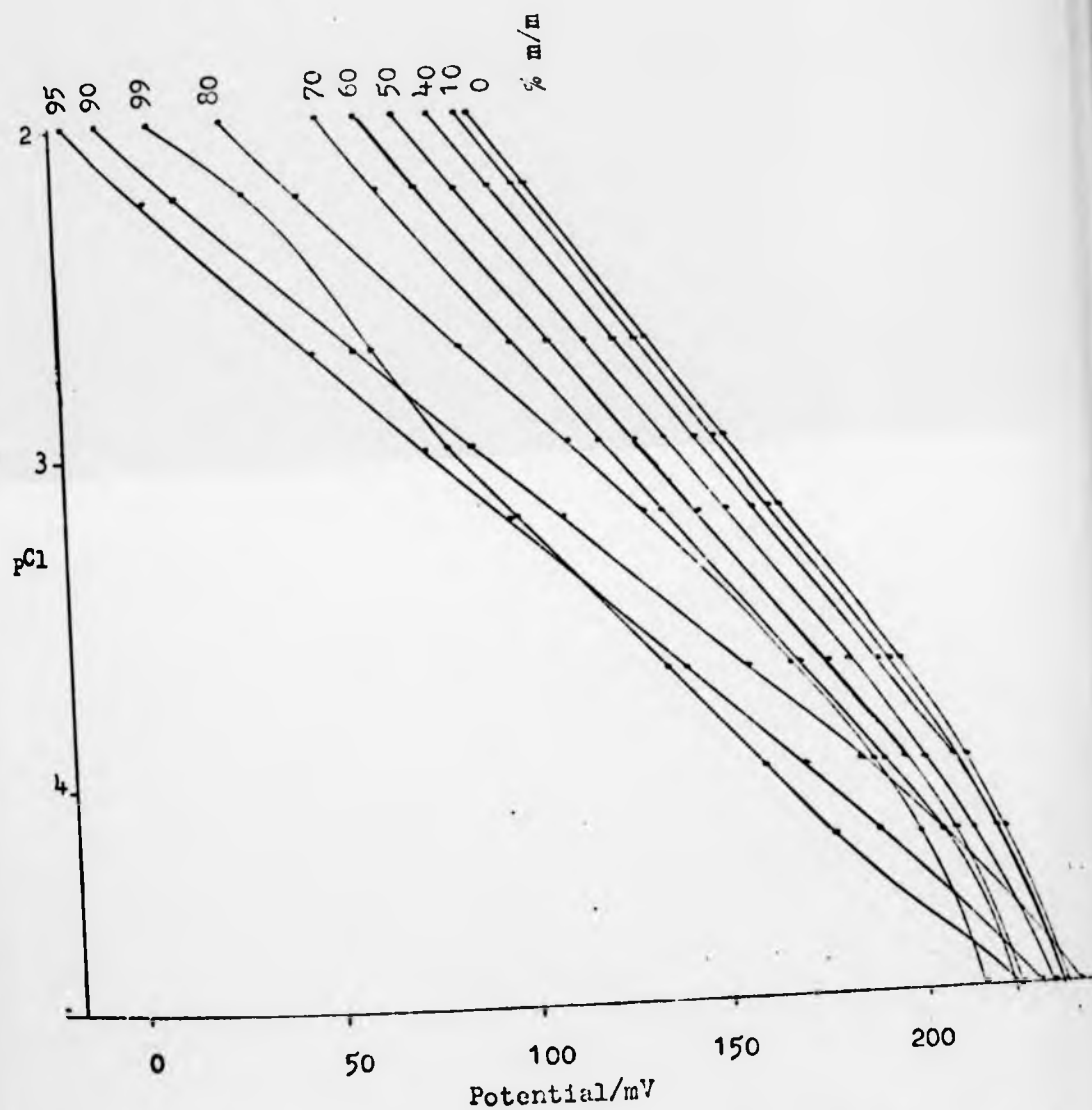


Fig. 38 Electrode calibration graphs for the system, NaCl—EtOH(H<sub>2</sub>O), in solutions of constant ethanol concentration and various sodium chloride concentrations, measured by using Silver chloride and mercury-mercurous sulphate (1M Na<sub>2</sub>SO<sub>4</sub>) electrodes.

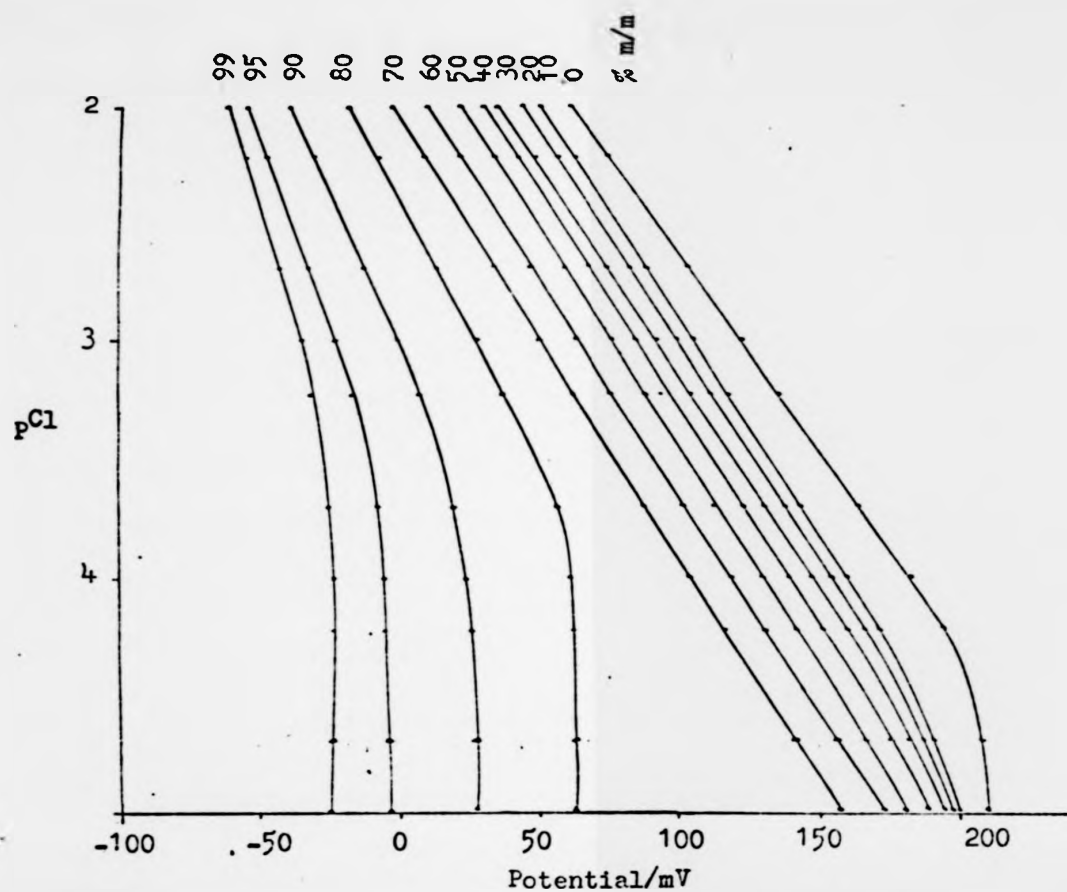


Fig. 39 Electrode calibration graphs for the system,  $\text{NaCl}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of constant acetic concentration and various sodium chloride concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

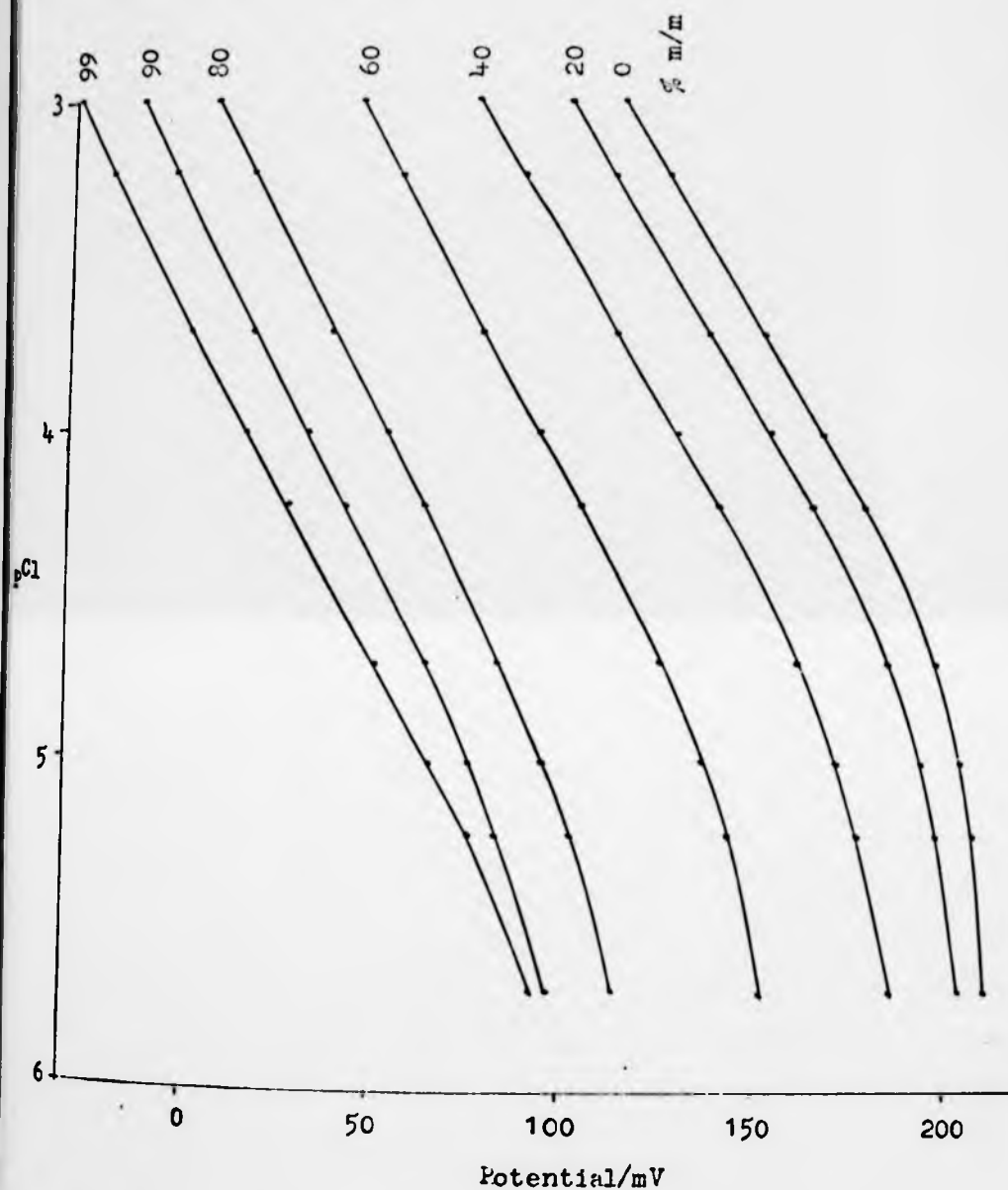


Fig. 40 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl-n-PrOH(H}_2\text{O)}$ , in solutions for constant n-propanol and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

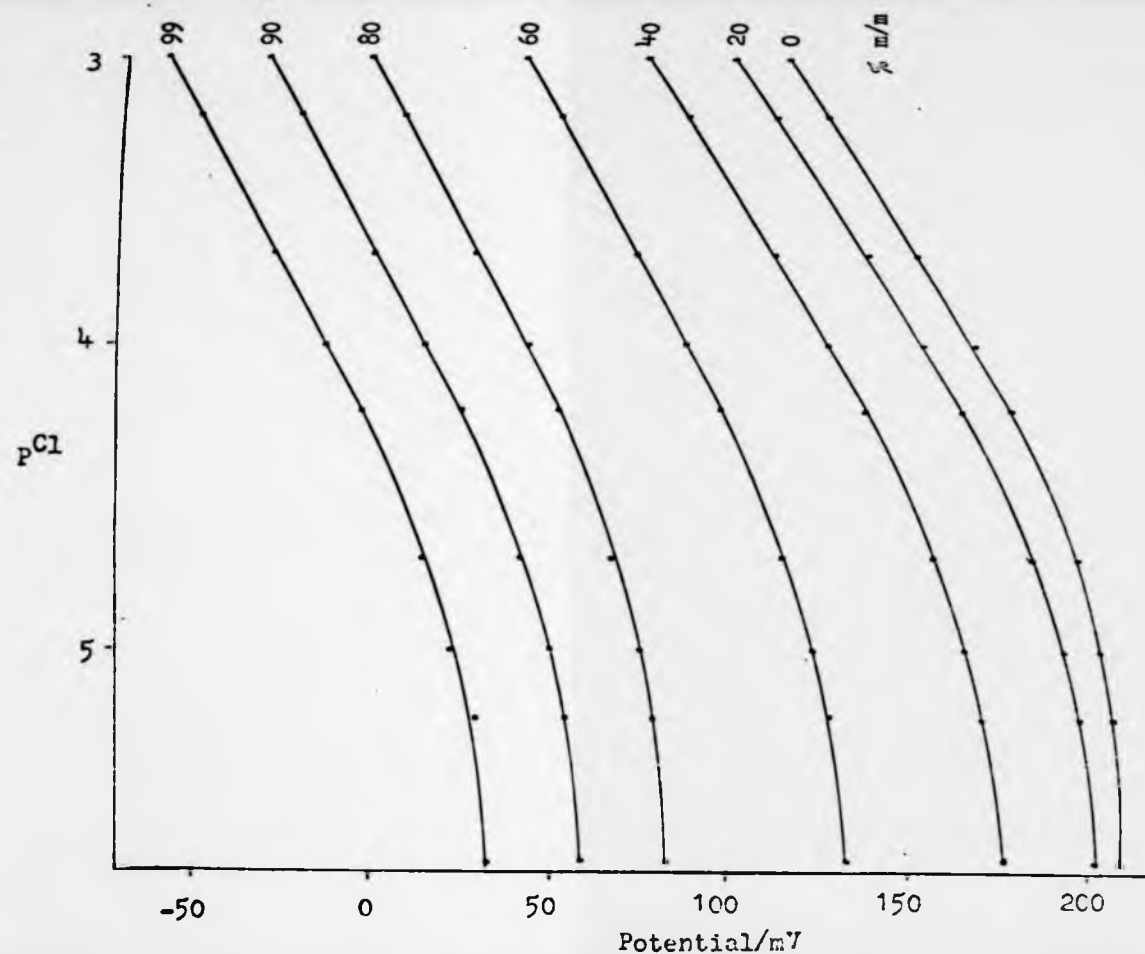


Fig. 41 Electrode calibration graphs for the system,  $Et_4NCl-1-PrOH(H_2O)$ , in solutions of constant iso-propanol concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

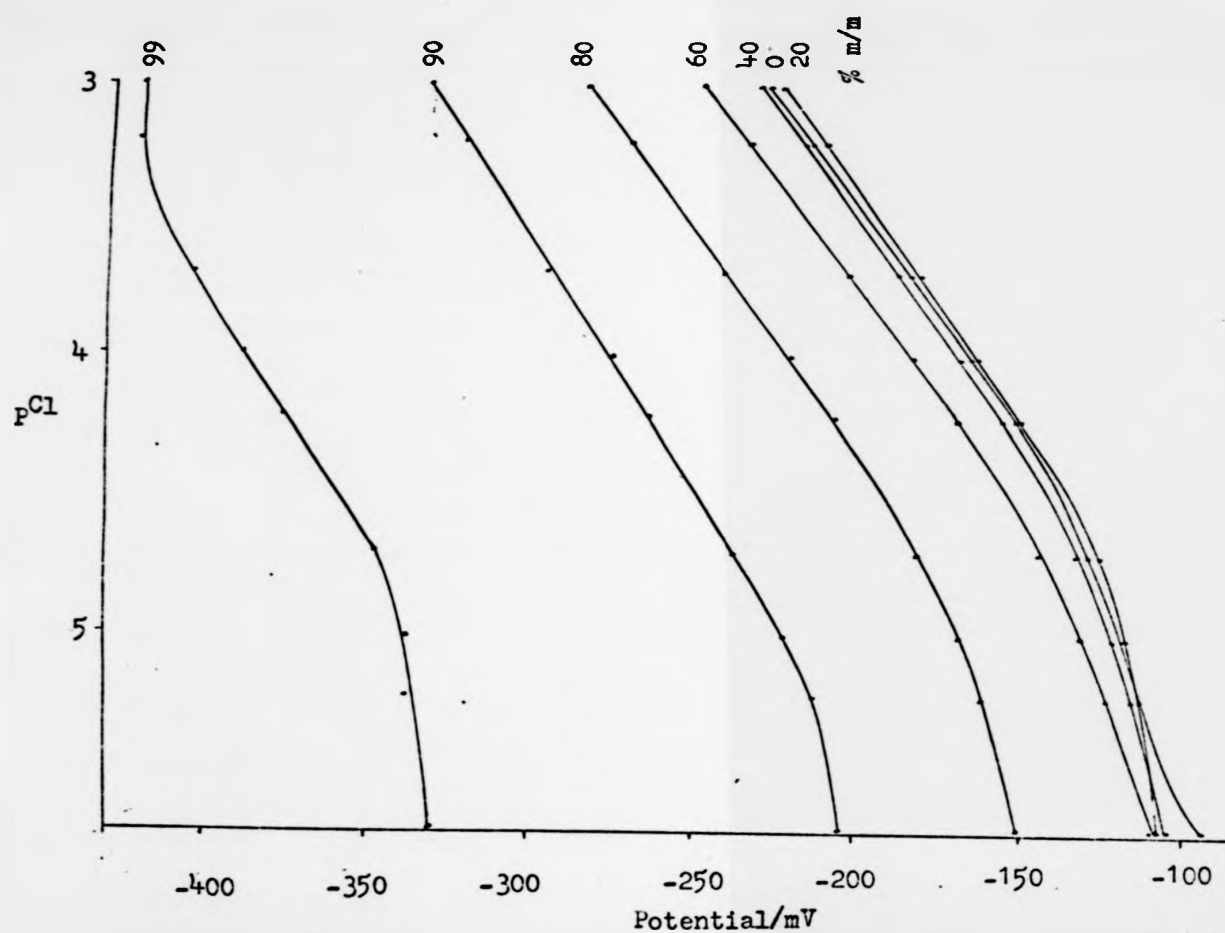


Fig. 42 Electrode calibration graphs for the system,  $Et_4NCl$ —acetone( $H_2O$ ), in solutions of constant acetone concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1M Na_2SO_4$ ) electrodes.

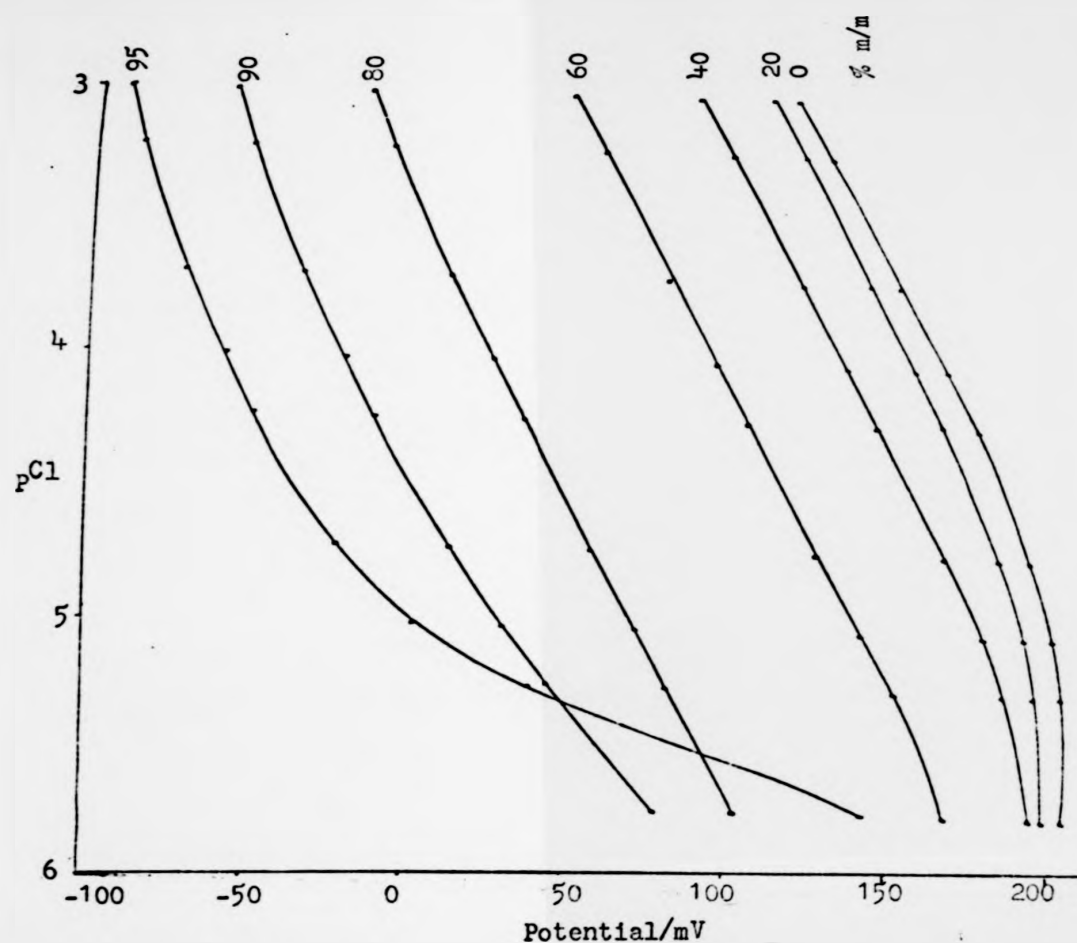


Fig. 43 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl}$ —1,4-dioxan( $\text{H}_2\text{O}$ ), in solutions of constant 1,4-dioxan concentration and various tetraethylammonium chloride concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

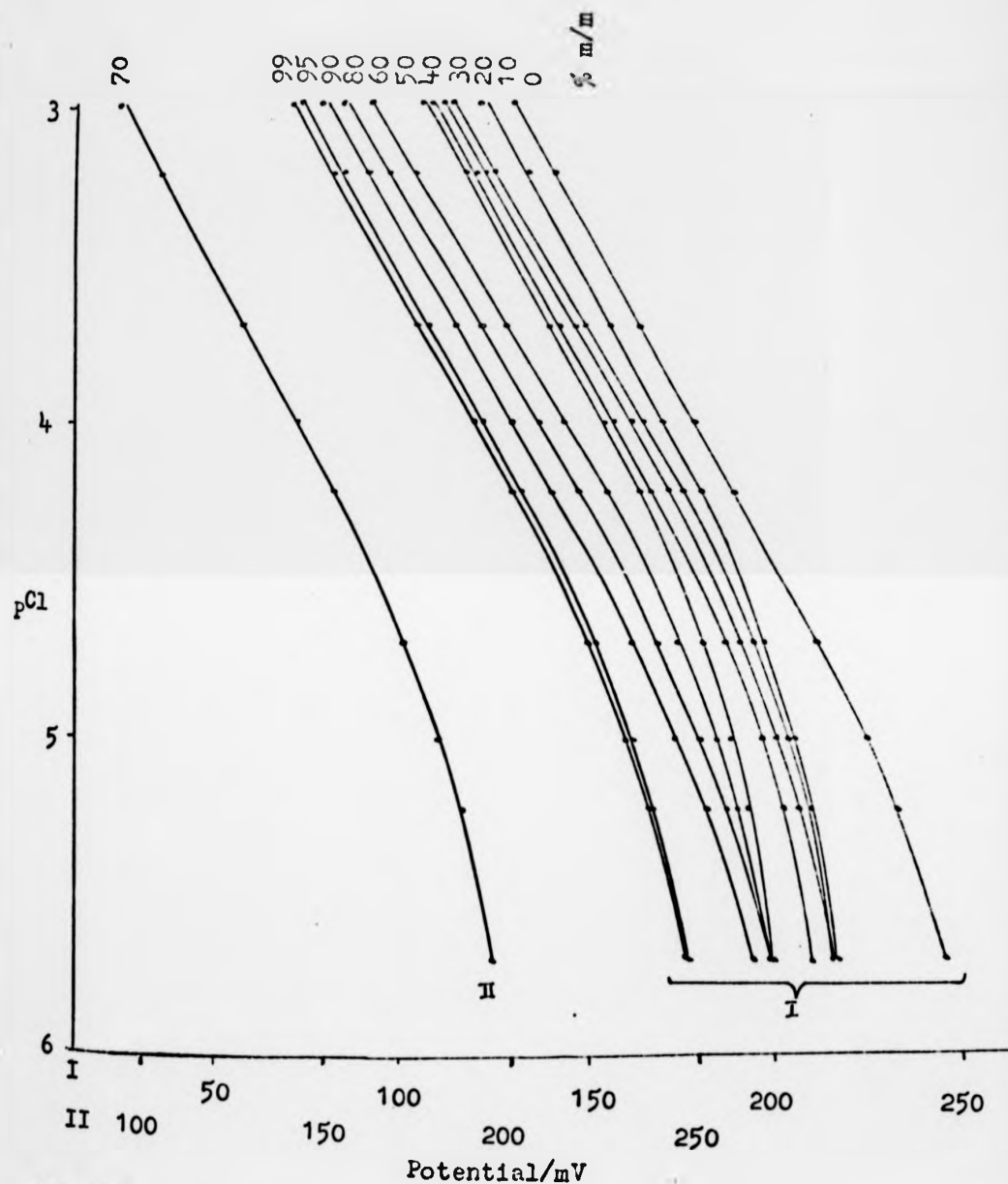


Fig. 44 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl}-\text{EtOH}(\text{MeOH})$ , in solutions of constant ethanol concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

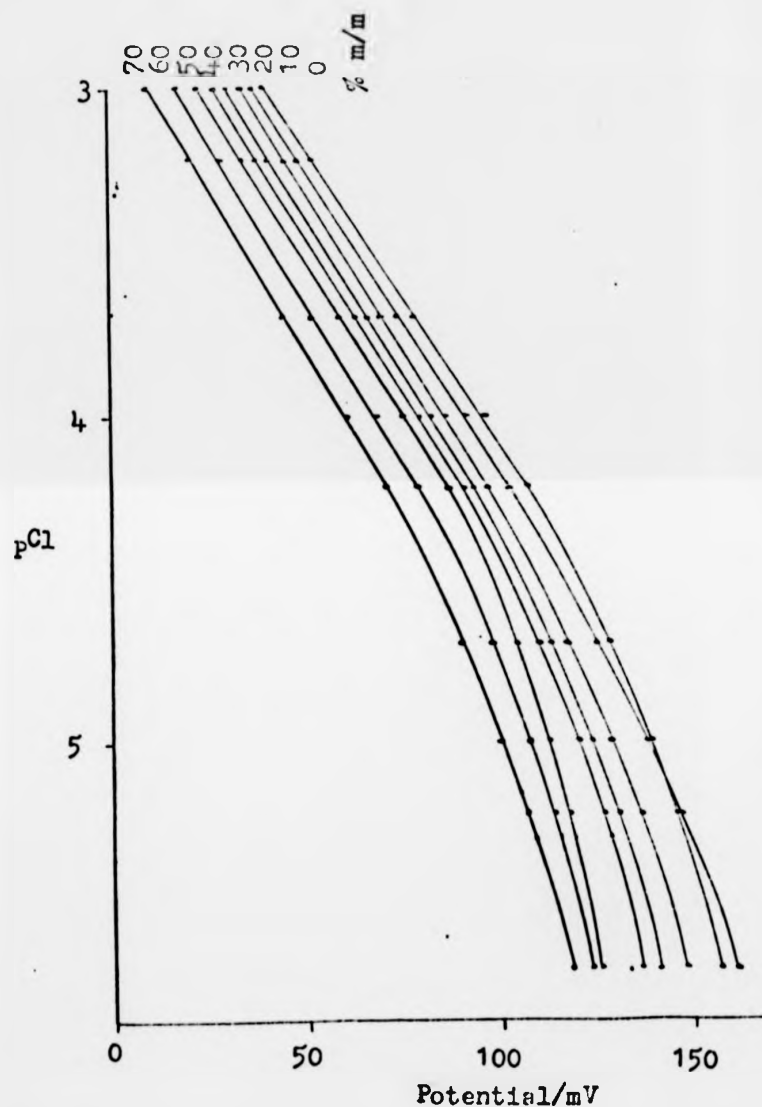


Fig. 45 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl}-\text{HOAc}(\text{MeOH})$ , in solutions of constant acetic acid concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.



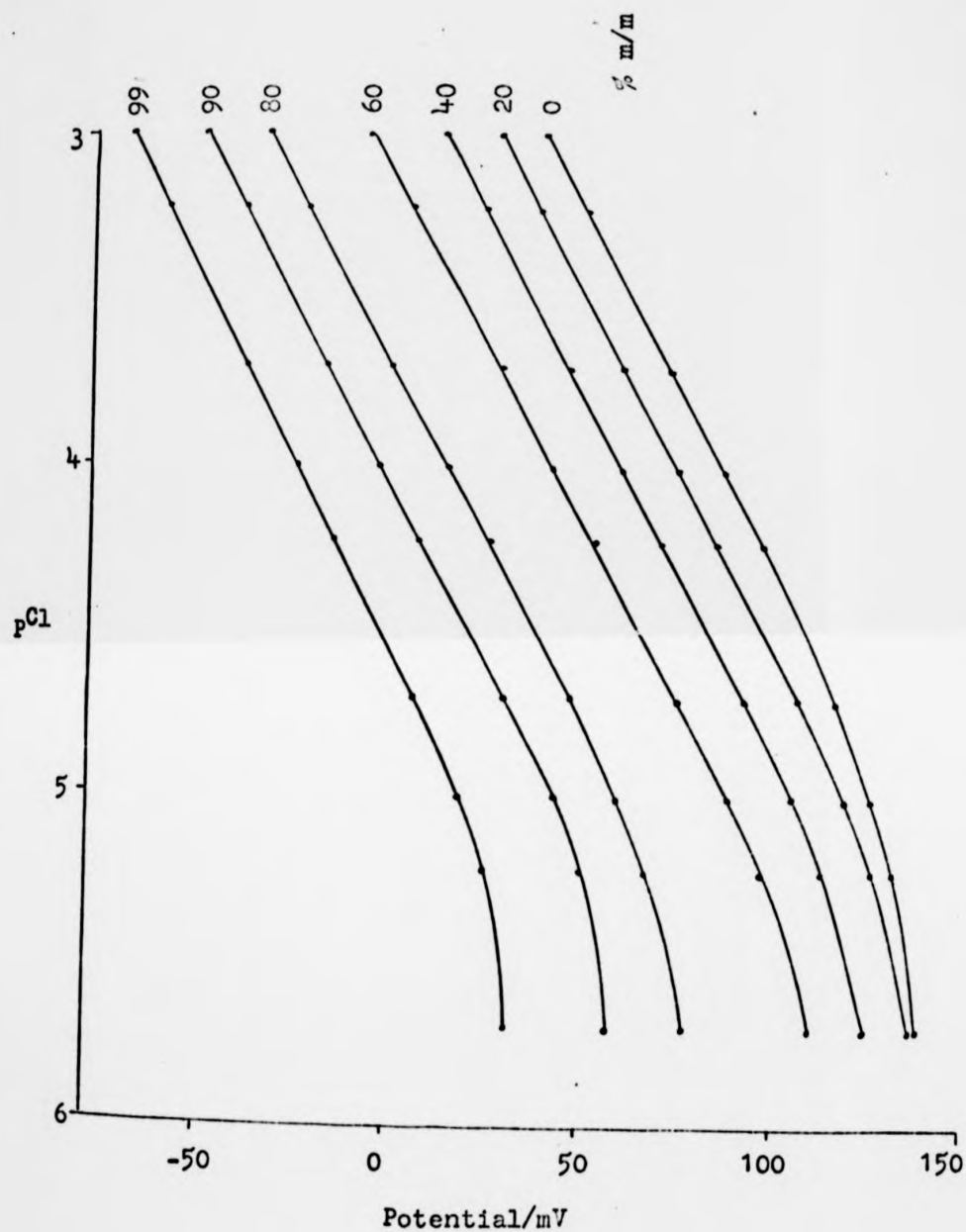


Fig. 46 Electrode calibration graphs for the system,  $Et_4NCl-1-PrOH(MeOH)$ , in solutions of constant iso-propanol concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

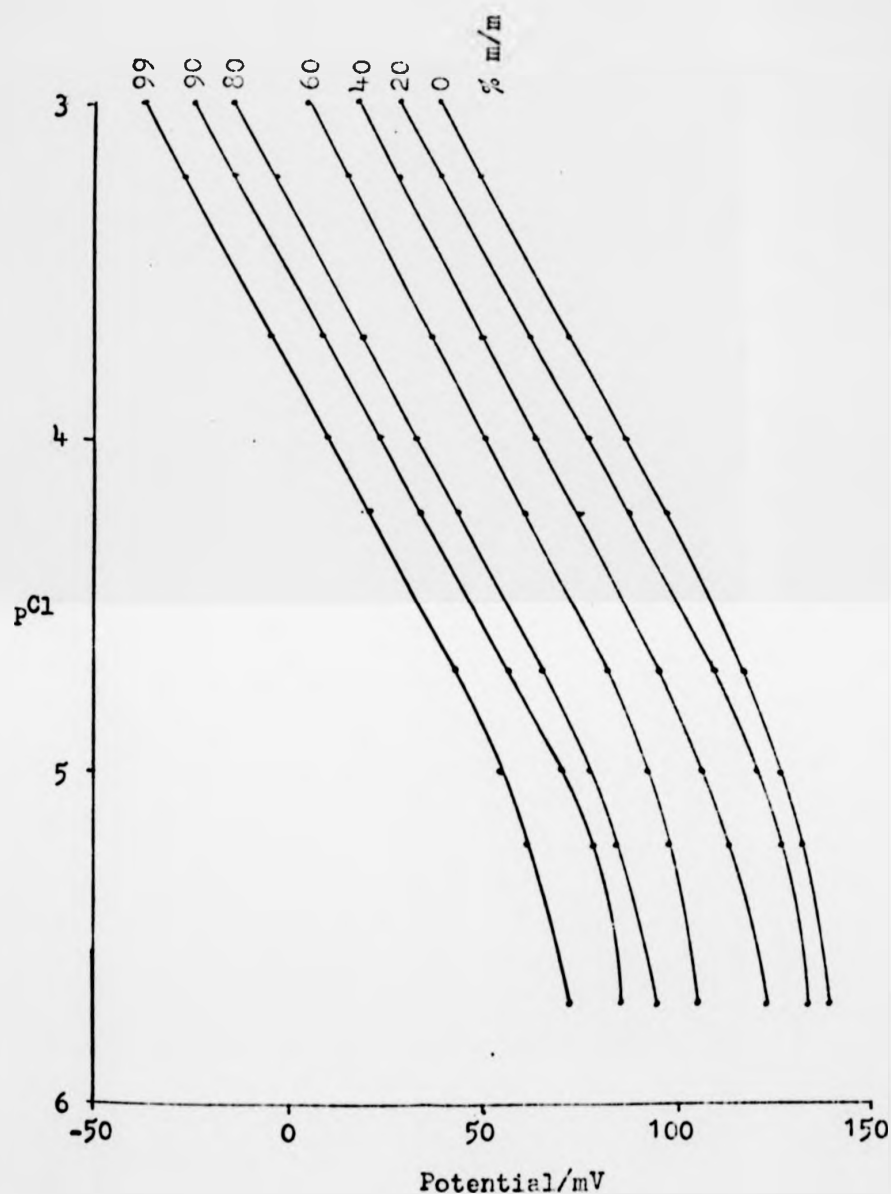


Fig. 47 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl}$ - $n$ - $\text{PrOH}$  ( $\text{MeOH}$ ), in solutions of constant  $n$ -propanol concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

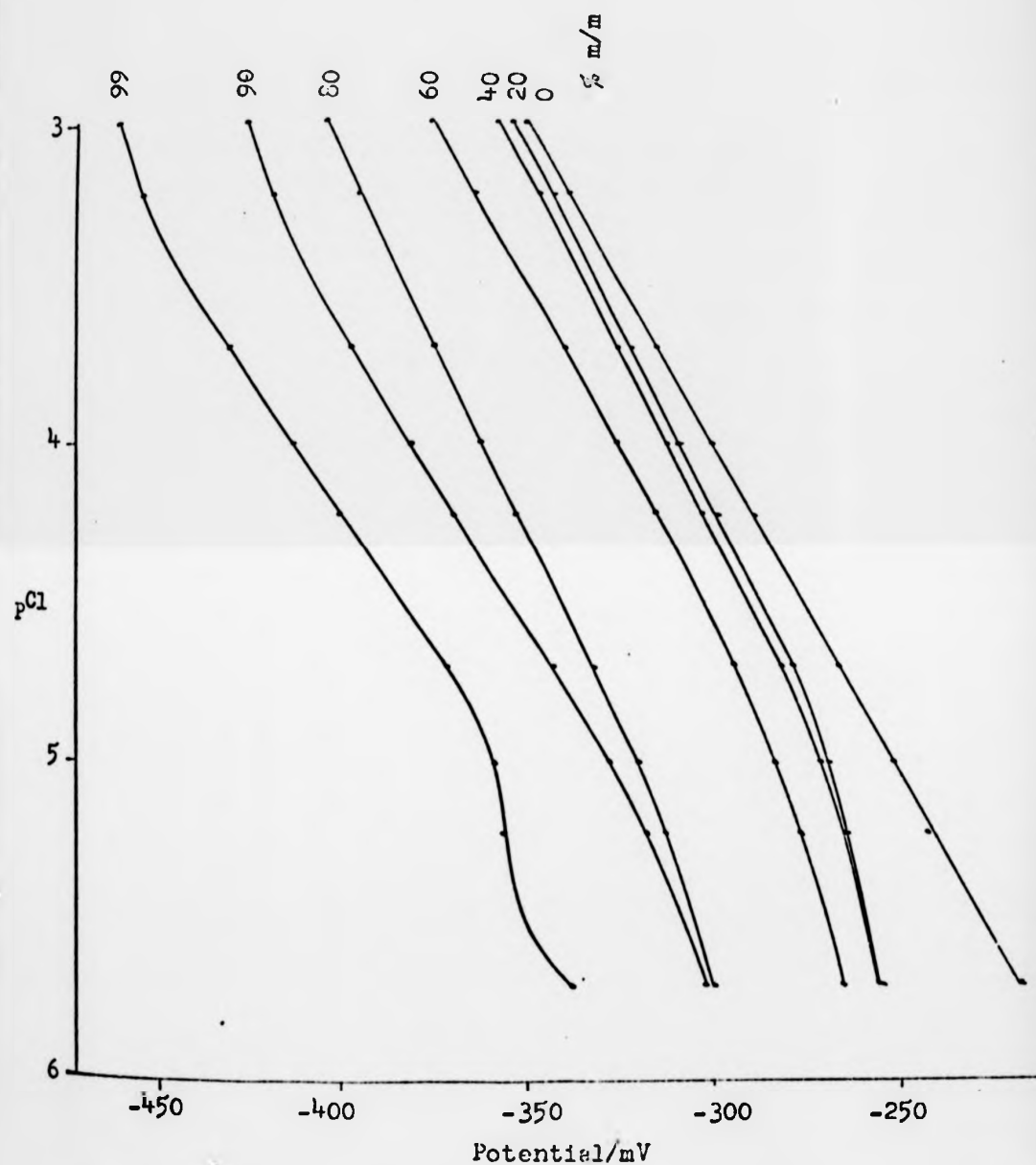


Fig. 48 Electrode calibration graphs for the system,  $\text{Et}_4\text{NCl}$ -acetone(MeOH), in solutions of constant acetone concentration and various tetraethylammonium chloride concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

2.2.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 58

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Et}_4\text{NCl}$  EtOH(MeOH), in  $10^{-3}$  M tetraethylammonium chloride for various methanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

ethanol % m/m	$\Delta E/\text{mV}$ (MeOH)		$\Delta\Delta E/\text{mV}$ (MeOH)
	Direct	Indirect	
0	0	0	0
10	-2	-9	7
20	-7	-16	9
30	-12	-18	6
40	-18	-22	4
50	-24	-24	0
60	-29	-37	8
70	-35	-37	2
80	-41	-45	4
90	-48	-51	3
95	-48	-56	8
99	-51	-58	7

Table 59

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the systems, NaCl-HOAc(H<sub>2</sub>O) and Et<sub>4</sub>NCl-HOAc(MeOH), in 10<sup>-3</sup> M solutions of electrolyte for various acetic acid concentrations measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

acetic acid % m/m	$\Delta E/mV$ (H <sub>2</sub> O)		$\Delta \Delta E$ (H <sub>2</sub> O)	$\Delta E/mV$ (MeOH)		$\Delta \Delta E$ (MeOH)
	Direct *	Indirect *		Direct	Indirect	
0	0	0	0	0	0	0
10	-7	-17	10	3.5	-3.1	6.6
20	-13	-23	10	-0.1	-6.0	5.9
30	-19	-30	11	-2.9	-10.1	7.2
40	-27	-39	12	-6.5	-12.8	6.3
50	-39	-47	8	-9.1	-17.0	7.9
60	-51	-60	9	-14.7	-22.4	7.7
70	-64	-72	8	-22.6	-30.0	7.4
80	-81	-94	13	-33.4		
90	-112	-123	11	-57.1	-	
95	-139	-145	6	-76.2	-	
99	-149	-157	8	-94.3	-	

(1). \* Hg, Hg<sub>2</sub>SO<sub>4</sub> reference electrode was used.

(2). - No measurement made.

Table 60

Comparison of changes in potential obtained by 'direct and 'indirect' measurements for the system,  $\text{Et}_4\text{NCl}-\text{n-PrOH}(\text{H}_2\text{O})$  and  $\text{Et}_4\text{NCl}-\text{n-PrOH}(\text{MeOH})$ , in  $10^{-3}$  M solutions of tetraethylammonium chloride for various n-propanol concentrations measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta\Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	-16.0	-14.4	-1.6	-11.0	-9.7	-1.3
40	-38.8	-36.8	-2.0	-23.3	-20.5	-2.8
60	-70.6	-67.9	-2.9	-35.5	-33.8	-1.7
80	-106.3	-105.9	-0.4	-54.1	-51.5	-2.6
90	-126.0	-127.1	1.1	-66.2	-62.1	-4.1
99	-146.5	-146.4	-0.1	-78.2	-74.4	-3.8

Table 61

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Et}_4\text{NCl}-1\text{-PrOH}(\text{H}_2\text{O})$  and  $\text{Et}_4\text{NCl}-1\text{-PrOH}(\text{MeOH})$ , in  $10^{-3}$  M solutions of tetraethylammonium chloride for various concentrations of iso-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

iso-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV}(\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	-11.7	-15.2	3.5	-13.3	-12.0	-1.3
40	-30.2	-39.0	8.8	-28.0	-26.5	-1.5
60	-65.5	-74.5	9.0	-49.8	-44.7	-5.1
80	-109.7	-117.9	8.2	-77.3	-70.8	-6.5
90	-138.6	-147.1	8.5	-95.8	-87.7	-8.1
99	-174.5	-175.1	0.6	-117.0	-106.9	-10.1

Table 62

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Et}_4\text{NCl}$  - acetone( $\text{H}_2\text{O}$ ) and  $\text{Et}_4\text{NCl}$  - acetone( $\text{MeOH}$ ), in  $10^{-3}$  M solutions of tetraethylammonium chloride for various acetone concentrations measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

acetone % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta\Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	0.5	1.6	-1.1	-12.4	-2.4	-10.0
40	-11.7	-3.3	-8.4	-27.2	-7.0	-20.2
60	-42.5	-20.9	-21.6	-55.1	-24.3	-30.8
80	-100.6	-55.9	-44.7	-98.1	-52.3	-45.8
90	-162.6	-103.8	-58.8	-143.	-73.6	-69.4
99	-250.6	-191.9	-58.7	-217.6	-111.2	-106.4



### 2.3 SILVER ION

2.3.1 Direct Measurements

2.3.2 Indirect Measurements

2.3.3 Comparison of Direct and Indirect Measurements

### 2.3.1 DIRECT MEASUREMENTS

Table 63

Comparison of changes in potential,  $\Delta E$ , for a given cell system (silver chloride/silver-silver chloride d/i.  $10^{-3}$  M silver nitrate) and various solvent concentrations in different solvent-water mixtures.

Solvent % m/m	$\Delta E/mV$					
	MeOH	EtOH	HOAc	n-PrOH	i-PrCH	acetone*
0	0**	0**	0**	0(346.7)	0(343.5)	0(6.5)
10	15	-1	4	4.9	3.8	12.8
20	28	-1	10	9.4	7.4	26.8
30	41	1	16	13.5	10.9	40.9
40	55	3	24	18.3	14.4	56.4
50	69	7	27	23.0	20.6	78.1
60	87	11	51	32.3	28.2	96.7
70	105	17	59	44.4	38.3	119.0
80	126	47	73	63.5	55.0	141.4
90	146	64	105	93.2	78.6	(144.3)
95	159	68	138	113.5	94.3	(145.9)
99	168	76	168	133.4	110.7	-

(1). \* SCE(LiCl) reference electrode was used.

(2). \*\* Absolute potential not available.

Table 64

Comparison of changes in potential,  $\Delta E$ , for a given cell system (silver chloride/silver-silver chloride d/1.  $10^{-3}$  M silver nitrate) and various solvent concentrations in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$				
	EtOH	HOAc	n-PrOH	i-PrCH	acetone
0	0*	*0(400.5)	0(474.3)	0(481.8)	0(167.2)
10	-1	9.8	1.1	-1.2	8.9
20	-2	16.1	2.2	-2.8	16.1
30	-3	23.8	3.1	-3.1	26.1
40	-5	32.4	3.8	-4.0	34.8
50	-5	41.4	5.6	-4.8	43.6
60	-1	53.6	7.4	-5.7	53.5
70	-3	68.3	8.7	-6.2	61.6
80	-6	85.5	9.3	-6.8	69.0
90	-8	105.7	9.9	-8.2	74.5
95	-10	114.9	11.5	-9.6	73.3
99	-11	122.0	12.4	-10.4	67.4

\* (1). Absolute potential not available.

(2).  $10^{-4}$  M  $AgNO_3$  was used.

# Lead acetate used.

$$\Delta E_{\max}/\text{mV} = 168$$

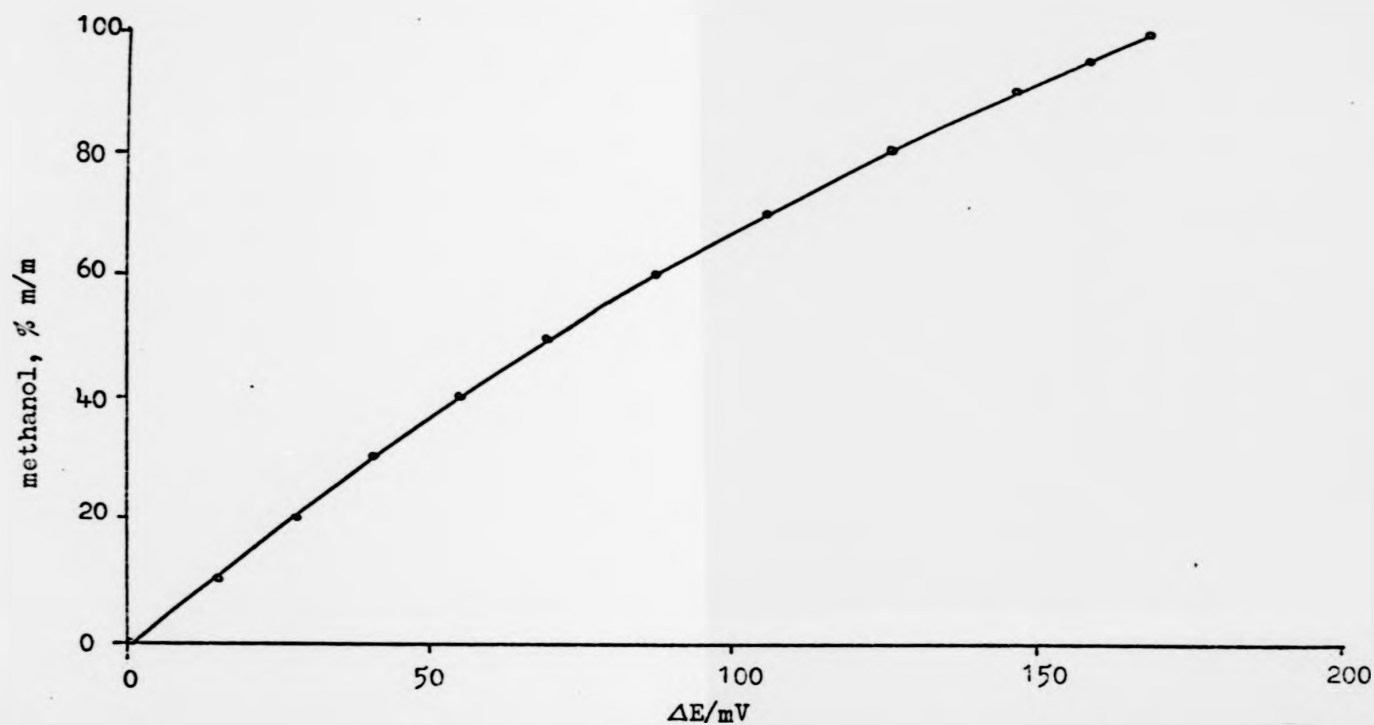


Fig. 49 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3\text{--MeOH(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M silver nitrate and various methanol concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

$$\Delta E_{\max}/mV = 154$$

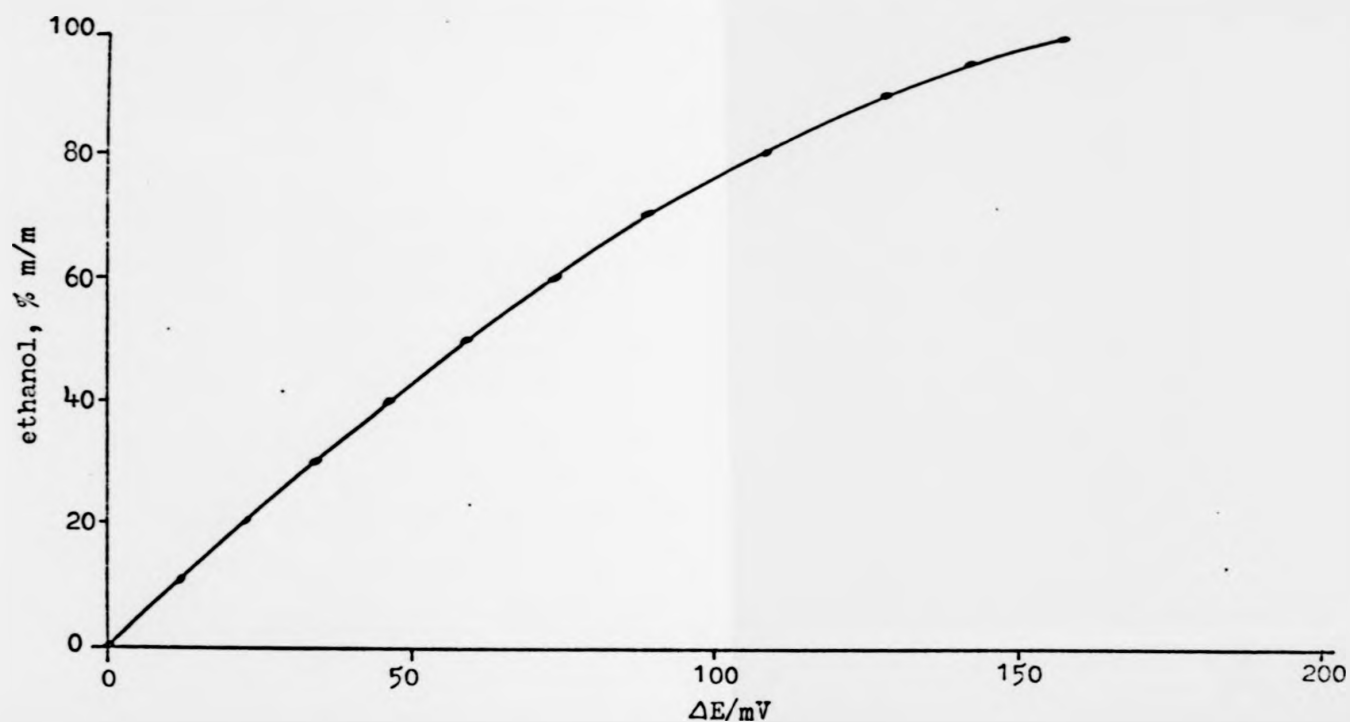


Fig. 50 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3 - \text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M silver nitrate and various ethanol concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

$$\Delta E_{\max}/\text{mV} = 186$$

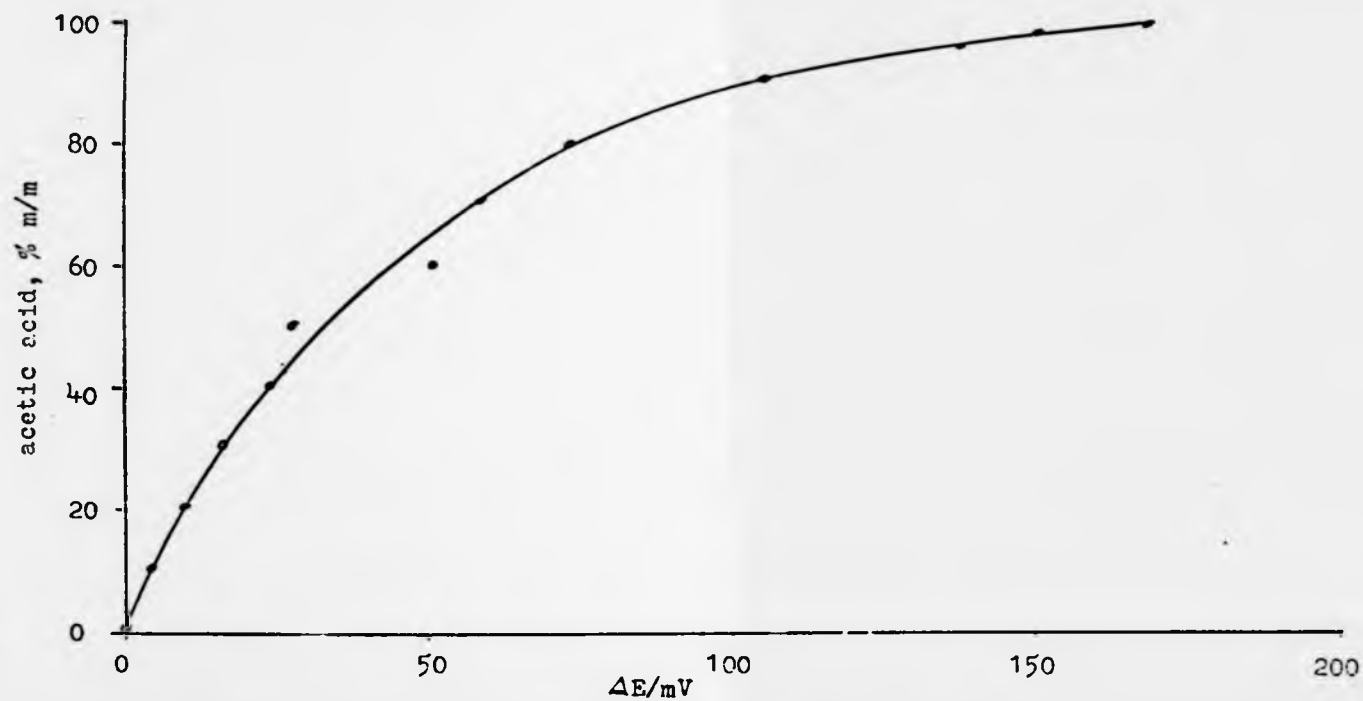


Fig. 51 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3\text{--HOAc(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M silver nitrate and various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (single-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 186$$

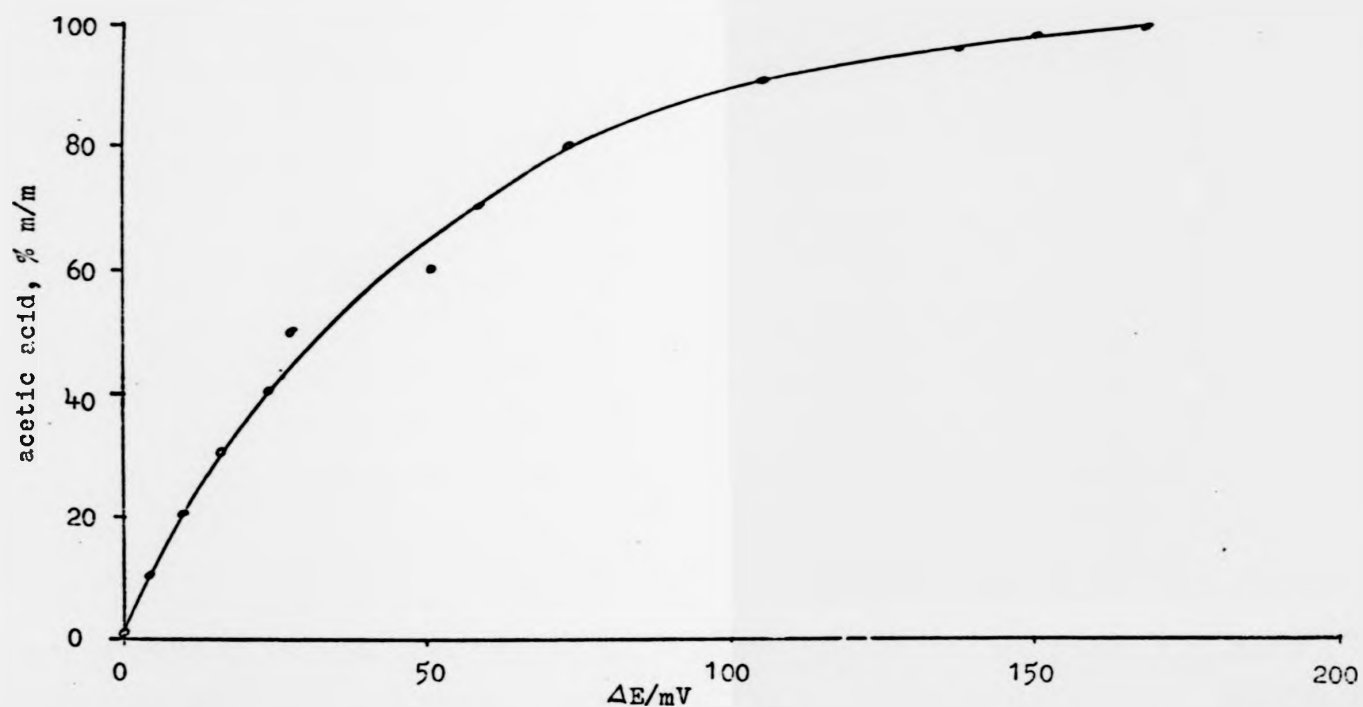


Fig. 51 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3\text{--HOAc(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M silver nitrate and various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (single-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 133.4$$

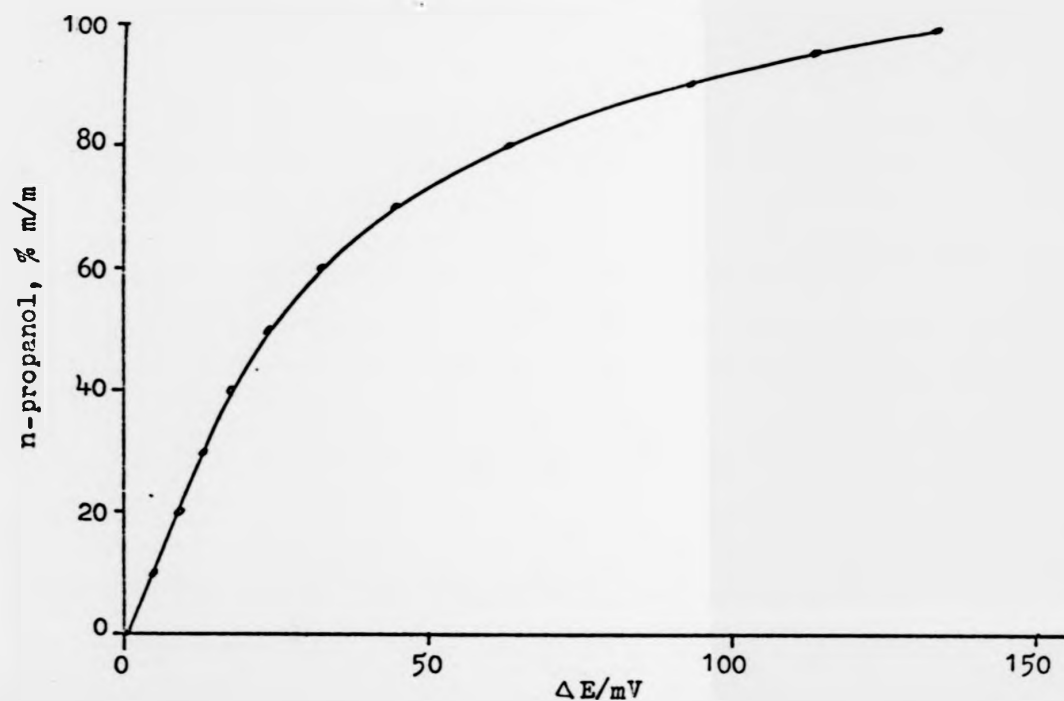


Fig.52 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ -n-PrOH( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M silver nitrate and various n-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.



$$\Delta E_{\max}/\text{mV} = 110.9$$

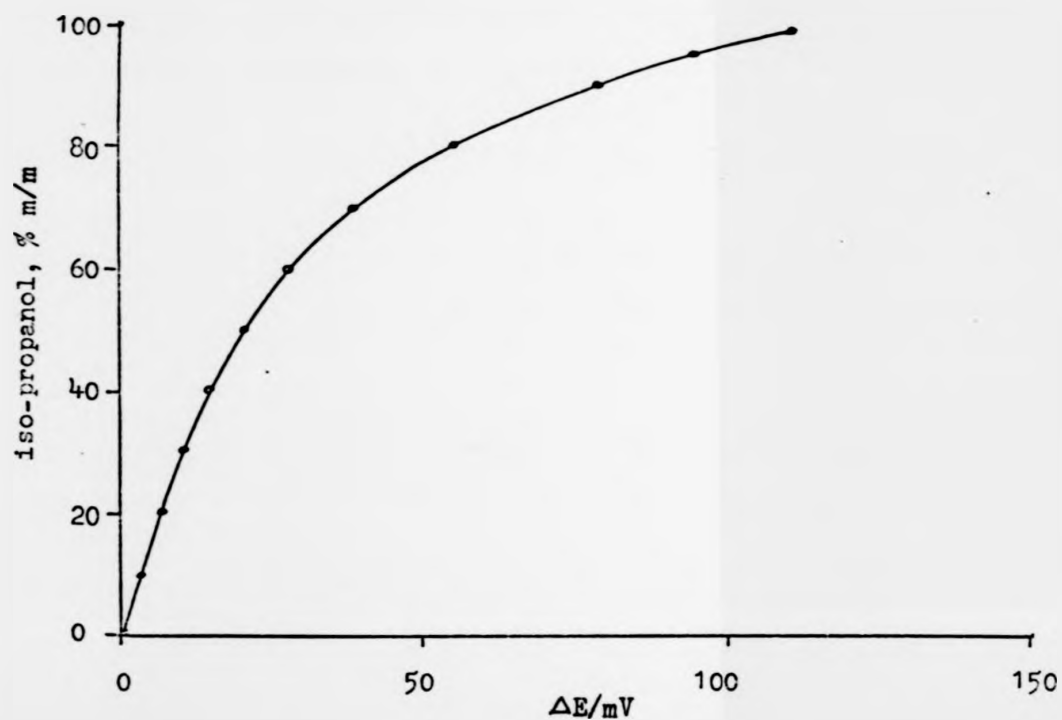


Fig.53 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ -1-PrCH( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M silver nitrate and various iso-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

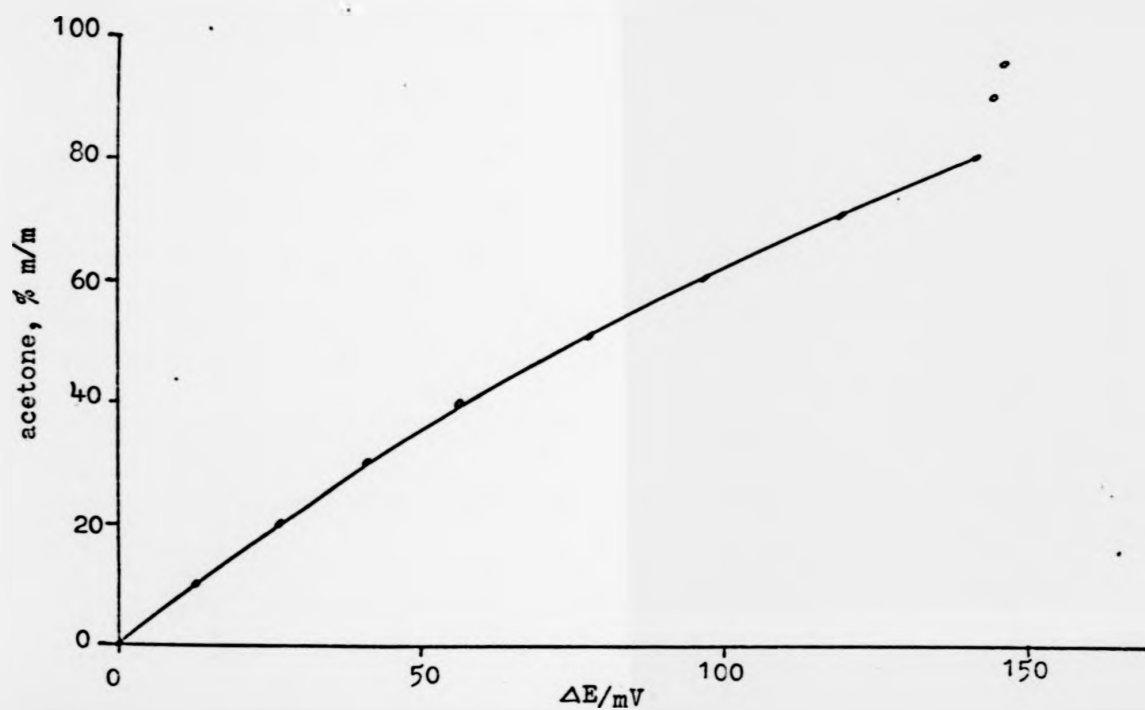


Fig. 54 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ —acetone( $\text{H}_2\text{O}$ ), in solutions, of  $10^{-3}$  M silver nitrate and various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

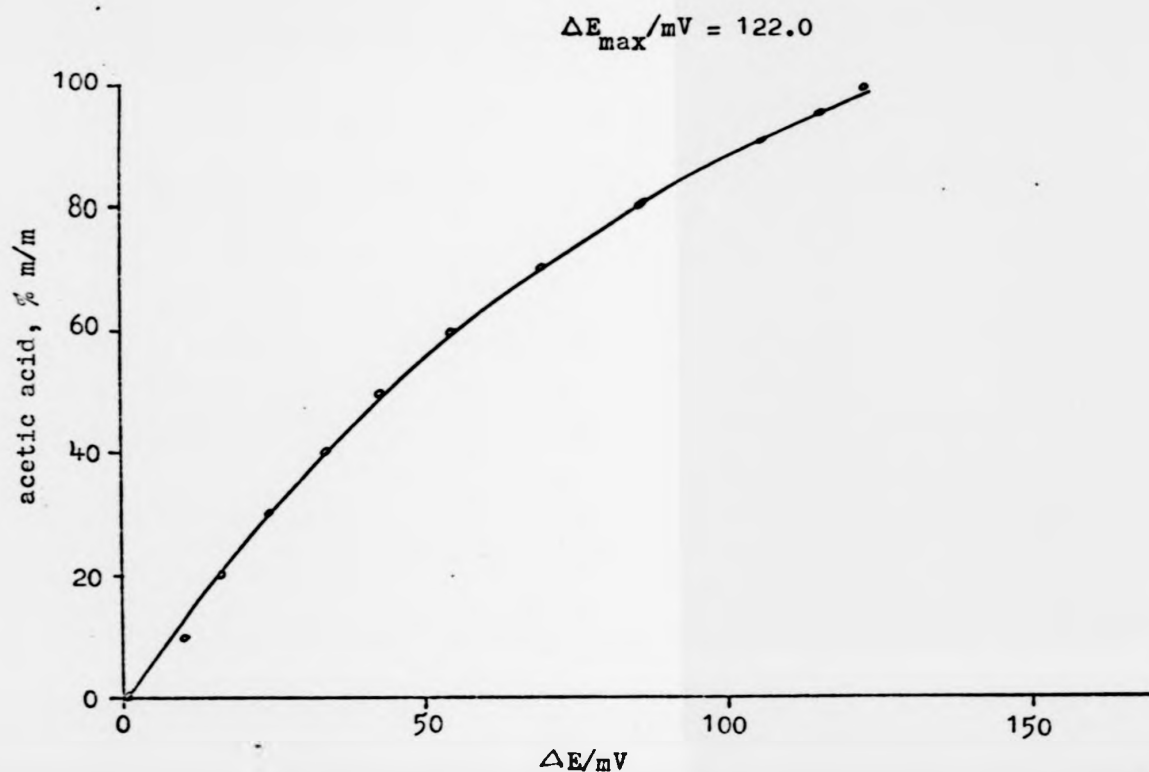


Fig. 55 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3 \text{ — HOAc}(\text{MeOH})$ , in solutions of  $10^{-4}$  M silver nitrate and various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/mV = 12.4$$

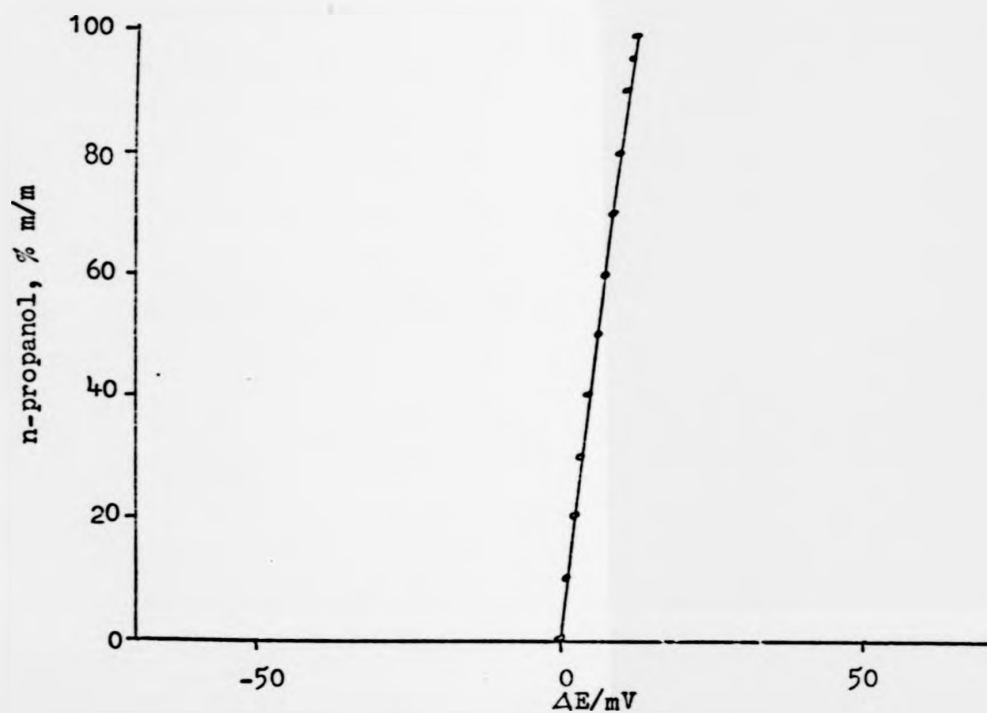


Fig.56 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ -n-PrOH(MeOH), in solutions, of  $10^{-3}$  M silver nitrate and various n-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\text{max}}/\text{mV} = -10.4$$

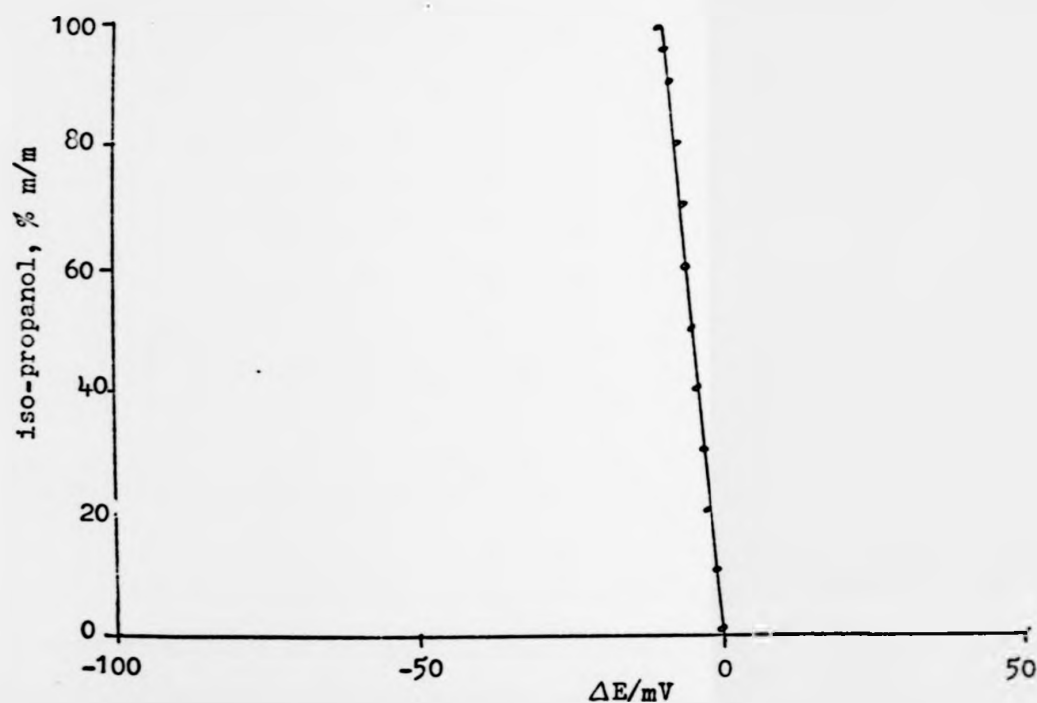


Fig.57 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ —1-PrOH(MeOH), in solutions of  $10^{-3}$  M silver nitrate and various iso-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

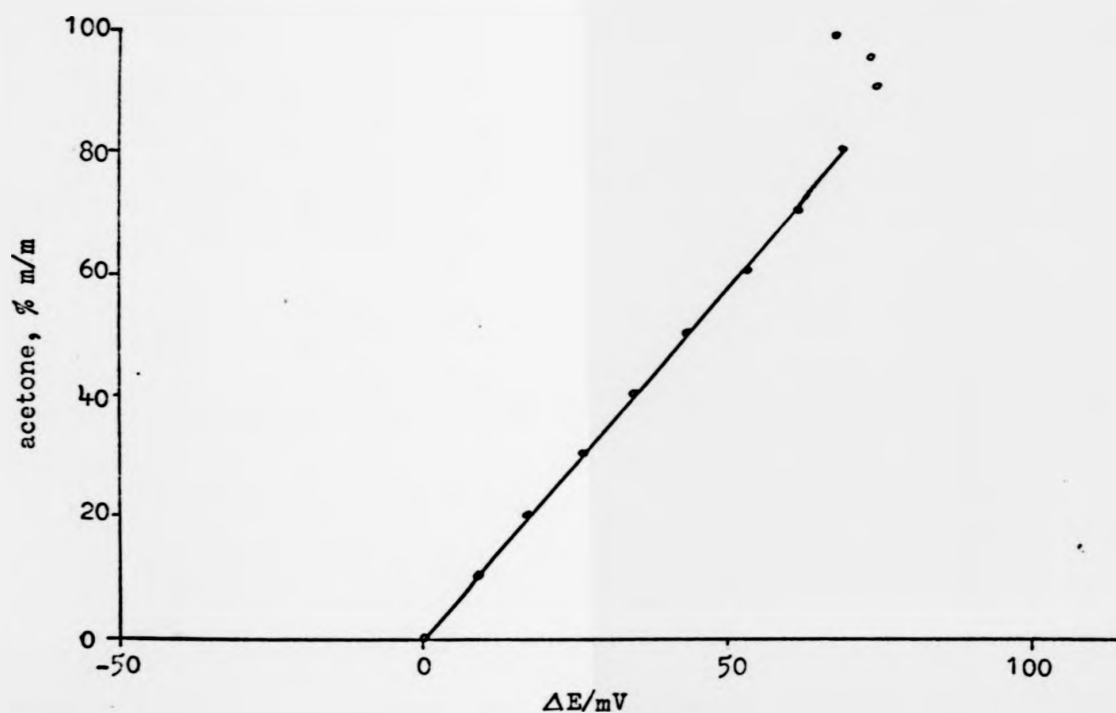


Fig.58 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3$ -acetone( $\text{MeOH}$ ), in solutions, of  $10^{-3}$  M silver nitrate and various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

### 2.3.2 INDIRECT MEASUREMENTS

Table 65

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3\text{--EtOH(H}_2\text{O)}$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various ethanol concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m ethanol	Potential/mV			Electrode slope /mV per decade	LLRP (LR)
	$10^{-3}$ MAg <sup>+</sup>	$10^{-4}$ MAg <sup>+</sup>	$10^{-5}$ MAg <sup>+</sup>		
0	144	92	41	51.5	$6 \times 10^{-6}$
10	157	104	51	52.0	$6 \times 10^{-6}$
20	167	116	63	51.5	$6 \times 10^{-6}$
30	178	129	74	53.5	$6 \times 10^{-6}$
40	194	142	88	53.0	$6 \times 10^{-6}$
50	202	154	105	49.0	$6 \times 10^{-6}$
60	215	167	98	58	$2 \times 10^{-6}$ - $2 \times 10^{-4}$
70	229	181	109	62.0	$2 \times 10^{-5}$ - $2 \times 10^{-4}$
80	248 (26)*	209 (49)*	136 (85)*	NL	-
90	258 (8)	231 (57)	136 (140)	NL	-
95	261 (2)	238 (53)	132	NL	-
99	266 (-2)	243 (38)	146	NL	-
$\Delta E_{\text{max/mV}}$	152	151	105		

(1). NL: Non-linear.

(2). ( )\*: Tangential slope at the given concentration point.

Table 66

Change in potential (obtained by the 'indirect method') for the system,  $\text{AgNO}_3$ --n-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various n-propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope /mV per decade	LLRR	$E^\circ$ /mV
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	344.5	278.5	227.9	66.0	$6 \times 10^{-5}$	542.5
20	352.4	289.3	241.8	63.0	$6 \times 10^{-5}$	541.4
40	359.1	293.6	233.0	66.0	$1 \times 10^{-5}$	557.1
60	369.7	301.8	229.9	67.9	$6 \times 10^{-6}$	573.4
80	396.0	328.8	239.7	67.2	$3 \times 10^{-5}$	597.6
90	421.0	358.5	240.2	65.0	$1 \times 10^{-4}$	615.0
99	455.5 (42)*	397.9 (72)*	225.6	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	111.0	119.4	-2.3			

(1) NL: Non-linear. 2. ( )\* Tangential slope.



Table 62

Change in potential (obtained by the 'indirect method') for the system,  $\text{AgNO}_3$ --1-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various isopropanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /mV per decade	LLLRR	$E^0$ /mV
	$10^{-3}$ MAg <sup>+</sup>	$10^{-4}$ MAg <sup>+</sup>	$10^{-5}$ MAg <sup>+</sup>			
0	344.5	278.5	227.9	66.0	$5 \times 10^{-5}$	542.5
20	349.2	286.1	230.9	63.1	$4 \times 10^{-5}$	538.5
40	355.7	290.4	229.7	65.0	$1 \times 10^{-5}$	550.7
60	365.3	298.9	225.7	67.5	$2 \times 10^{-5}$	567.8
80	387.5	522.7	235.6	64.8	$6 \times 10^{-5}$	581.9
90	408.6 (47)*	347.4 (68)*	((225.5))**	NL	-	
99	433.1 (38)	380.2 (62)	((211.8))	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	88.6	101.7	-16.1			

NL: Non-linear.

( )\*: Tangential slope at the given concentration point.

(( ))\*\*: Unstable.

Table 68

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ --acetone( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLRR	$E^0$ /mV
	$10^{-3}$ MAg <sup>+</sup>	$10^{-4}$ MAg <sup>+</sup>	$10^{-5}$ MAg <sup>+</sup>			
0	-23.6	-74.3	-115.6	50.7	$5 \times 10^{-5}$	123.5 (167.3)**
20	0.1	-54.6	-101.8	54.7	$4 \times 10^{-5}$	164.2 (186.8)
40	33.6	-20.6	-79.8	56.0	$6 \times 10^{-6}$	201.6 (214.7)
60	74.9	22.2	-40.0	57.5	$2 \times 10^{-6}$	247.4 (249.2)
80	119.3 (28)*	80.6 (47)*	20.8 (72)*	NL	-	
90	122.8 (18)	90.2 (44)	19.3 (114)	NL	-	
99	143.6 (14)	113.1 (28)	68.6 (91)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	167.2	187.4	184.2			

1. NL: Non-linear. 2. ( )\* Tangential slope. 3. ( )\*\*  $E^0$  normalised w.r.t.d/j.

Table 69

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ --EtOH(MeOH), in solutions  
 $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various ethanol concentrations, measured by  
using silver chloride and silver-silver chloride (double-junction)  
electrodes

% m/m ethanol	Potential/mV			Electrode slope /mV per decade	LLPR
	$10^{-3}$ $\text{M Ag}^+$	$10^{-4}$ $\text{M Ag}^+$	$10^{-5}$ $\text{M Ag}^+$		
0	297	238	169	64.0	$6 \times 10^{-6}$
10	294	231	167	63.5	$6 \times 10^{-6}$
20	291	229	165	63.0	$6 \times 10^{-6}$
30	290	229	165	62.5	$6 \times 10^{-6}$
40	289	225	163	63.0	$6 \times 10^{-6}$
50	288	226	167	62.0	$2 \times 10^{-5}$
60	287	225	165	62.0	$2 \times 10^{-5}$
70	288	255	164	62.0	$6 \times 10^{-6}$
80	291	229	171	62.0	$1 \times 10^{-5}$
90	295	233	175	62.0	$1 \times 10^{-5}$
95	300	239	175	62.5	$6 \times 10^{-6}$
$\Delta E/\text{mV}$	3	1	6		

Table 70

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ -- $\text{HOAc}(\text{MeOH})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver chloride and of various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m acetic acid	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0$ /mV
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	470.0	406.6	341.5	63.4	$1 \times 10^{-5}$	660.2
10	475.1	412.6	359.5	62.5	$6 \times 10^{-5}$	662.6
20	480.4	418.7	364.2	62.0	$6 \times 10^{-5}$	666.4
30	487.3	425.0	372.8	62.3	$6 \times 10^{-5}$	674.2
40	494.1	435.7	392.2	58.5	$6 \times 10^{-5}$	669.6
50	501.9	440.8	391.1	61.0	$6 \times 10^{-5}$	684.9
60	511.7	454.9	407.9	57.0	$6 \times 10^{-5}$	682.7
70	522.2	467.9	418.7	64.5	$6 \times 10^{-5}$	685.7
$\Delta E_{\text{max/mV}}$	52.2	61.3	77.2			

Table 70

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3\text{--HOAc}(\text{MeOH})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver chloride and of various acetic acid concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m acetic acid	Potential/mV			Electrode slope /mV per decade	LLRR	$E^\circ/\text{mV}$
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	470.0	406.6	341.5	63.4	$1 \times 10^{-5}$	660.2
10	475.1	412.6	359.5	62.5	$6 \times 10^{-5}$	662.6
20	480.4	418.7	364.2	62.0	$6 \times 10^{-5}$	666.4
30	487.3	425.0	372.8	62.3	$6 \times 10^{-5}$	674.2
40	494.1	435.7	392.2	58.5	$6 \times 10^{-5}$	669.6
50	501.9	440.8	391.1	61.0	$6 \times 10^{-5}$	684.9
60	511.7	454.9	407.9	57.0	$6 \times 10^{-5}$	682.7
70	522.2	467.9	418.7	64.5	$6 \times 10^{-5}$	685.7
$\Delta E_{\text{max}}/\text{mV}$	52.2	61.3	77.2			

Table 71

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ -- $n$ -PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various  $n$ -propanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m $n$ -propanol	Potential/mV			Electrode slope /mV per decade	LLRR	$E^\circ$ /mV
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	479.6	410.6	351.6	69.0	$6 \times 10^{-5}$	686.6
20	483.6	415.7	360.9	68.0	$6 \times 10^{-5}$	687.6
40	487.0	419.4	361.2	60.0	$2 \times 10^{-4}$	667.0
60	490.4	423.5	361.3	59.0	$2 \times 10^{-4}$	667.4
80	493.2	427.2	359.6	53.0	$2 \times 10^{-4}$	652.2
90	494.2	429.9	366.5	52.0	$2 \times 10^{-4}$	650.2
99	494.5	431.1	(351.6)*	51.0	$2 \times 10^{-4}$	647.5
$\Delta E_{\text{max}}/\text{mV}$	14.9	20.5	(0)			

(\*)\*: Unstable

Table 72

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ --1-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various isopropanol concentrations, measured by using silver chloride and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential /mV			Electrode slope /mV per decade	LLRR (LR)	$E^\circ$ /mV
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	479.6	410.6	351.6	64.0	1 X 10	671.6
20	471.6	403.7	342.4	64.6	1 X 10	665.4
40	471.2	403.8	345.4	62.9	1 X 10	659.9
60	473.2	407.0	348.1	62.6	1 X 10	661.0
80	473.9	411.0	347.2	64.8	1 X 10	668.3
90	473.4	413.7	344.4	69.3	$1 \times 10^{-5}$ - $2 \times 10^{-4}$	690.9
99	472.0	414.9	342.6	68.3	$2 \times 10^{-5}$ - $2 \times 10^{-4}$	688.1
$\Delta E_{\text{max}}/\text{mV}$	-7.6	4.3	-9.0			

LR: Linear region

Table 23

Change in potential (obtained by 'indirect method') for the system,  $\text{AgNO}_3$ --acetone (MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in silver nitrate and of various acetone concentrations, measured by using silver chloride and mercury-mercurous sulphate electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0$ /mV
	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$			
0	97.2	30.7	-32.4	64.8	$1 \times 10^{-5}$	291.6 (344.8)**
20	109.8	46.6	-5.9	62.0	$5 \times 10^{-5}$	295.8 (337.8)
40	127.7	67.6	11.4	58.2	$2 \times 10^{-6}$	302.3 (336.7)
60	147.5	95.1	42.0	52.8	$6 \times 10^{-6}$	305.9 (331.0)
80	(84.6)	120.9	124.2	NL	-	
90	(140.2)*	159.0	138.8	NL	-	
99	(96.5)	(90.2)*	120.0	NL	-	
$\Delta E/\text{mV}$	50.3	64.4	74.4			

1. ( )\* Unstable      2. ( )\*\*  $E^0$  normalised w.r.t.d/j.

NL: Non-linear



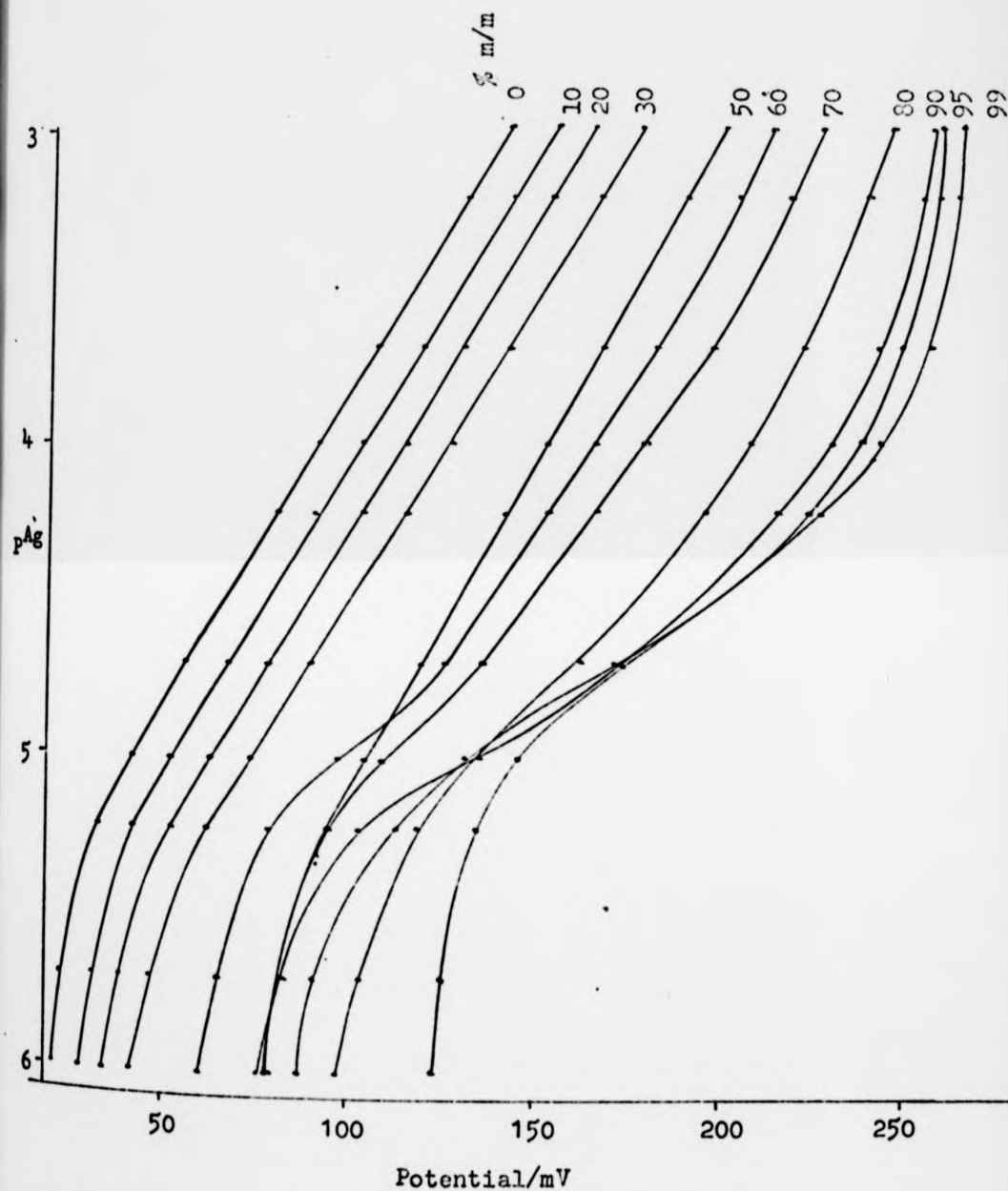


Fig.59 Electrode calibration graphs for the system,  $AgNO_3-EtOH(H_2O)$ , in solutions of constant ethanol concentration and various silver nitrate concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1M Na_2SO_4$ ) electrodes.

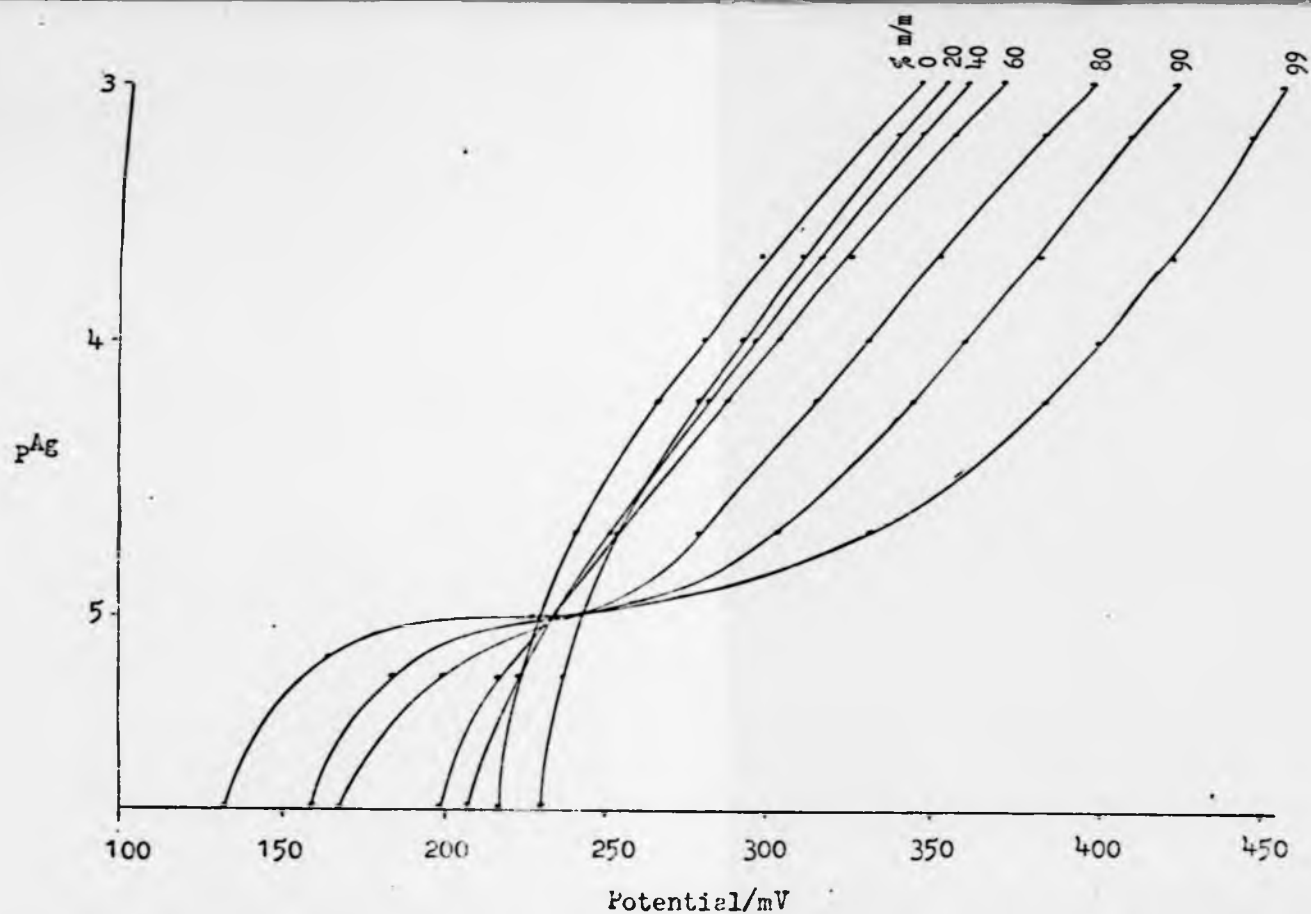


Fig.60 Electrode calibration graphs for the system,  $\text{AgNO}_3\text{--nPrOH(H}_2\text{O)}$ , in solutions of constant n-propanol concentration and various silver nitrate concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

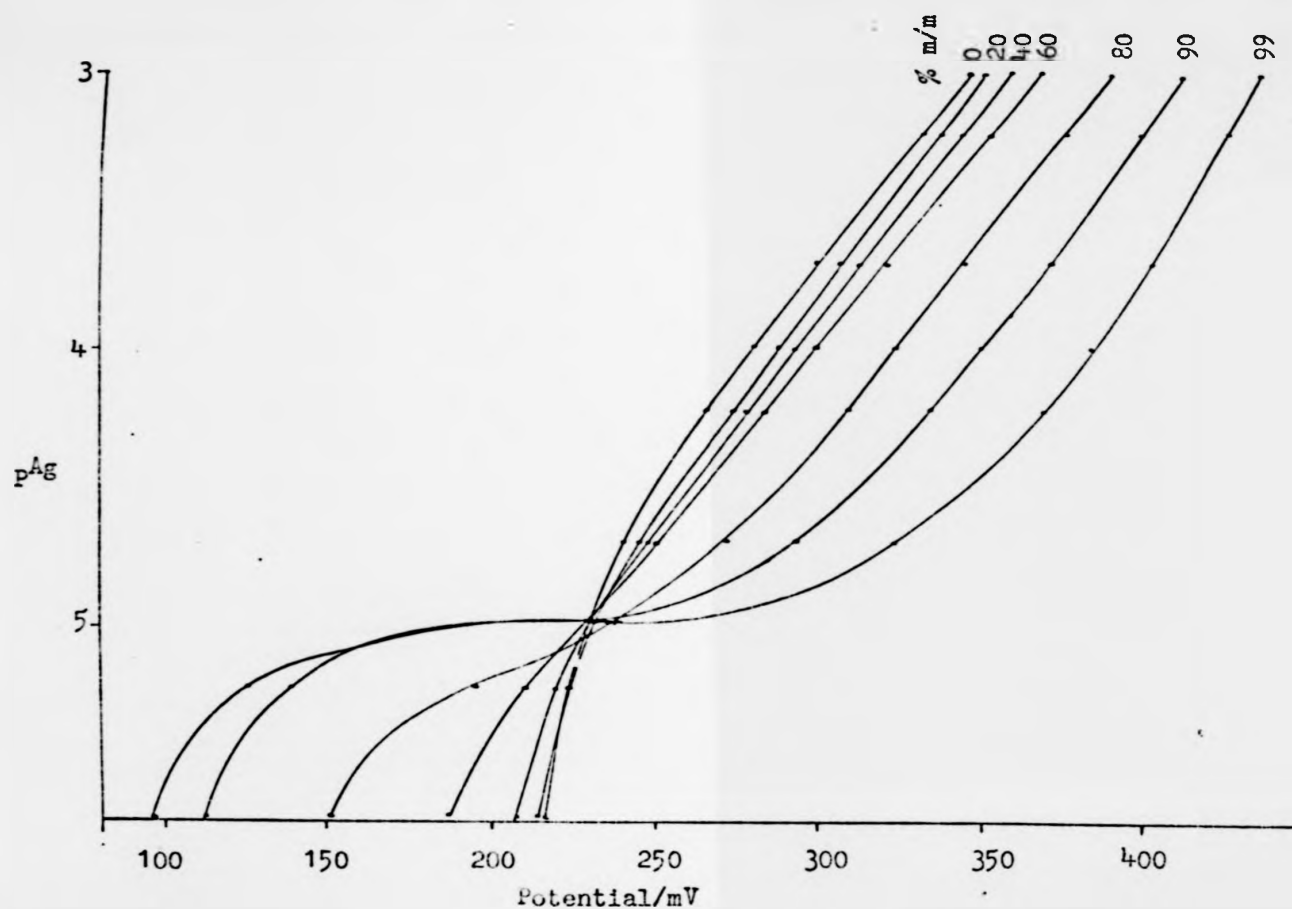


Fig. 61 Electrode calibration graphs for the system,  $\text{AgNO}_3$ -1- $\text{PrOH}(\text{H}_2\text{O})$ , in solutions of constant iso-propanol concentration and various silver nitrate concentrations, measured by using silver chloride and silver-silver chloride (double junction) electrodes.

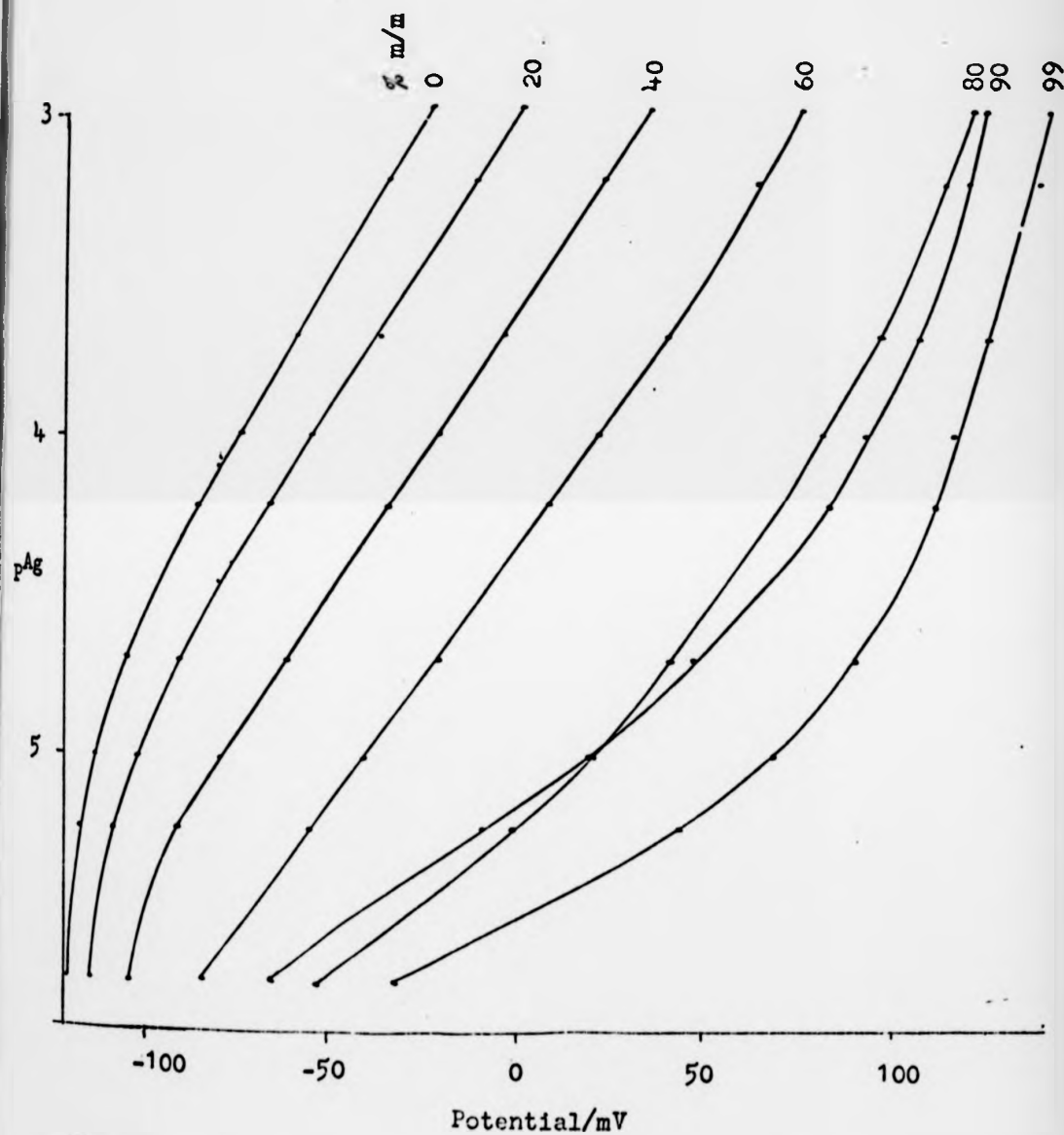


Fig. 62 Electrode calibration graphs for the system,  $\text{AgNO}_3$ --acetone( $\text{H}_2\text{O}$ ), in solutions of constant acetone concentration and various silver nitrate concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

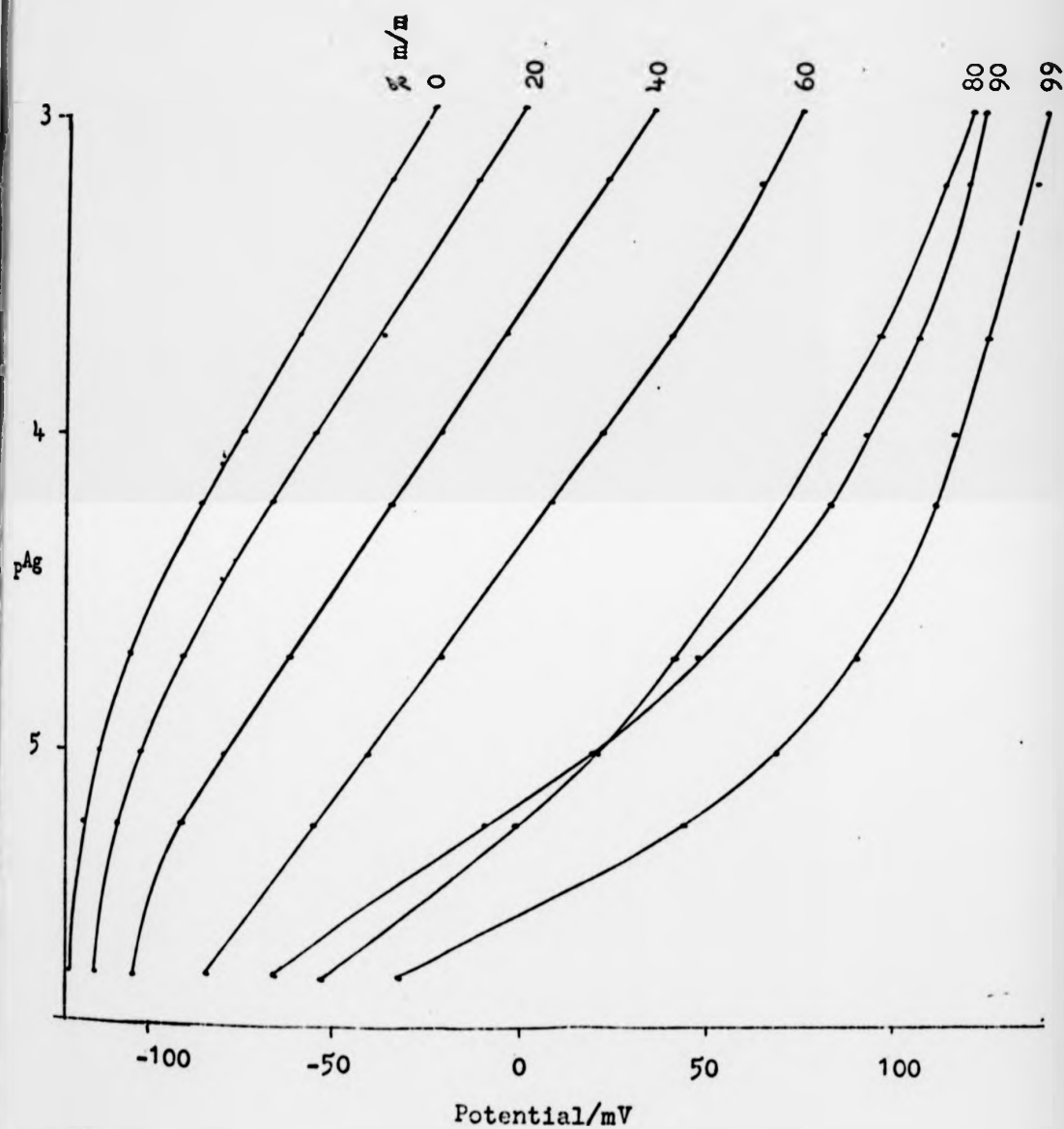


Fig. 62 Electrode calibration graphs for the system,  $\text{AgNO}_3$ --acetone( $\text{H}_2\text{O}$ ), in solutions of constant acetone concentration and various silver nitrate concentrations, measured by using Silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

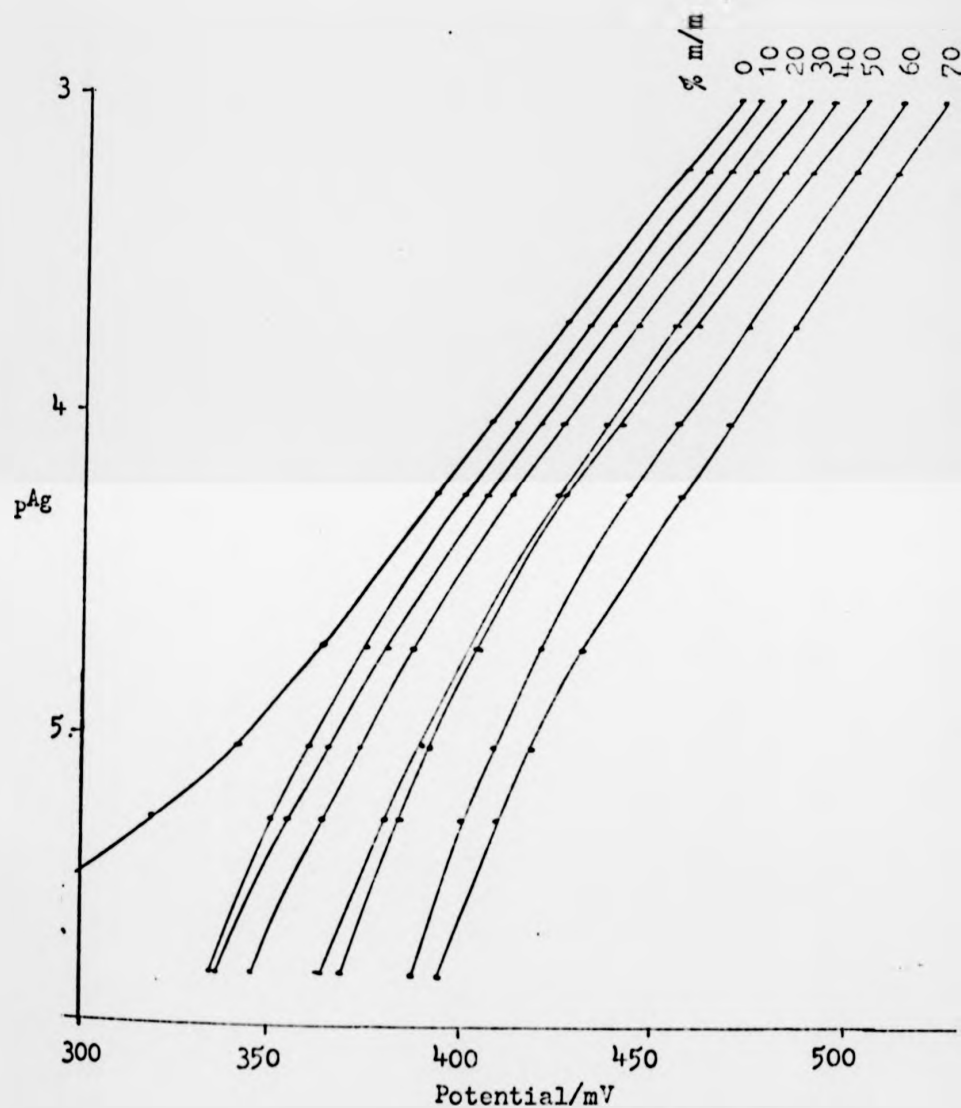


Fig.63 Electrode calibration graphs for the system,  $\text{AgNO}_3$ -- $\text{HOAc}(\text{MeOH})$  in solutions of constant acetic acid concentration and various silver nitrate concentrations, measured by using Silver chloride and silver-silver chloride (double-junction) electrodes.

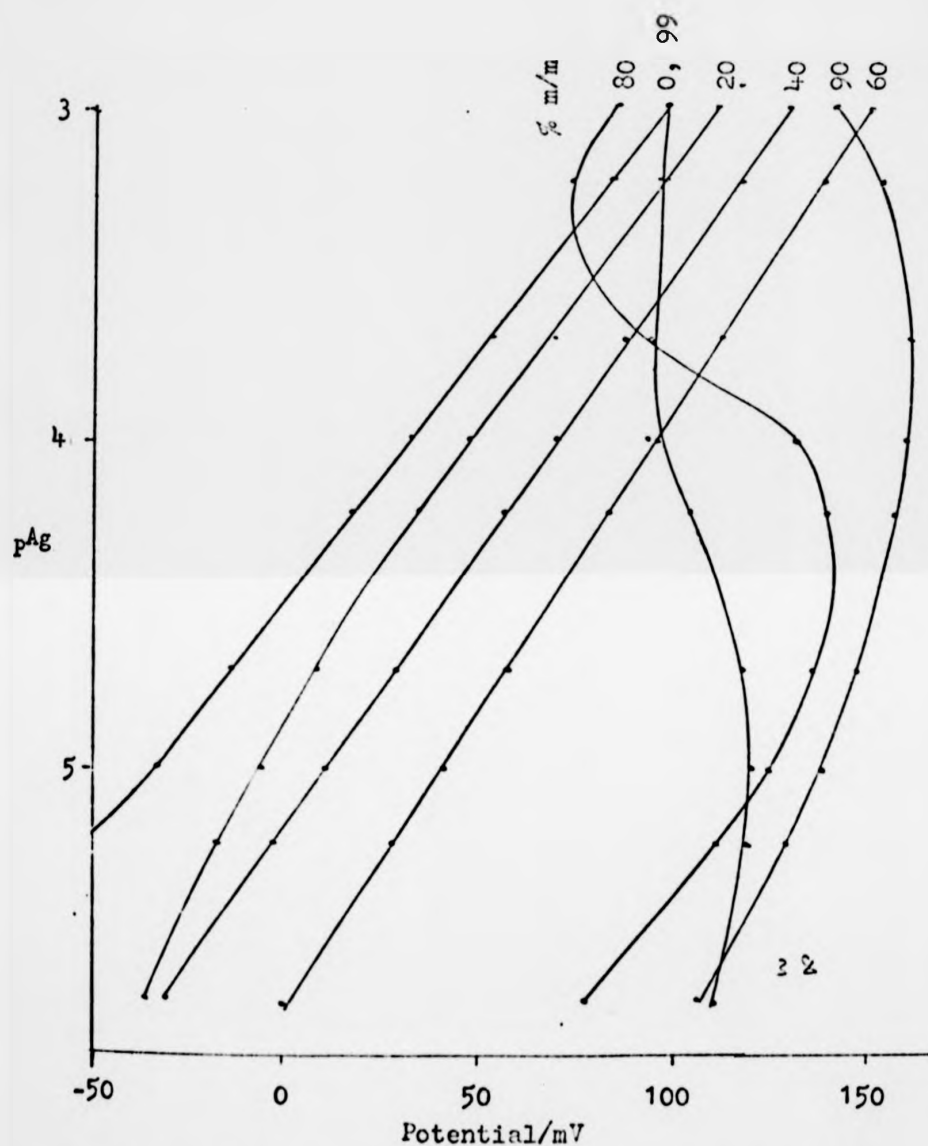


Fig. 64 Electrode calibration graphs for the system,  $\text{AgNO}_3$ --acetone(MeOH) in solutions of constant acetone and various silver nitrate concentrations, measured by using Silver chloride and mercury-mercurous ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

### 2.3.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 74

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the systems,  $\text{AgNO}_3$ -HOAc( $\text{H}_2\text{O}$ ) and  $\text{AgNO}_3$ -HOAc( $\text{MeOH}$ ), in  $10^{-3}$  M solutions of silver nitrate for various concentrations of acetic acid measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

acetic acid % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct*	Indirect*		Direct	Indirect	
0	0	0	0	0	0	0
10	4	-7	11	9.8	5.1	4.7
20	10	-4	14	16.1	10.4	5.7
30	16	0	16	23.8	17.3	6.5
40	24	9	15	32.4	24.1	8.3
50	27	17	10	41.4	31.9	9.5
60	51	30	21	53.6	41.7	11.9
70	59	39	20	68.3	52.2	16.1
80	73	66	6	85.5	+	
90	105	95	10	105.7	+	
95	138	119	19	114.9	+	
99	168	140	28	122.0	+	

(1). \*  $\text{Hg}, \text{Hg}_2\text{SO}_4$  reference electrode was used.

(2). + No measurement made.



### 2.3.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 74

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the systems,  $\text{AgNO}_3\text{--HOAc(H}_2\text{O)}$  and  $\text{AgNO}_3\text{--HOAc(MeOH)}$ , in  $10^{-3}$  M solutions of silver nitrate for various concentrations of acetic acid measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

acetic acid % m/m	$\Delta E/\text{mV (H}_2\text{O)}$		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV (MeOH)}$		$\Delta\Delta E$ (MeOH)
	Direct <sup>*</sup>	Indirect <sup>*</sup>		Direct	Indirect	
0	0	0	0	0	0	0
10	4	-7	11	9.8	5.1	4.7
20	10	-4	14	16.1	10.4	5.7
30	16	0	16	23.8	17.3	6.5
40	24	9	15	32.4	24.1	8.3
50	27	17	10	41.4	31.9	9.5
60	51	30	21	53.6	41.7	11.9
70	59	39	20	68.3	52.2	16.1
80	73	66	6	85.5	+	
90	105	95	10	105.7	+	
95	138	119	19	114.9	+	
99	168	140	28	122.0	+	

(1). \*  $\text{Hg, Hg}_2\text{SO}_4$  reference electrode was used.

(2). + No measurement made.

Table 75

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{AgNO}_3$ -n-PrOH( $\text{H}_2\text{O}$ ), and  $\text{AgNO}_3$ -n-PrOH(MeOH), in  $10^{-3}$  M solutions of silver nitrate for various n-propanol concentrations measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/\text{mV}$ ( $\text{H}_2\text{O}$ )		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV}$ (MeOH)		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	9.4	7.9	1.5	2.2	4.0	-1.8
40	18.3	14.6	3.7	3.8	7.4	-3.6
60	32.3	25.2	7.2	7.4	10.8	-3.4
80	63.5	51.5	12.0	9.3	13.6	-4.3
90	93.2	76.5	16.7	9.9	14.6	-4.7
99	133.4	111.0	22.4	12.4	14.9	-2.5

Table 76

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{AgNO}_3$ -1-PrOH( $\text{H}_2\text{O}$ ) and  $\text{AgNO}_3$ -1-PrOH(MeCH), in  $10^{-3}$  M solutions of silver nitrate for various iso-propanol concentrations measured by using silver chloride and silver-silver chloride (double-junction) electrodes.

iso-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ (MeCH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	7.4	4.7	2.7	-2.8	-8.0	5.2
40	14.4	11.2	3.2	-4.0	-4.0	4.4
60	28.2	20.8	7.4	-5.7	-5.7	0.0
80	55.0	43.0	12.0	-6.8	-5.7	-1.1
90	78.6	64.1	14.5	-8.2	-6.2	-2.0
99	110.7	88.6	22.1	-10.4	-7.6	-2.8

Table 72

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{AgNO}_3$ -Acetone( $\text{H}_2\text{O}$ ) and  $\text{AgNO}_3$ -Acetone( $\text{MeOH}$ ), in  $10^{-3}$  M solutions of silver nitrate for various acetone concentrations measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

acetone % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta\Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	26.8	23.7	3.1	16.1	12.6	3.5
40	56.4	57.2	-0.8	34.8	30.5	4.3
60	96.7	98.5	-1.8	53.5	50.3	3.2
80	141.4	142.9	-1.5	69.0	(-12.6)	(81.6)
90	(144.3)*	146.4	(-2.1)	74.5	(43.0)	(31.5)

(\*)\*: unstable

2.4      LEAD ION

2.4.1      Direct Measurements

2.4.2      Indirect Measurements

2.4.3      Comparison of Direct and Indirect Measurements.

# 2.4.1 DIRECT MEASUREMENTS

Table 78

Comparison of changes in potential,  $\Delta E$ , for a given cell system (lead sulphide/silver-silver chloride d/j,  $10^{-3}$  M lead perchlorate) and various solvent concentrations in different solvent-water mixtures.

Solvent % m/m	$\Delta E/mV$					
	MeOH	EtOH	n-PrOH	i-PrOH	acetone	1,4-dioxan
0	0(-205.7)	0*	0(-197.4)	0(-190.4)	0(-162.9)	0(-200.0)
10	8.0	-5	8.4	7.0	14.3	8.9
20	14.5	-3	14.0	14.4	28.7	15.7
30	21.1	-2	18.6	20.9	43.3	23.9
40	27.7	0	22.8	25.8	60.9	32.1
50	36.2	0	27.4	32.3	88.1	41.8
60	45.5	0	36.4	42.9	112.9	55.2
70	56.5	30	49.6	58.3	143.4	72.7
80	71.9	27	71.7	82.7	186.2	98.3
90	93.3	39	113.0	127.2	255.8	133.2
95	108.9	66	149.0	158.3	324.0	169.8
99	123.9	99	199.9	233.7	427.5	(266)

\*Absolute potentials not available.

Table 79

Comparison of changes in potential,  $\Delta E$ , for a given cell system (lead sulphide/silver-silver chloride d/i,  $10^{-3}$  M lead perchlorate) and various solvent concentrations in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$					
	EtOH	HOAc	n-PrOH	i-PrOH	acetone	1,4-dioxan
0	*0(-178.1)	*0(187.4)	0(-62.7)	0(-67.4)	0(14.8)	0(-72.4)
10	0.3	14.8	6.4	11.6	16.3	22.6
20	0.7	25.9	13.9	23.6	30.1	36.7
30	-1.2	38.7	21.7	40.9	43.9	49.0
40	1.5	51.3	29.7	53.3	61.4	61.3
50	2.1	64.4	38.6	65.8	79.4	74.1
60	2.2	78.5	48.3	82.4	99.4	86.4
70	2.2	96.3	59.3	99.3	123.5	99.0
80	2.2	114.0	76.1	117.7	152.1	105.2
90	1.7	131.7	91.1	142.4	192.3	158.8
95	2.2	139.0	99.1	156.8	231.5	174.8
99	-2.0	149.4	106.6	170.6	288.3	-

\*Lead acetate was used.

$$\Delta E_{\max}/\text{mV} = 124$$

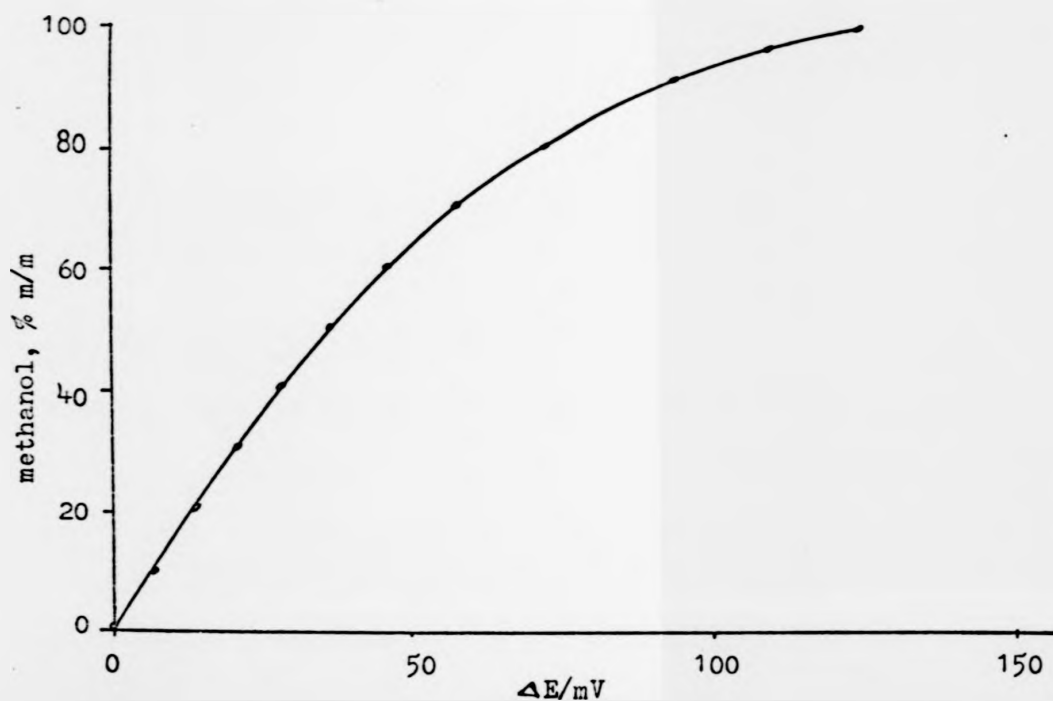


Fig.65 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2 - \text{MeOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M lead perchlorate and various methanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.



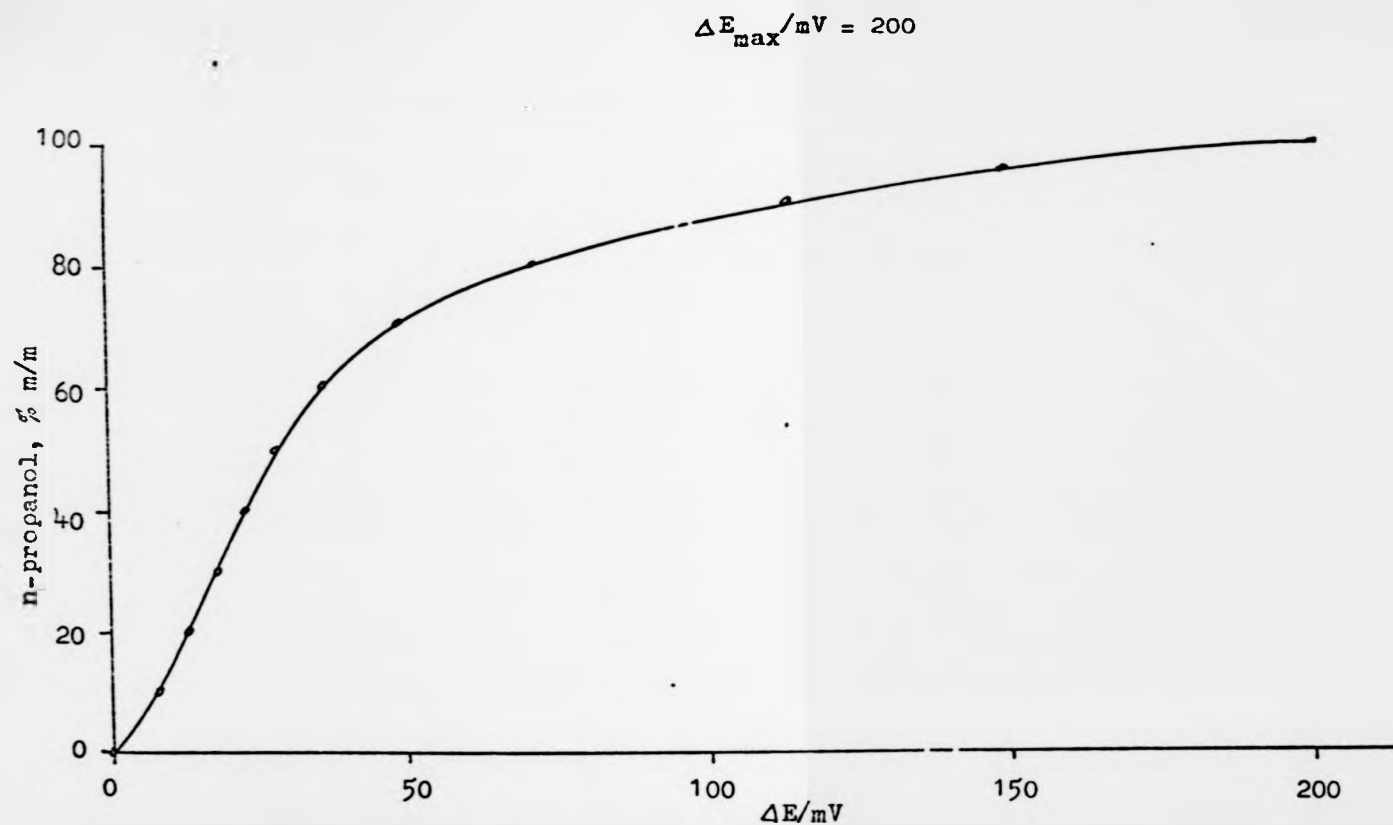


Fig. 66 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2 - \text{n-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M lead perchlorate and various n-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 234$$

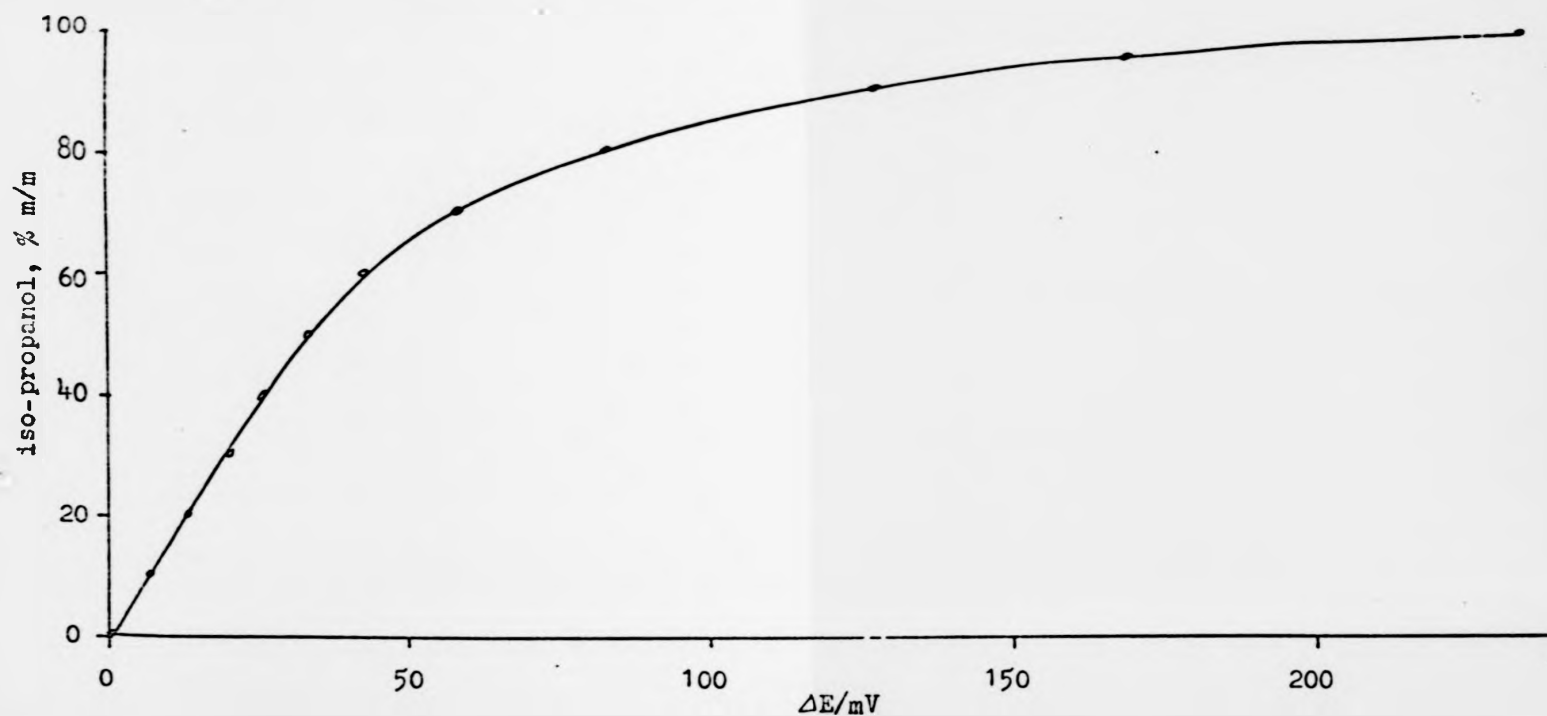


Fig. 67 Change in potential,  $\Delta E$ , for the system  $\text{Pb}(\text{ClO}_4)_2 - 1\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M lead perchlorate and various iso-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

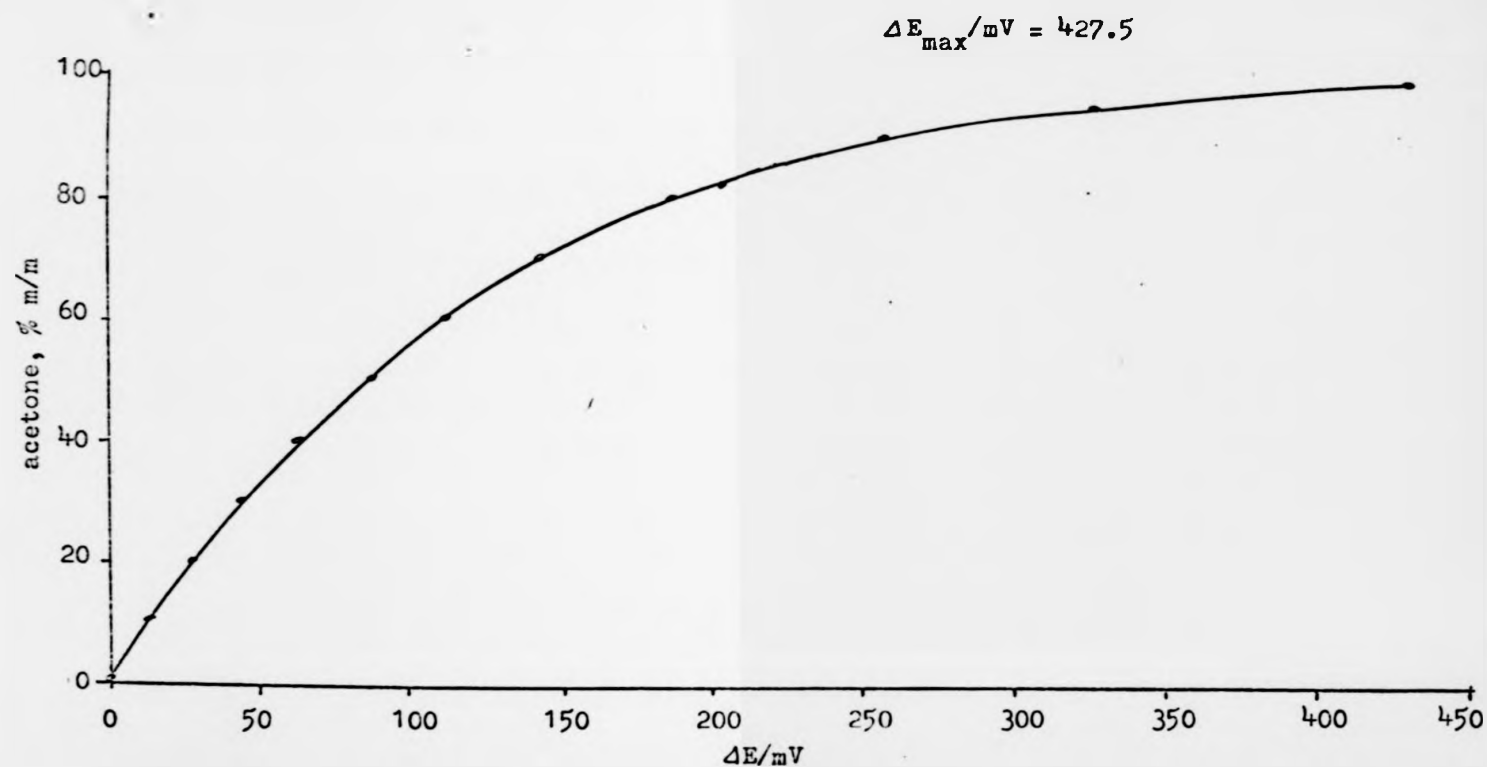


Fig. 68 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2$ -acetone( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M lead perchlorate and various acetone concentrations, measured by using lead sulphide and SCE(LiCl) electrodes.

$$\Delta E_{\max}/\text{mV} = 266$$

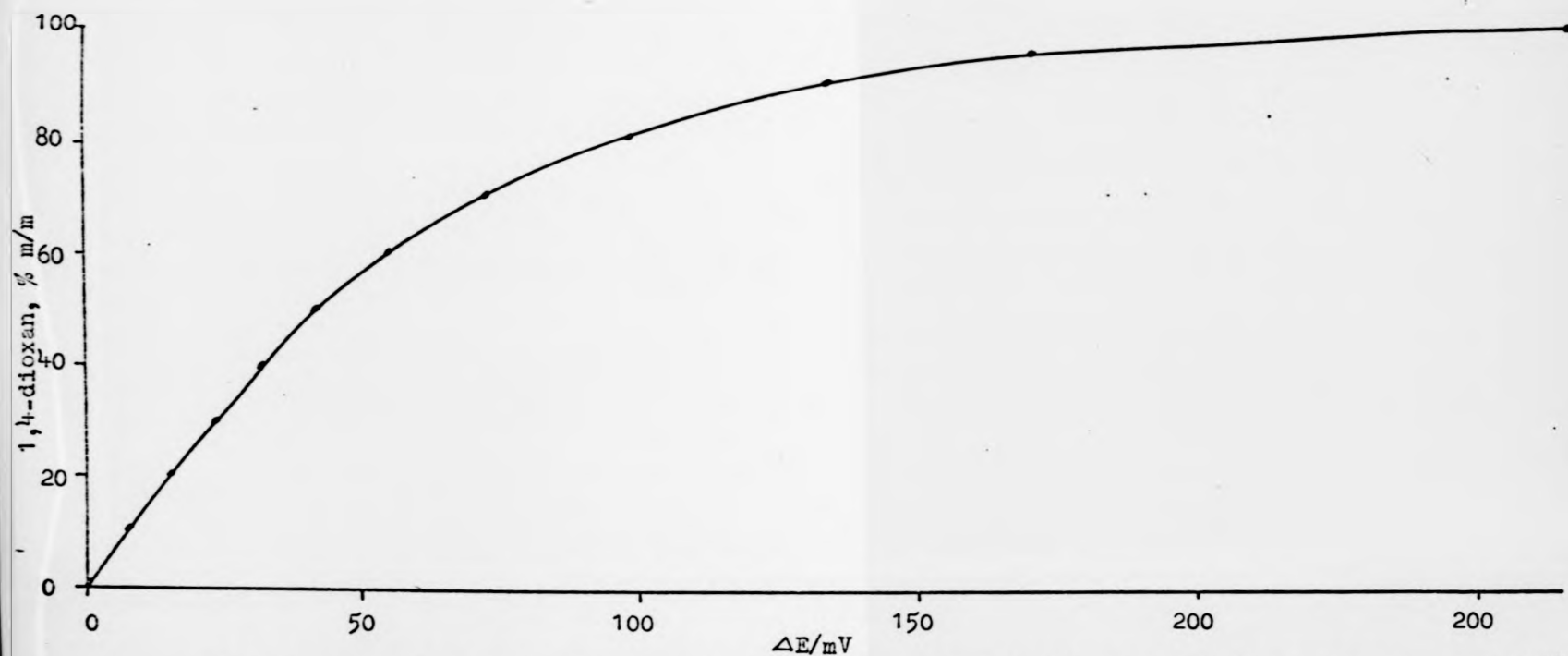


Fig. 69 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2$  / 1,4-dioxan( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M lead perchlorate and various 1,4-dioxan concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\text{max}}/\text{mV} = 139.4$$

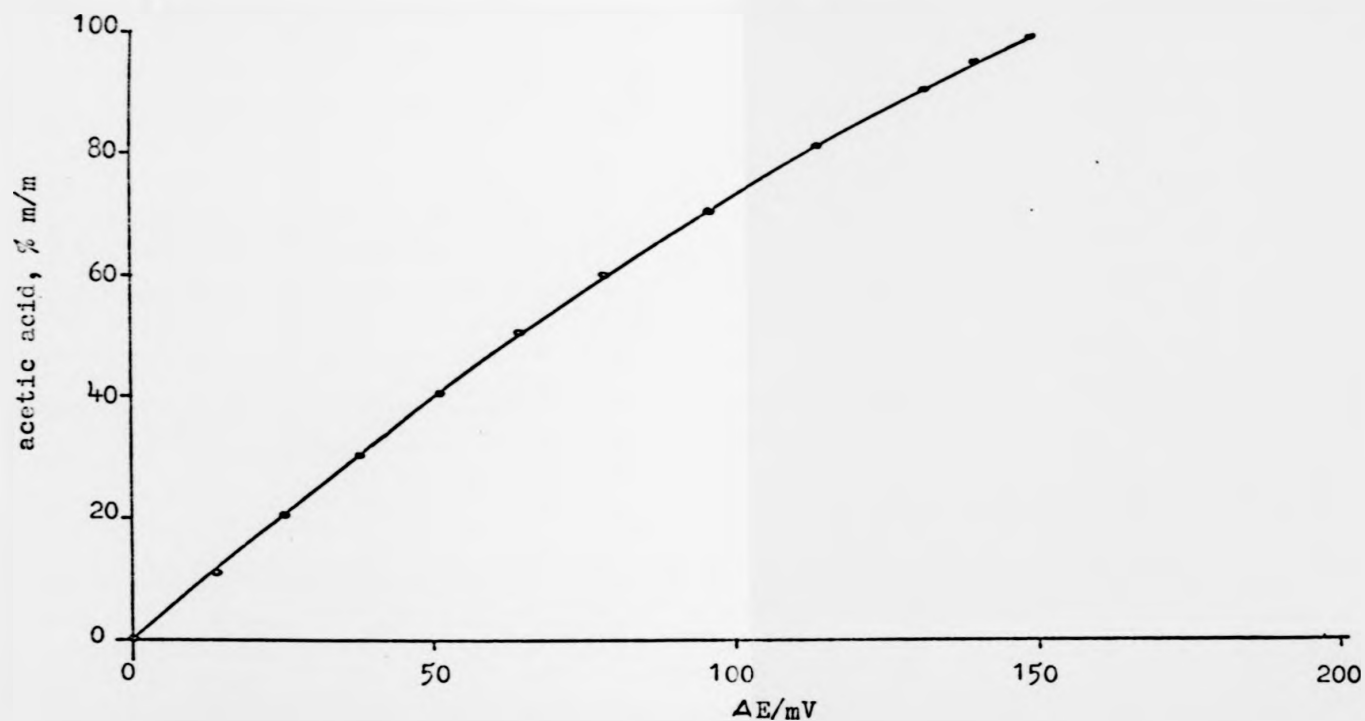


Fig. 70 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{OAc})_2 - \text{HOAc}(\text{MeOH})$ , in solutions of  $10^{-4}$  M lead acetate and various acetic acid concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

\*\* There is no fig. 71.

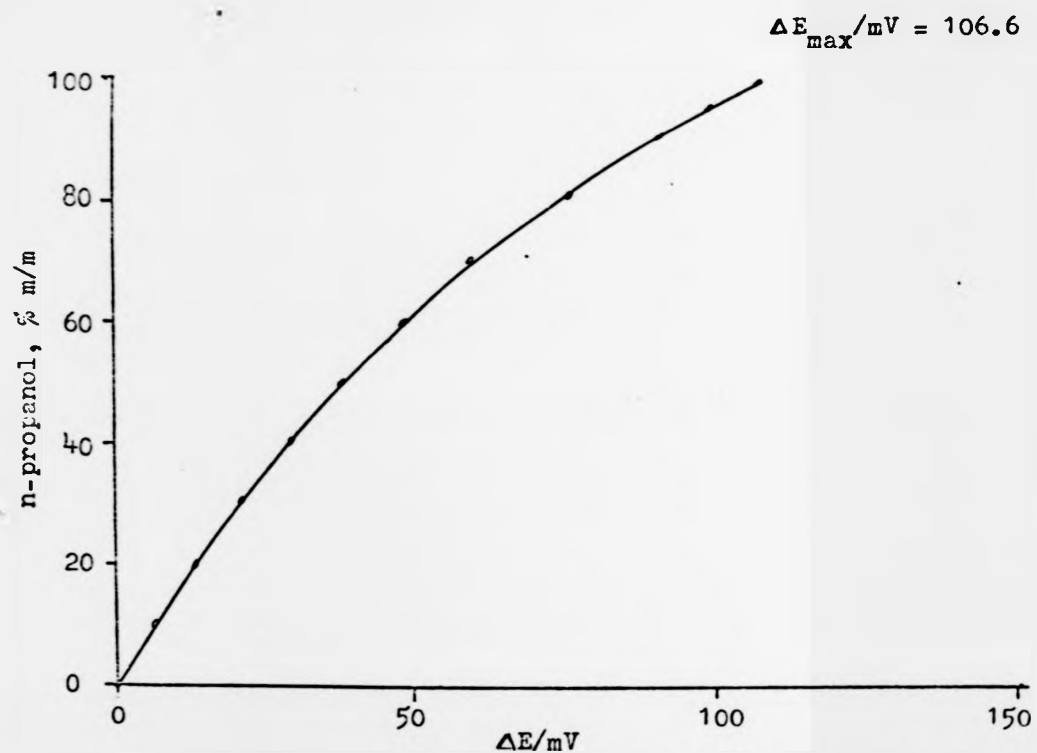


Fig. 72 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2 - n\text{-PrCH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M lead perchlorate and various n-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

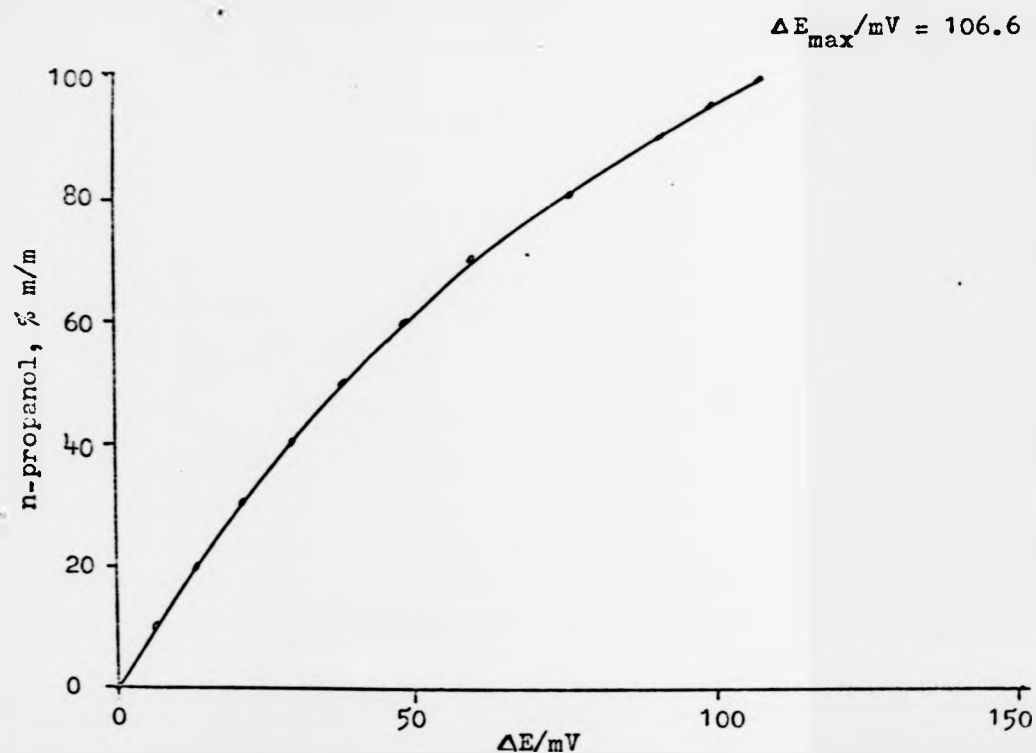


Fig. 72 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2 - \text{n-PrCH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M lead perchlorate and various n-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\text{max}}/\text{mV} = 170.6$$

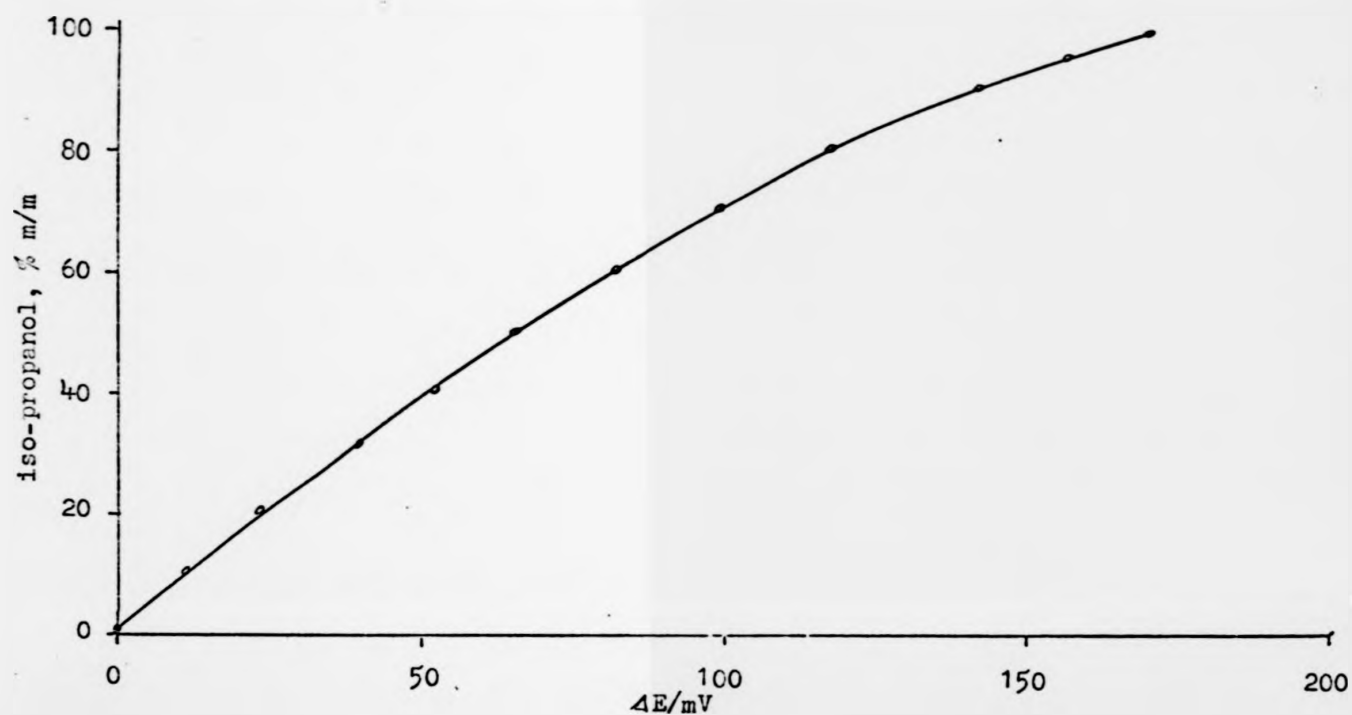


Fig. 73 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2 - 1\text{-PrOH}(\text{MeOH})$ , in solutions of  $10^{-3}$  M lead perchlorate and various iso-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.



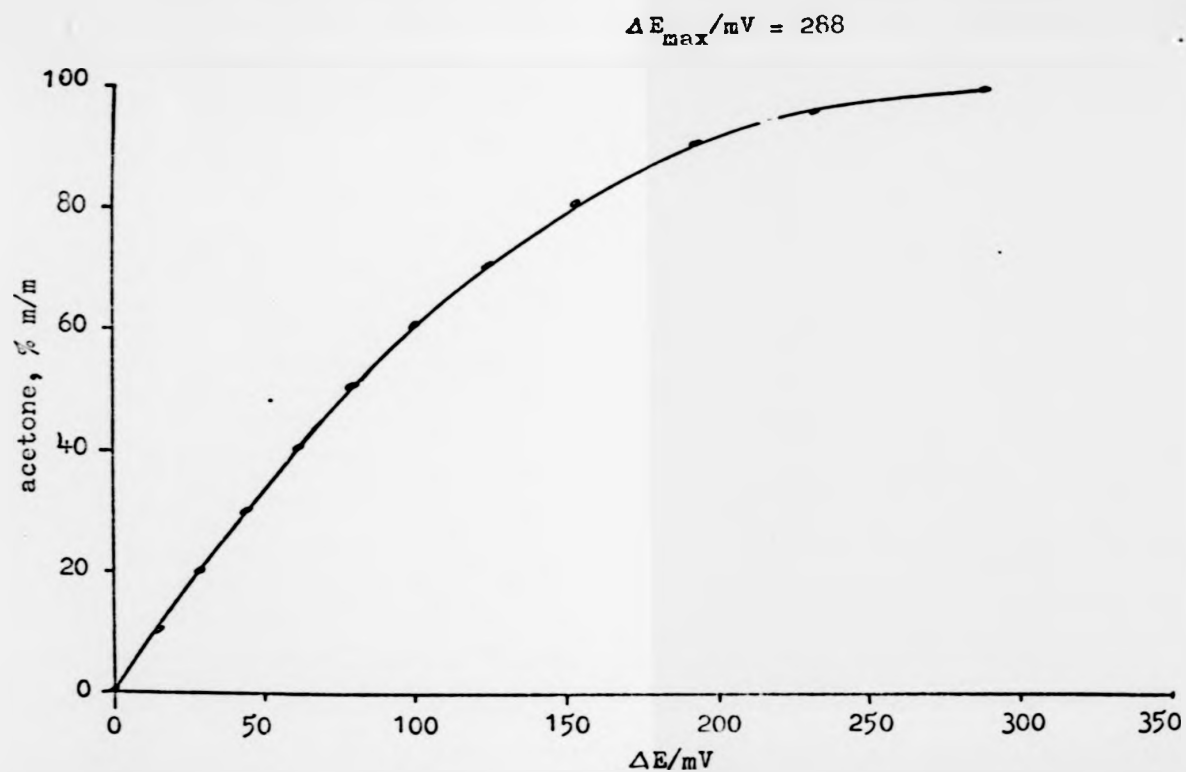


Fig. 74a Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2$ -acetone(MeOH), in solutions of  $10^{-3}$  M lead perchlorate and various acetone concentrations, measured by using lead sulphide and SCE(LiCl) electrodes.

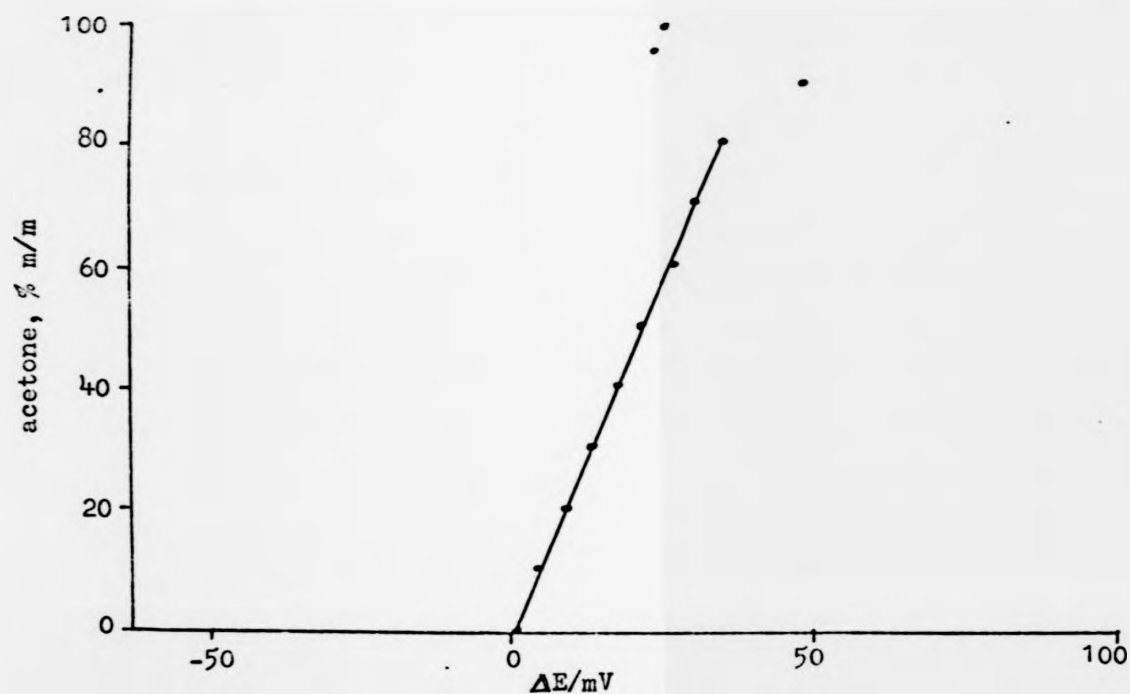


Fig. 74b Change in potential,  $\Delta E$ , for the system,  $Pb(OAc)_2$ -acetone(MeOH), in solutions of  $10^{-3}$  M lead acetate and various acetone concentrations, measured by using lead sulphide and SCE(LiCl) electrodes.

$$\Delta E_{\max}/\text{mV} = 174.8$$

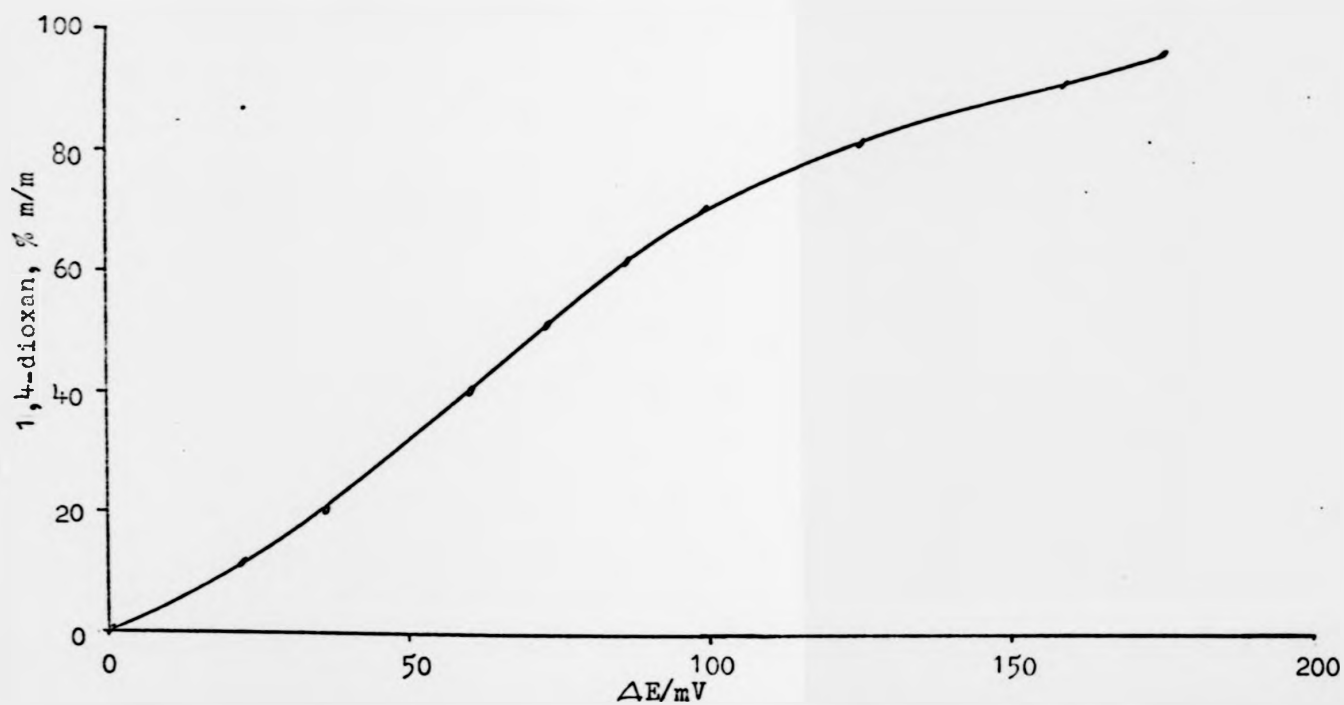


Fig.75 Change in potential,  $\Delta E$ , for the system,  $\text{Pb}(\text{ClO}_4)_2$ -1,4-dioxan(MeOH), in solutions of  $10^{-3}$  M lead perchlorate and various 1,4-dioxan concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

# 2.4.2 INDIRECT MEASUREMENTS

Table 80

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2\text{--MeOH}(\text{H}_2\text{O})$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various methanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes

% m/m methanol	Potential/mV			Electrode slope /mV per decade	LLLRR (LR)	$E^0/\text{mV}$
	$10^{-3}$ $\text{MPb}^{2+}$	$10^{-4}$ $\text{MPb}^{2+}$	$10^{-5}$ $\text{MPb}^{2+}$			
0	-194.7	-229.7	-263.5	34.4	$6 \times 10^{-6}$	-91.5
20	-181.2	-216.5	-248.8	33.8	$8 \times 10^{-6}$	-79.8
40	-169.0	-203.6	-236.8	33.9	$8 \times 10^{-6}$	-67.3
60	-154.6	-188.0	-222.0	33.7	$4 \times 10^{-6}$	-53.5
80	-131.2	-163.6	-200.8	37.2	$2 \times 10^{-6}$ - $2 \times 10^{-4}$	-14.8
90	-112.8 (22)	-145.0 (38)	-186.8 (46)	NL	NL	
99	-86.6 (23)	-117.0 (36)	-170.0 (74)	NL	NL	
$\Delta E_{\text{max}}/\text{mV}$	108.1	112.7	93.5			

NL: Non-linear

( )\* Tangential slope at the given concentration points.

Table 81

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2\text{--EtOH}(\text{H}_2\text{O})$ , in solutions  $6 \times 10^{-4} \text{ M}$ ,  $6 \times 10^{-5} \text{ M}$  and  $6 \times 10^{-6} \text{ M}$  in lead perchlorate and of various ethanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes

% m/m ethanol	Potential/mV			Electrode slope / mV per decade	LLRR
	$6 \times 10^{-4} \text{ MPb}^{2+}$	$6 \times 10^{-5} \text{ MPb}^{2+}$	$6 \times 10^{-6} \text{ MPb}^{2+}$		
00	144	120	89	27.5	$6 \times 10^{-6}$
10	139	114	87	26.0	$2 \times 10^{-6}$
20	137	112	85	26.0	$6 \times 10^{-6}$
30	138	113	84	27.0	$6 \times 10^{-6}$
40	143	116	84	28.5	$6 \times 10^{-6}$
50	151	123	80	28.0	$6 \times 10^{-5}$
60	154	125	52	29.0	$6 \times 10^{-5}$
70	159	130	30	29.0	$6 \times 10^{-5}$
80	174	145	14	29.0	$6 \times 10^{-5}$
90	192	161	3	31.0	$6 \times 10^{-6} - 6 \times 10^{-4}$
95	200 (20)	170 (52)	-2	NL	-
99	225 (4)	194 (57)	23	NL	-
$\Delta E_{\text{max/mV}}$	81	74	91		

( )\*: Tangential slope at the given concentration point.

Table 82

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$  --n-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various n-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-unction) electrodes

% m/m n-propanol	Potential /mV			Electrode slope /mV per decade	LLLR	$E^\circ$ /mV
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$			
0	-194.5	-228.6	-251.3	34.1	$2 \times 10^{-5}$	-92.2
20	-184.0	-218.6	-249.6	34.6	$6 \times 10^{-6}$	-80.2
40	-176.8	-211.3	-248.7	34.5	$2 \times 10^{-6}$	-73.3
60	-163.4	-198.7	-269.2	35.3	$6 \times 10^{-5}$	-57.5
80	-133.0	-164.6	-293.7	31.6	$6 \times 10^{-5}$	-38.2
90	-100.9 (12)	-134.1 (92)	-284.6	NL	-	
99	-46.5 (-12)	-95.2 (104)	((-240.2))	NL	-	
$\Delta E/\text{mV}(90\% \text{ m/m})$	93.6	94.5	-33.3			

NL: Non-linear

( )\*: Tangential slope at the given concentration point.

Table 83

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ --i-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various isopropanol concentrations, measured by using lead sulphide and silver-silver chloride (double-function) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /mV per decade	LLRR	$E^0$ /mV
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$			
0	-194.5	-228.6	-251.3	32.0	$2 \times 10^{-5}$	-98.5
20	-179.9	-213.1	-243.4	31.8	$6 \times 10^{-6}$	-84.5
40	-169.6	-201.6	-233.0	31.7	$6 \times 10^{-6}$	-74.5
60	-152.0	-184.0	-218.0	32.0	$6 \times 10^{-6}$	-56.0
80	-116.9	-146.2	-189.3	29.3	$5 \times 10^{-5}$	-29.0
90	-80.0 (14)	-108.9 (37)	-167.3 (102)	NL	-	
99	-20.0 (-6)	-50.2 (86)	-138.6 (86)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	174.5	228.4	112.7			

NL: Non-linear

( ) \* Tangential slope at the given concentration point.

Table 84

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ --acetone( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various acetone concentrations, measured by using lead sulphide and SCE(LiCl) electrodes

% m/m acetone	Potential /mV			Electrode slope / mV per decade	LLLRR	$E^0$ / mV
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$			
0	-166.0	-208.4	-250.6	42.3	$6 \times 10^{-6}$	-39.1 (-54.1)
20	-139.8	-180.0	-218.1	39.2	$5 \times 10^{-6}$	-22.2 (-56.4)
40	-109.4	-147.0	-186.7	38.7	$2 \times 10^{-6}$	6.7 (-50.9)
60	-62.5	-95.0	-134.4	+32.5	$2 \times 10^{-5}$	35.0 (-55.2)
80	6.1	-17.5	-56.7	23.6	$4 \times 10^{-5}$	76.9 (-53.0)
90	60.8	45.4	9.5	18.0	$5 \times 10^{-5}$	114.8 (-44.1)
95 **	92.5 ( $\infty$ )	84.0 (14)	0.7 (73)	NL	-	
99	162.2 (-29)	171.3 (-10)	((-10.0))(280)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	328.2	379.7	260.1			

(( ))\*: Unstable

( ): Tangential slope at the given concentration point

\*\* : Measured separately;

NL: Non-linear



Table 85

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ -1,4-dioxan( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M lead perchlorate and of various 1,4-dioxan concentrations, measured by using lead sulphide and silver-silver chloride (double-unction) electrodes

% m/m 1,4-dioxan	Potential/mV			Electrode slope /mV per decade	LLLRR	$E^0$ / mV
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$			
0	-195.0	-230.8	-263.2	35.8	$3 \times 10^{-5}$	-87.6
20	-178.7	-211.6	-239.9	33.9	$3 \times 10^{-5}$	-77.0
40	-159.0	-192.3	-220.9	33.3	$4 \times 10^{-5}$	-59.1
60	-133.3	-162.0	-192.9	28.7	$2 \times 10^{-6}$	-47.2
80	-91.6 (9)	-110.3(33)	-153.7 (36)	NL	-	
90	-68.0 (4)	-81.3(29)	-143.3 (53)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	127	149.5	119.9			

NL: Non-linear

( )\* Tangential slope at the given concentration point.

Table 86

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ -n-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various n-propanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope /mV per decade	LLRR (LR)	$E^0$ /mV
	$10^{-3}$ $\text{MPb}^{2+}$	$10^{-4}$ $\text{MPb}^{2+}$	$10^{-5}$ $\text{MPb}^{2+}$			
0	-75.5	-108.5	-150.7	34.0	$2 \times 10^{-6}$	27.5
20	-60.5	-96.5	-158.2	36.1	$6 \times 10^{-6}$	73.4
40	-42.5 (26)	-80.3 (78)	-165.8 (84)	NL	-	
60	-22.3 (12)	-57.9 (75)	-176.2 (128)	NL	-	
80	0.5 (14)	-38.5 (90)	-192.0 (126)	NL	-	
90	13.5 (14)	-51.8 (116)	-211.2 (168)	NL	-	
99	23.3 (10)	-47.0 (120)	-222.5 (200)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	98.8	61.5	-72.0			

NL: Non-linear

( )\* Tangential slope at the given concentration point.

Table 82

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ --1-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various isopropanol concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes

% m/m iso-propanol	Potential/mV			Electrode slope /mV per decade	LLRR (LR)	$E^0$ /mV
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$			
0	-75.5	-108.5	-150.7	33.0	$2 \times 10^{-6}$ - $6 \times 10^{-5}$	23.5
20	-51.1	-88.3	-139.1	37.0	$6 \times 10^{-6}$ - $10^{-4}$	59.9
40	-30.3	-90.2	-139.7	53.5	$6 \times 10^{-6}$ - $10^{-4}$	130.2
60	0.6 (10)	-58.9 (62)	-124.5	NL	-	
80	35.9 (4)	-19.0 (132)	-115.0 (112)	NL	-	
90	52.7 (16)	36.6 (108)	-119.4 (156)	NL	-	
99	78.6 (6)	2.9 (148)	-122.6 (178)	NL	-	
$\Delta E_{\text{max}}/\text{mV}$	154.1	111.4	28.1			

LR: Linear region

NL: Non-linear

( ): Tangential slope at the given concentration point.

Table 88

Change in potential (obtained by 'indirect method') for the system,  $\text{Pb}(\text{ClO}_4)_2$ --acetone (MeOH), in solutions,  $6 \times 10^{-4}$  M,  $6 \times 10^{-5}$  M and  $6 \times 10^{-6}$  M in lead perchlorate and of various acetone concentrations, measured by using lead sulphide and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLLR
	$6 \times 10^{-4}$ $\text{MPb}^{2+}$	$6 \times 10^{-5}$ $\text{MPb}^{2+}$	$6 \times 10^{-6}$ $\text{MPb}^{2+}$		
0	12.4 (18)	-32.6 (68)	-87.8	NL	-
20	40.4 (26)	8.5 (62)	-62.3	NL	-
40	73.4 (24)	42.9 (68)	-50.1	NL	-
50	113.6 (13)	88.0 (60)	-31.3	NL	-
80	166.6 (13)	146.2 (68)	-25.4	NL	-
90	210.4 (6)	193.7 (68)	-19.2	NL	-
99	279.6 (-20)	276.8 (28)	10.1	NL	-
$\Delta E_{\text{max/mV}}$	267.2	309.4	97.9		

NL: Non-linear

( )\* Tangential slope at the given concentration points.

Table 89

Change in potential (obtained by 'indirect method' for the system,  $\text{Pb}(\text{ClO}_4)_2$ -- 1,4-dioxan(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in lead perchlorate and of various 1,4-dioxan concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes

% m/m 1,4-dioxan	Potential/mV			Electrode slope /mV per decade	LLRR
	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-5}$ MPb $^{2+}$		
0	-63.3 (26)	-99.9 (46)	-168.4 (59)	NL	-
20	-24.8 (22)	-59.8 (55)	-140.2 (84)	NL	-
40	0.8 (20)	-40.1 (73)	-123.0 (85)	NL	-
60	21.9 (18)	-3.8 (64)	-109.5 (66)	NL	-
80	44.9 (12)	18.1 (74)	-114.9 (105)	NL	-
90	76.0 (7)	59.0 (38)	-43.0 (148)	NL	-
$\Delta E_{\text{max}}/\text{mV}$	139.3	158.9	125.4		

( )\* Tangential slope at the given concentration point

NL: Non-linear

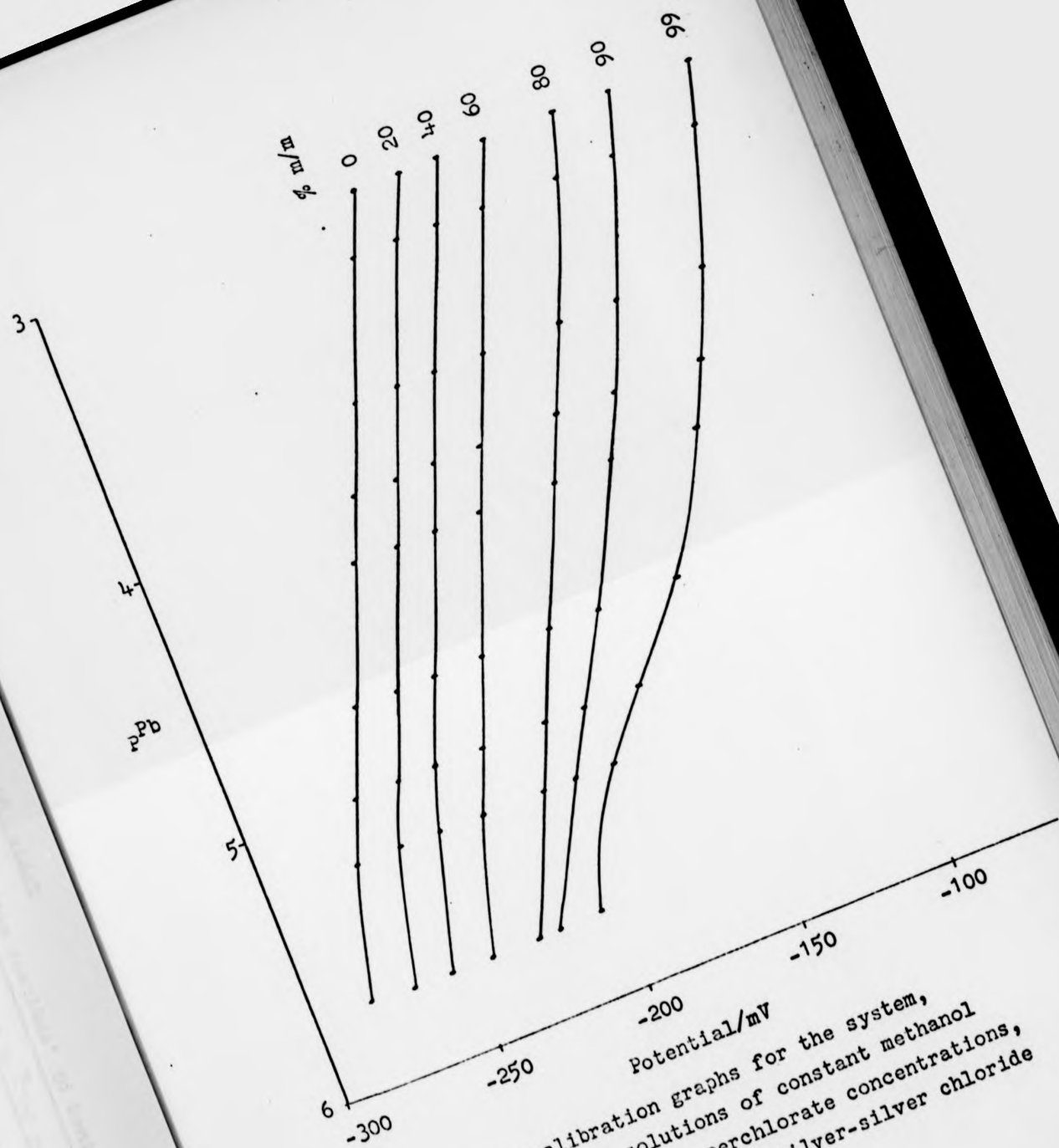


Fig.76 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2$ -MeOH( $\text{H}_2\text{O}$ ), in solutions of constant methanol concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

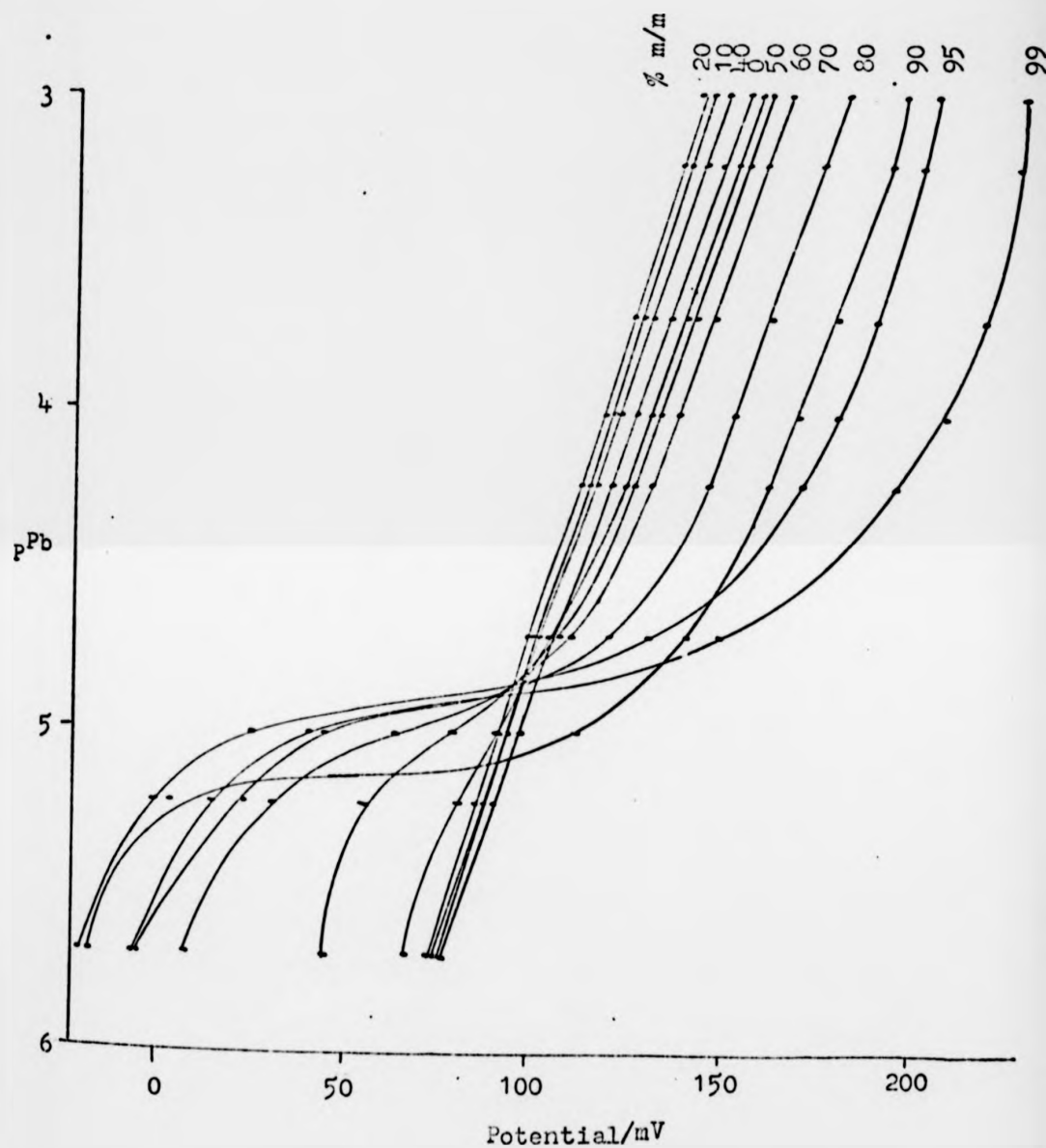


Fig. 77 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2\text{-EtOH}(\text{H}_2\text{O})$ , in solutions of constant ethanol concentration and various lead perchlorate concentrations, measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

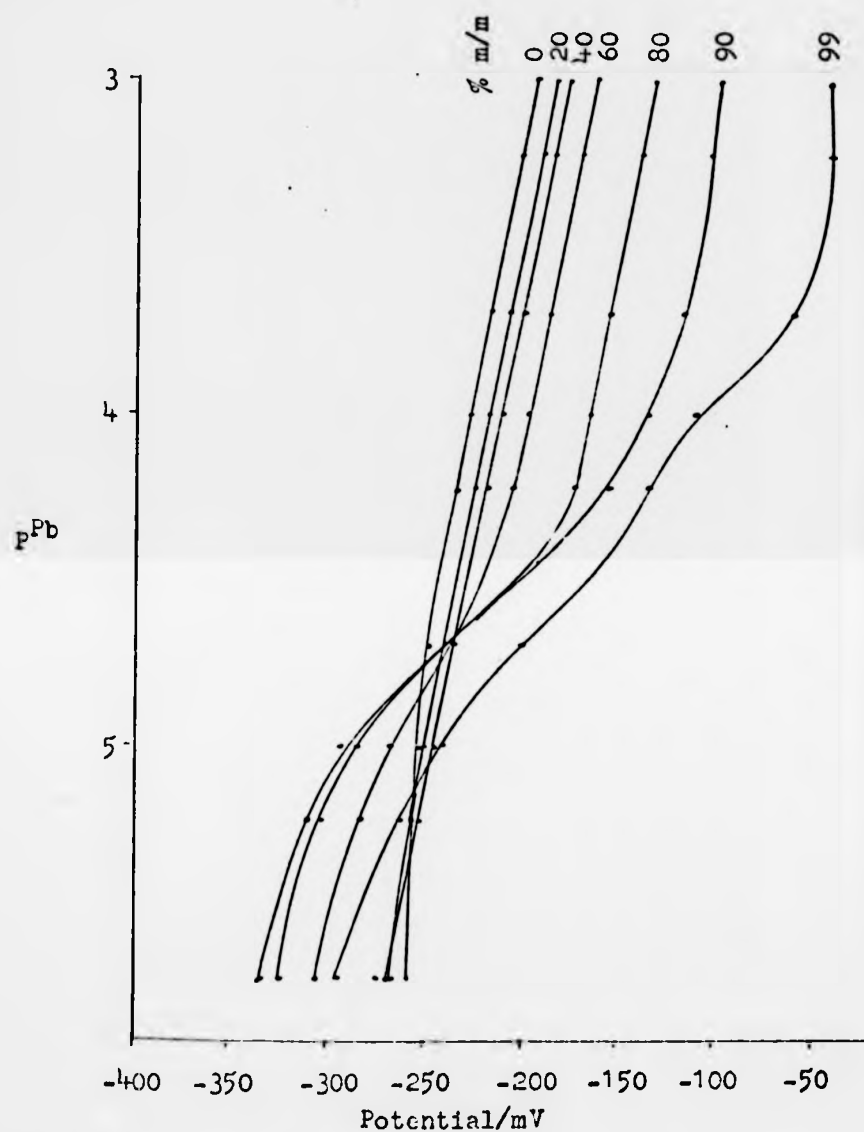


Fig. 78 Electrode calibration graphs for the system,  $\text{Pb(ClO}_4)_2$ -- $\text{n-PrOH(H}_2\text{O)}$ , in solutions of constant n-propanol concentration and various Lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.



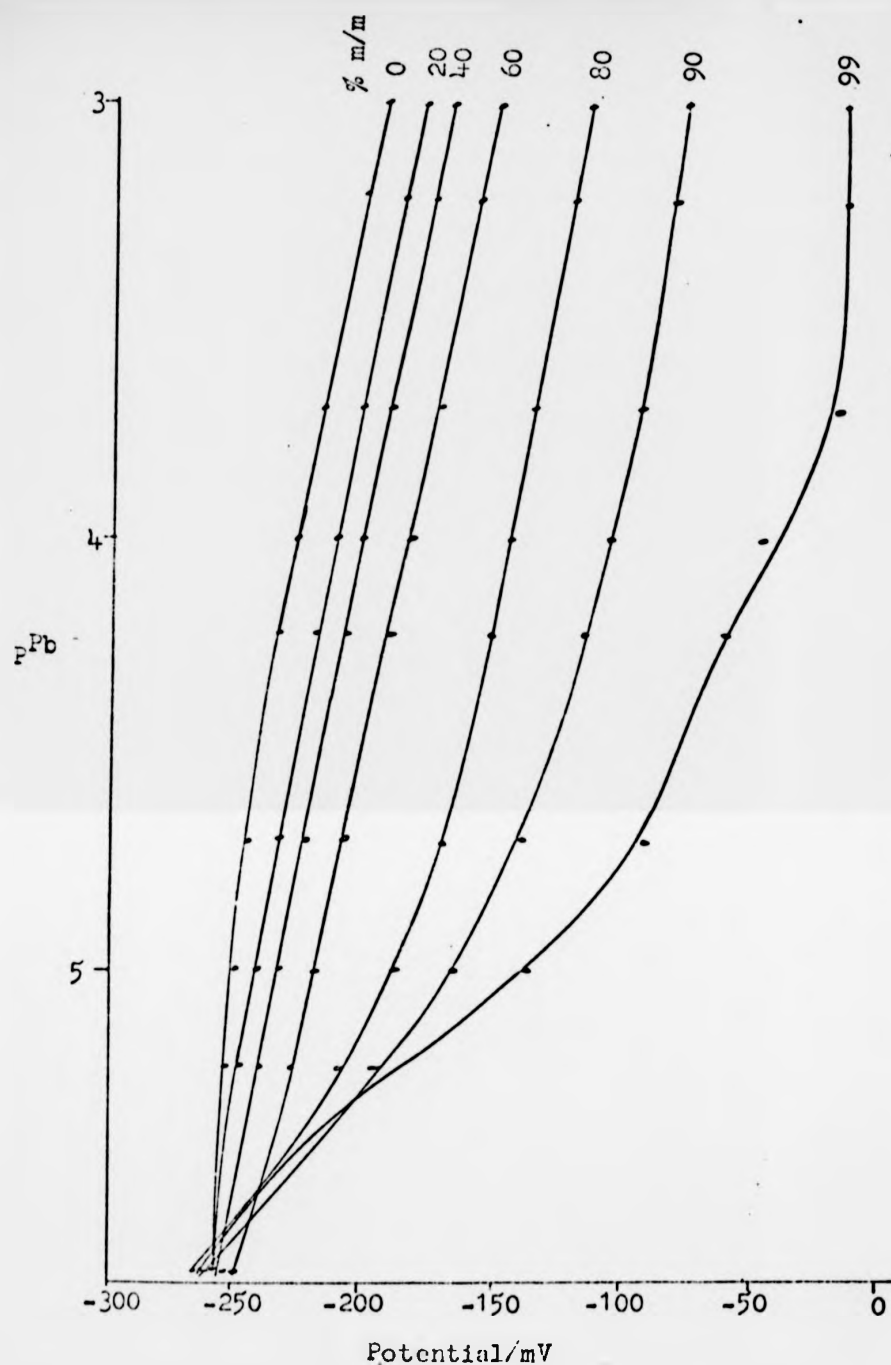


Fig. 79 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2$ --i-PrOH( $\text{H}_2\text{O}$ ), in solutions of constant iso-propanol concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

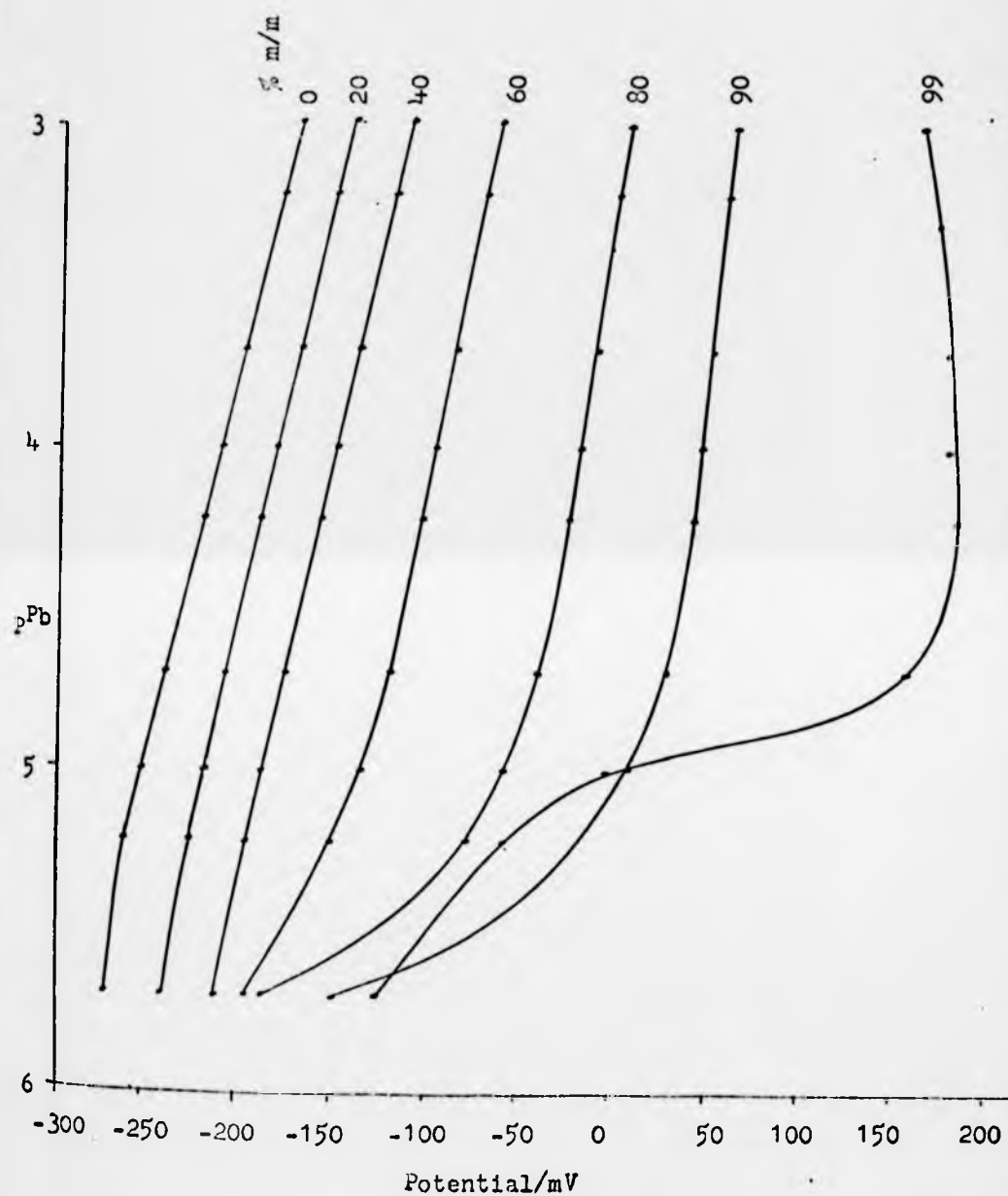


Fig.80 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2$ -acetone( $\text{H}_2\text{O}$ ), in solutions of constant acetone concentration and various lead perchlorate concentrations, measured by using Lead sulphide and SCE( $\text{LiCl}$ ) electrodes.

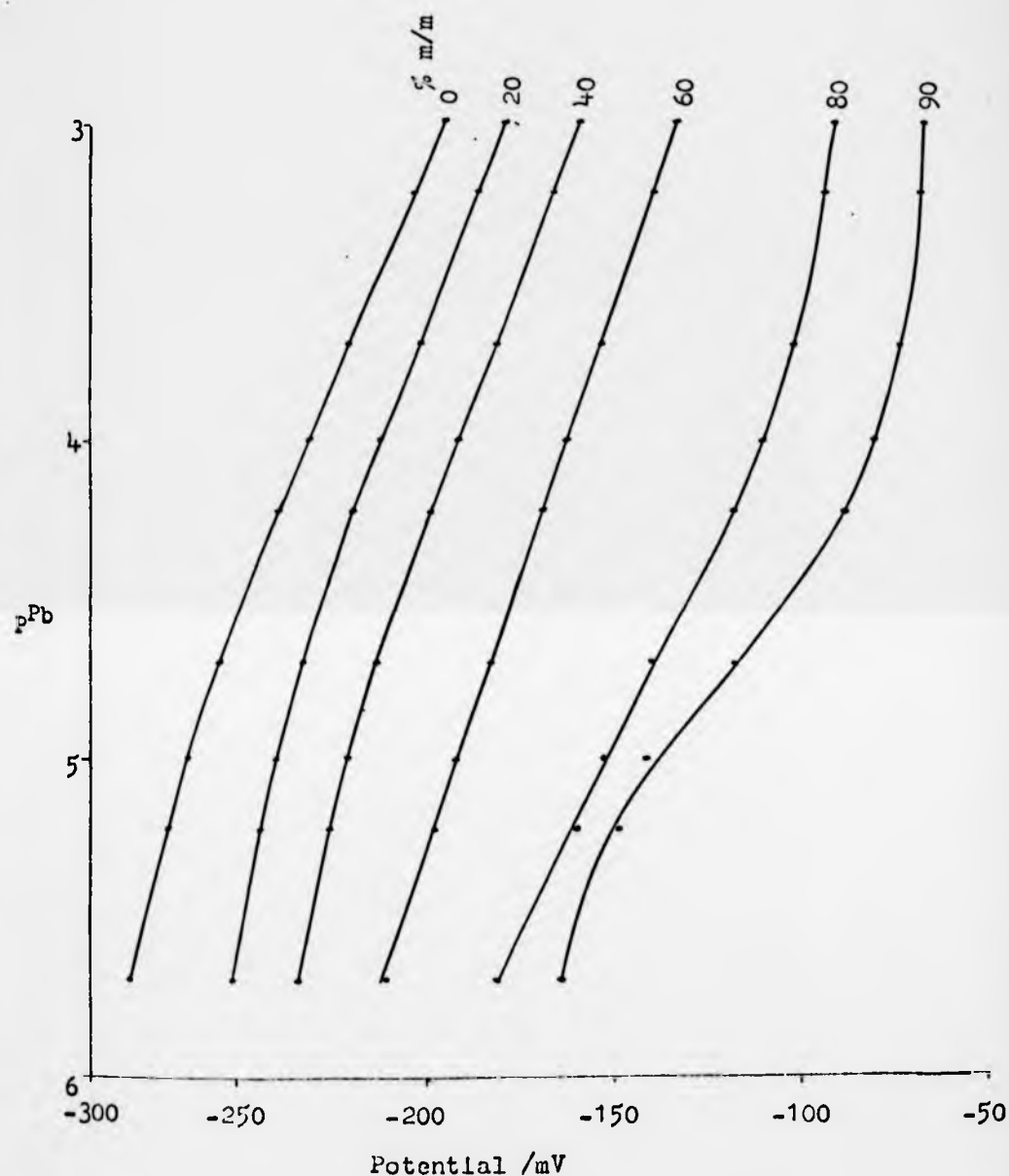


Fig.81 Electrode calibration graphs for the system,  $Pb(ClO_4)_2$ -1,4-dioxan( $H_2O$ ), in solutions of constant 1,4-dioxan concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

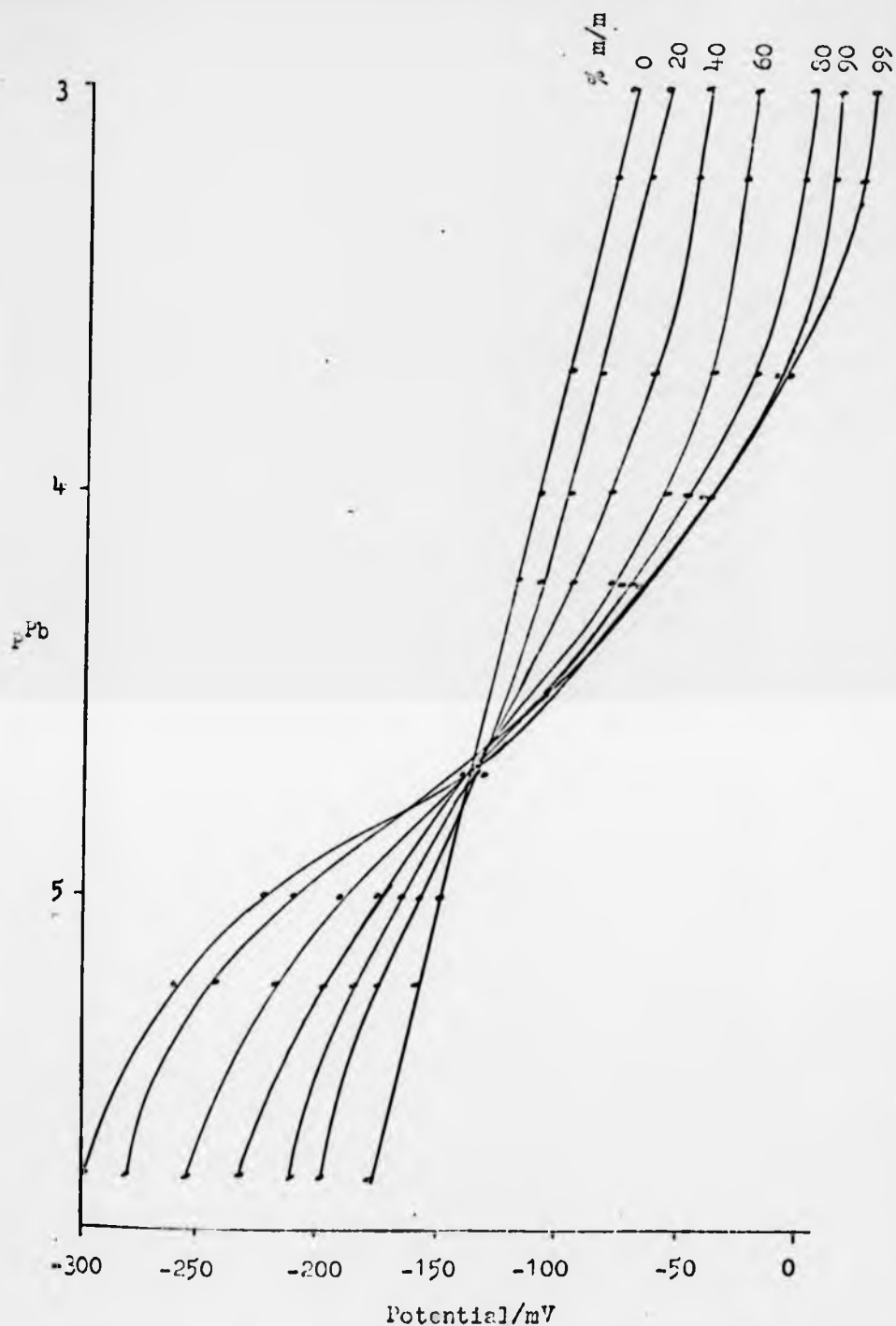


Fig. 82 Electrode calibration graphs for the system,  $\text{Pb(ClO}_4)_2$ --n-PrOH(MeOH), in solutions of constant n-propanol concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

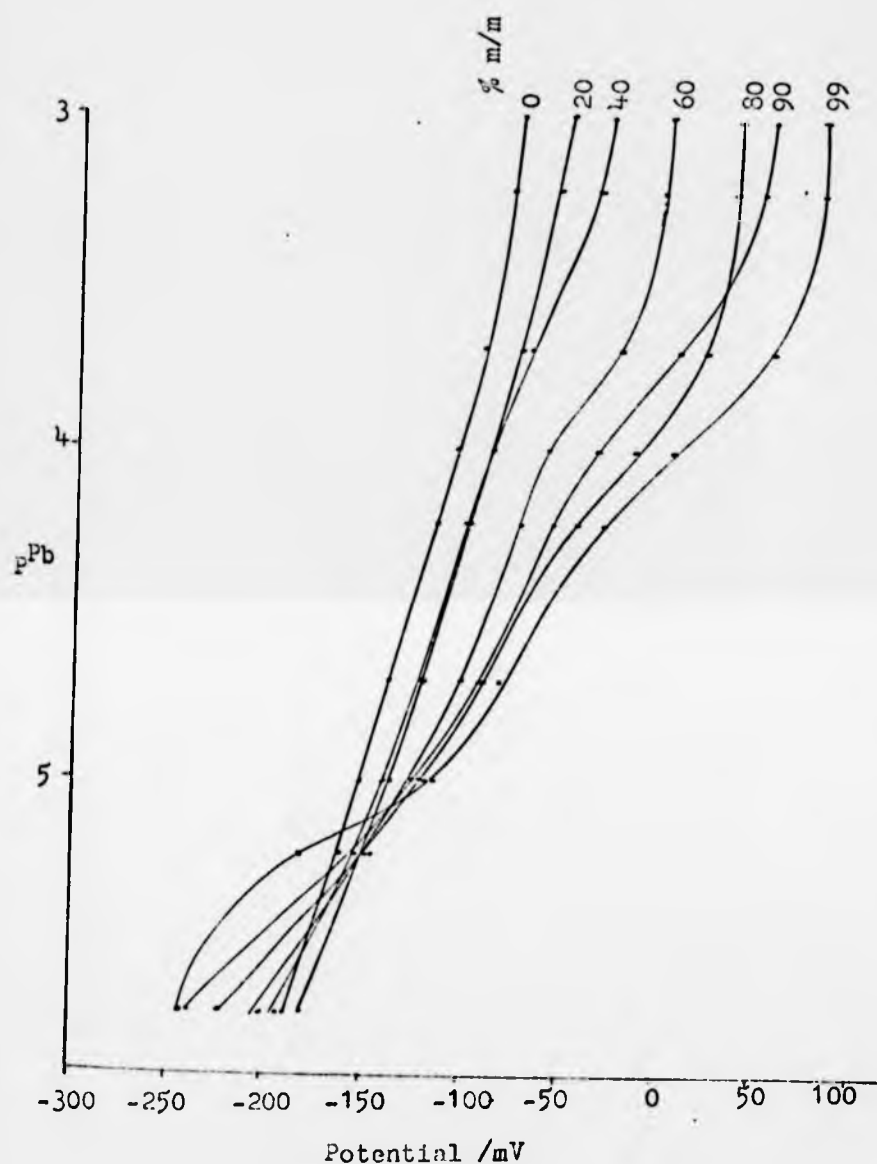


Fig.83 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2$ -1-PrOH(MeOH), in solutions of constant iso-propanol concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

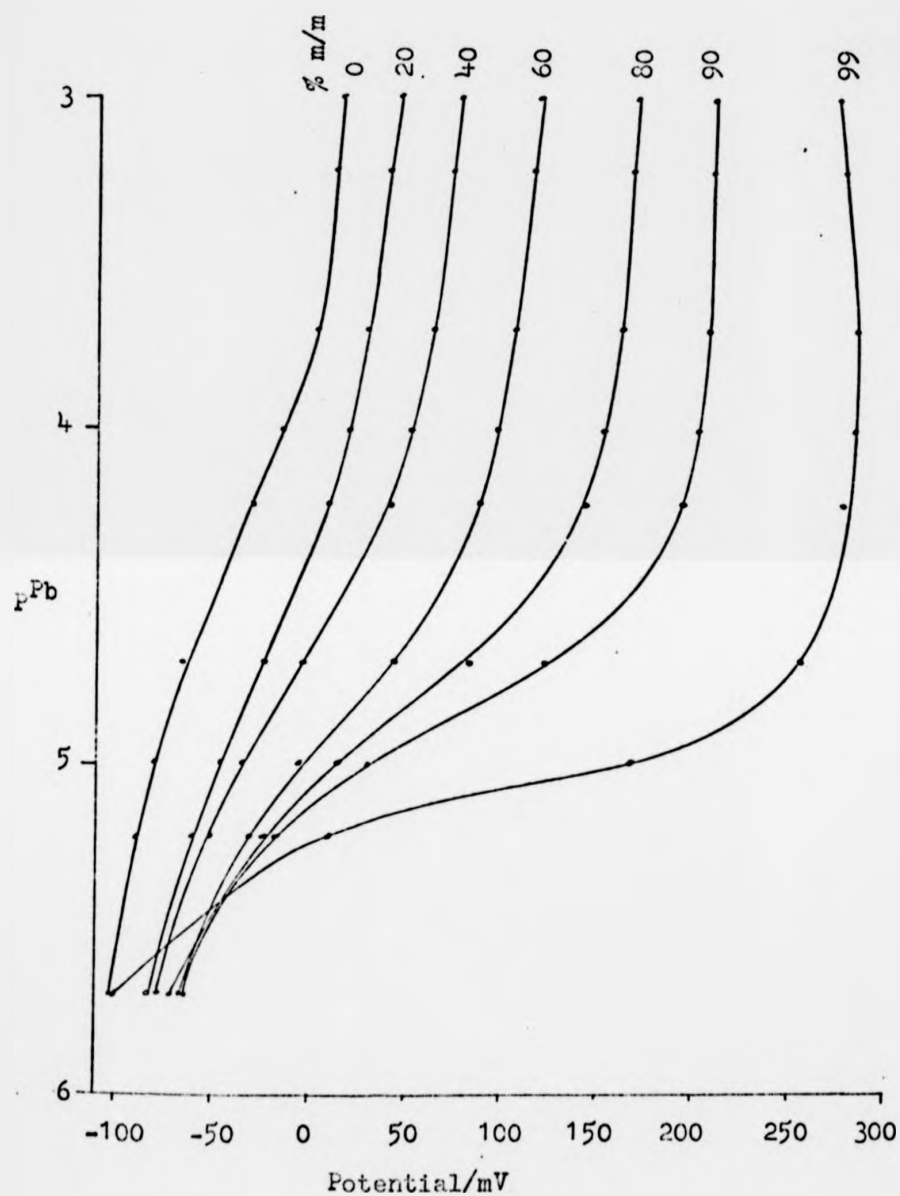


Fig. 84 Electrode calibration graphs for the system,  $\text{Pb}(\text{ClO}_4)_2$ --acetone(MeOH), in solutions of constant acetone concentration and various lead perchlorate concentrations, measured by using Lead sulphide and SCE(LiCl) electrodes.

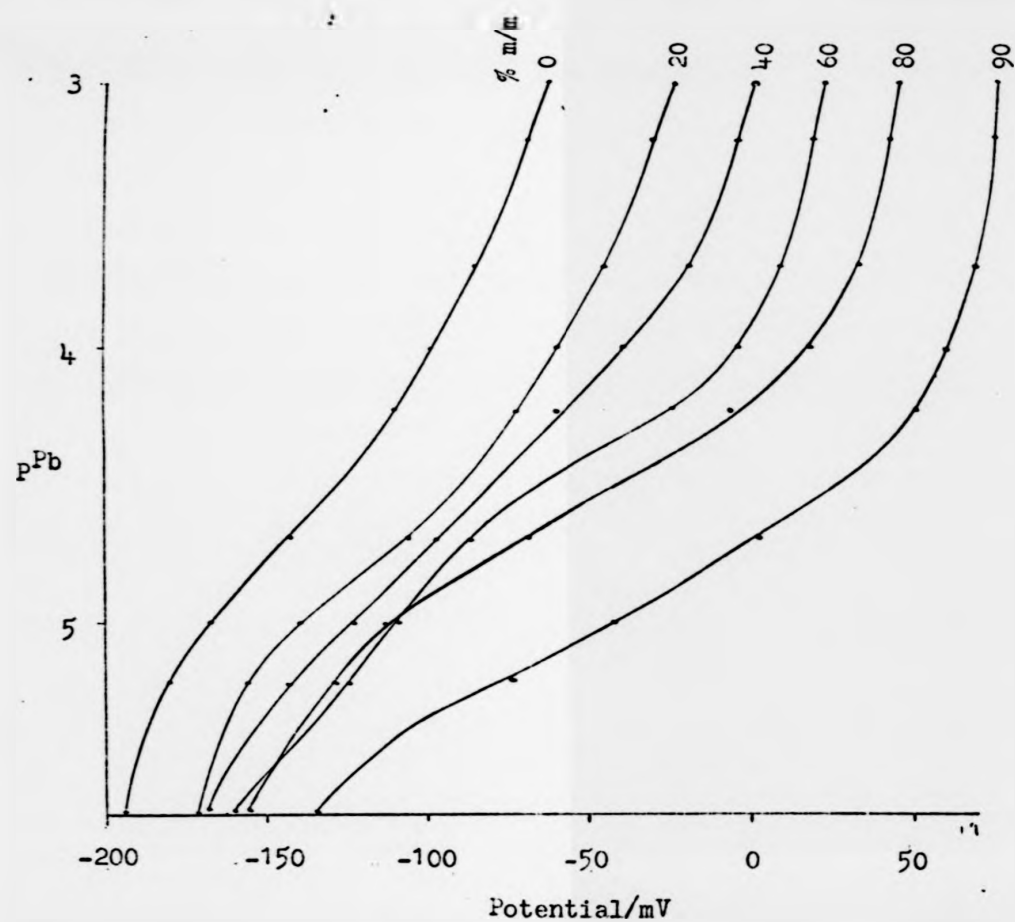


Fig.85 Electrode calibration graphs for the system,  $Pb(ClO_4)_2$ -1,4-dioxan(MeOH), in solutions of constant 1,4-dioxan concentration and various lead perchlorate concentrations, measured by using Lead sulphide and silver-silver chloride (double-junction) electrodes.

### 2.4.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 90

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Pb}(\text{ClO}_4)_2$ -n-PrOH( $\text{H}_2\text{O}$ ), and  $\text{Pb}(\text{ClO}_4)_2$ -n-PrOH(MeOH), in  $10^{-3}$  M solutions of lead perchlorate for various n-propanol concentrations measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	14.0	10.5	3.5	13.9	15.0	-1.1
40	22.8	17.7	5.1	29.7	33.0	-3.3
60	36.4	31.1	5.3	48.3	53.2	-4.9
80	71.7	61.5	10.2	76.1	76.0	0.1
90	113.0	93.6	19.4	91.1	89.0	2.1
99	199.9	148.0	51.9	106.6	98.8	7.8



Table 91

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Pb}(\text{ClO}_4)_2$  - acetone( $\text{H}_2\text{O}$ ) and  $\text{Pb}(\text{ClO}_4)_2$  - acetone( $\text{MeOH}$ ) in  $10^{-3}$  M solutions of lead perchlorate for various acetone concentrations measured by using lead sulphide and SCE( $\text{LiCl}$ ) electrodes.

acetone % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	28.7	26.2	2.5	30.1	27.2	2.9
40	60.9	56.6	4.3	61.4	59.3	2.1
60	112.9	103.5	9.4	99.4	98.3	1.2
80	186.2	172.1	14.1	152.1	149.4	2.7
90	255.8	226.8	29.0	192.3	191.2	1.1
99	427.5	328.2	99.3	288.3	225.6	62.7

Table 92

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the systems,  $\text{Pb}(\text{ClO}_4)_2 - \text{i-PrOH}(\text{H}_2\text{O})$  and  $\text{Pb}(\text{ClO}_4)_2 - \text{i-PrOH}(\text{MeOH})$ , in  $10^{-3}$  M solutions of lead perchlorate for various iso-propanol concentrations measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

iso-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	14.4	14.6	-0.2	23.6	24.4	-0.8
40	25.8	24.9	0.9	53.3	45.2	8.1
60	42.9	42.5	0.4	82.4	76.1	6.3
80	82.7	77.6	5.1	117.7	111.4	6.3
90	127.2	114.5	12.7	142.4	128.2	14.2
99	233.7	174.5	59.2	170.6	154.1	16.5

Table 93

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{Pb}(\text{ClO}_4)_2$ -1,4-dioxan( $\text{H}_2\text{O}$ ) and  $\text{Pb}(\text{ClO}_4)_2$ -1,4-dioxan( $\text{MeOH}$ ), in  $10^{-3}$  M solutions of lead perchlorate for various 1,4-dioxan concentrations measured by using lead sulphide and silver-silver chloride (double-junction) electrodes.

1,4-dioxan % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	15.7	16.3	-0.6	36.7	38.5	-1.8
40	32.1	36.0	-3.9	61.3	64.1	-2.8
60	55.2	61.7	-6.5	86.4	85.2	1.2
80	98.3	103.4	-5.1	125.2	108.2	17.0
90	133.2	127.0	6.2	158.8	139.3	19.5

2.5      SODIUM ION

2.5.1      Direct Measurements

2.5.2      Indirect Measurements

2.5.3      Comparison of Direct and Indirect Measurements.

2.5      SODIUM ION

2.5.1      Direct Measurements

2.5.2      Indirect Measurements

2.5.3      Comparison of Direct and Indirect Measurements.

### 2.5.1 DIRECT MEASUREMENTS

Table 94

Comparison of changes in potential,  $\Delta E$ , for a given cell system (sodium-selective glass/silver-silver chloride d/i,  $10^{-3}$  M sodium nitrate) and various solvent concentrations in different solvent-water mixtures

Solvent % m/m	$\Delta E/mV$				
	MeOH	EtOH	n-PrOH	i-PrOH	acetone
0	0(25.6)	0*	0(-18.3)	0(-13.4)	0(-13.0)
10	5.4	11	5.8	3.3	11.9
20	9.4	23	11.8	9.2	24.9
30	15.0	34	18.3	14.1	37.3
40	22.4	41	25.5	21.2	56.1
50	31.9	48	33.2	30.9	88.4
60	42.3	63	47.1	43.1	115.7
70	54.8	78	65.5	61.2	145.8
80	67.8	100	95.1	91.6	185.9
90	83.3	136	144.5	141.5	244.6
95	93.0	152	182.4	179.7	292.8
99	99.1	166	220.5	223.0	302.6

(1) \*  $10^{-3}$  M NaCl was used.

(2) Absolute potentials not available.

Table 95

Comparison of changes in potential,  $\Delta E$ , for a given cell system (sodium-selective glass/silver-silver chloride d/i.  $10^{-3}$  M sodium nitrate) and various solvent concentrations in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$		
	n-PrOE	i-PrOE	acetone*
0	0(74.9)	0(76.3)	0(186.3)
10	8.0	4.7	4.0
20	16.7	12.7	10.1
30	26.4	31.3	18.3
40	34.4	26.7	28.8
50	44.0	39.2	43.2
60	54.7	53.5	57.9
70	66.3	67.8	75.9
80	79.0	85.0	100.8
90	93.0	100.9	133.3
95	100.6	134.4	160.9
99	106.6	142.2	194.4

\* SCE(LiCl) reference electrode was used.

$$\Delta E_{\max}/mV = 99.1$$

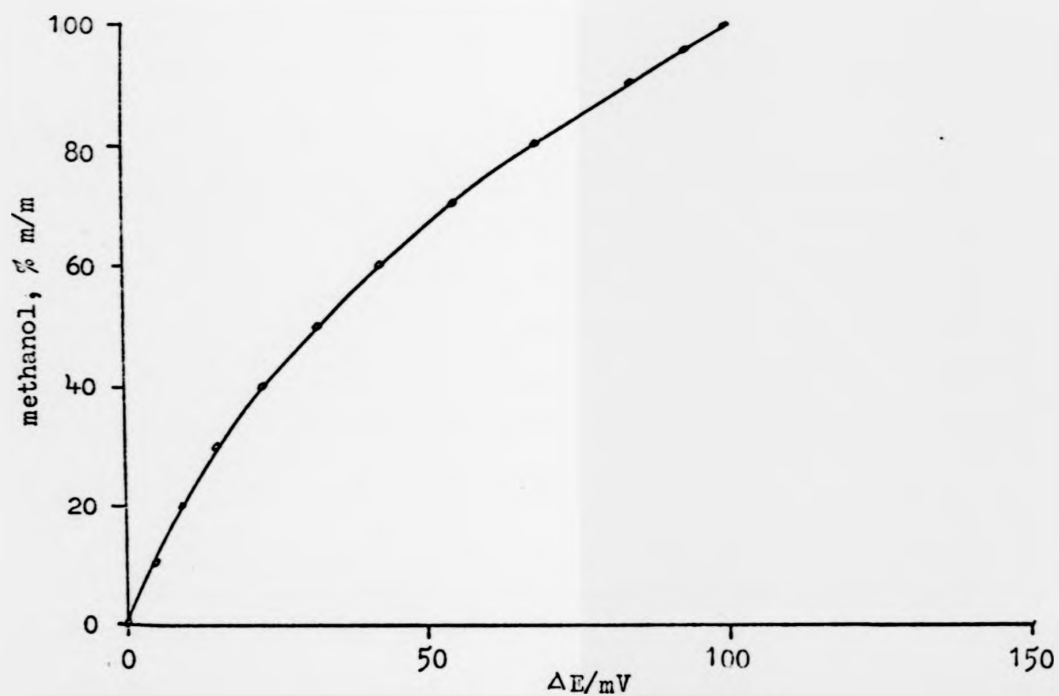


Fig.86 Change in potential,  $\Delta E$ , for the system,  $\text{NaNO}_3\text{--MeOH(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M sodium nitrate and various methanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.



$$\Delta E_{\text{max}}/\text{mV} = 166$$

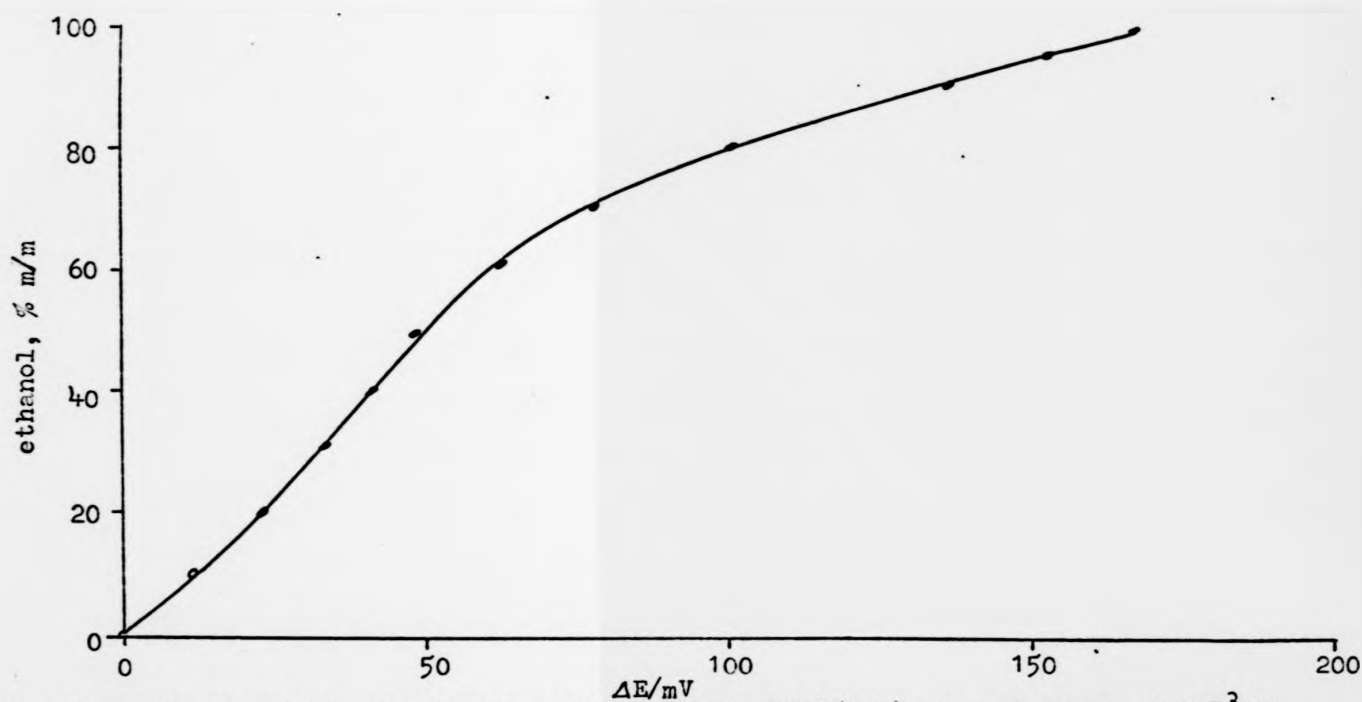


Fig.87 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various ethanol concentrations, measured by using sodium-selective glass and silver-silver chloride (single-junction) electrodes.

$$\Delta E_{\text{max}}/\text{mV} = 220.5$$

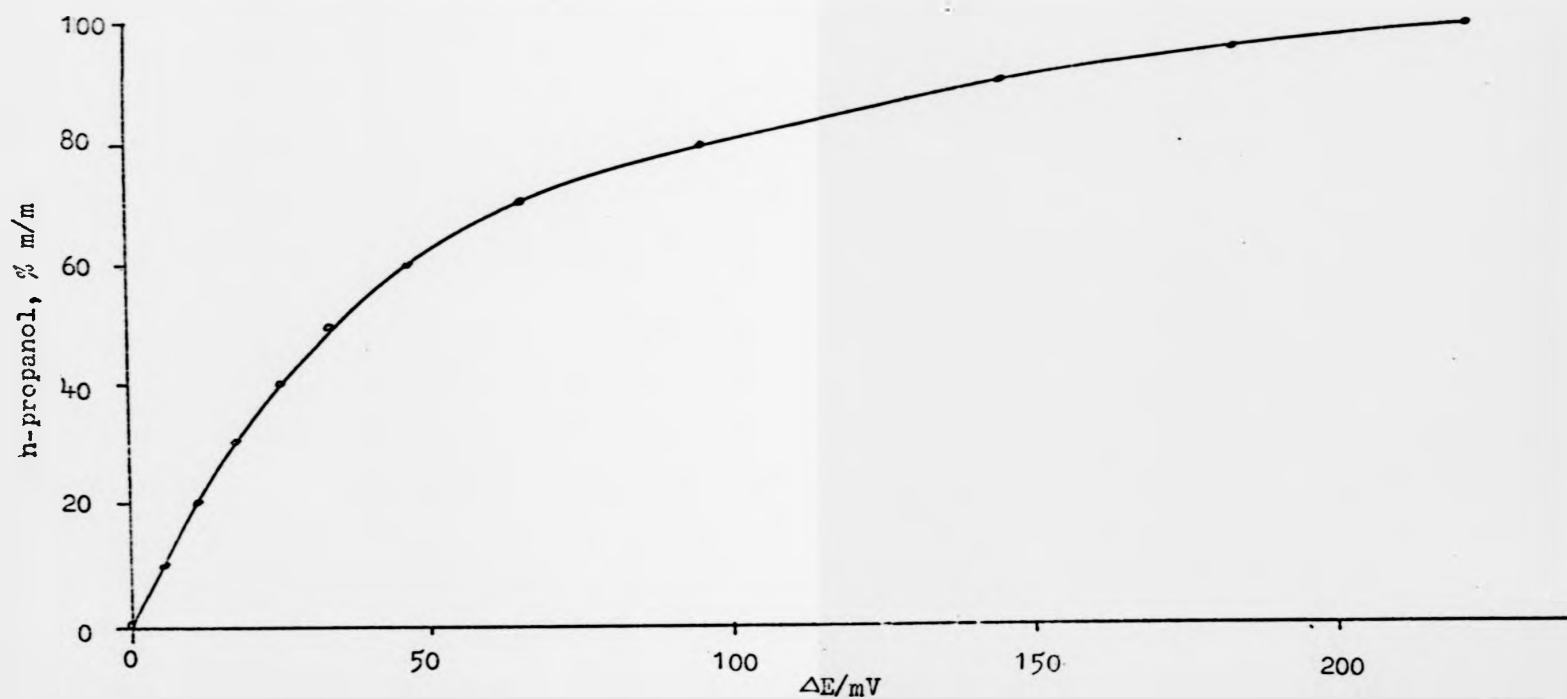


Fig. 88 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-n\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various n-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/mV = 223.0$$

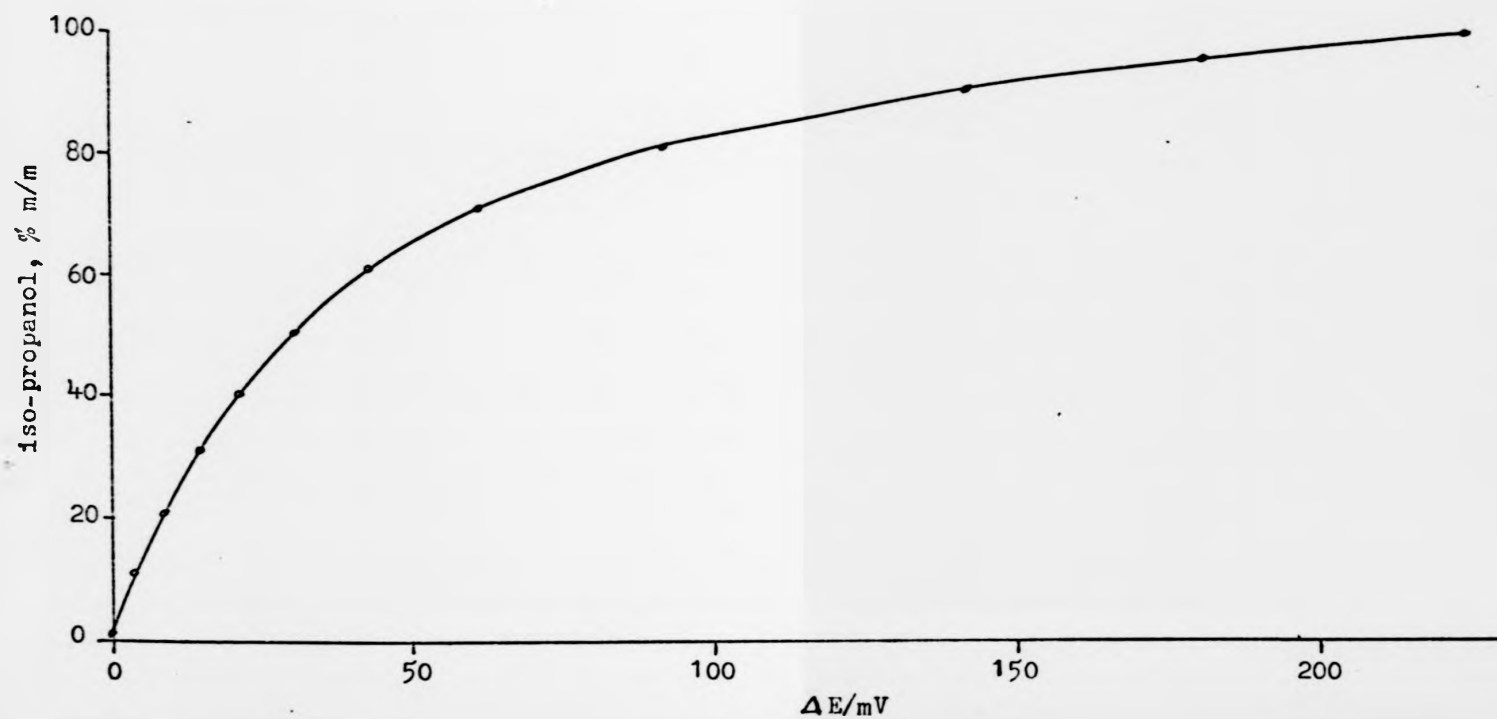


Fig.89 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-i\text{-PrOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various iso-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

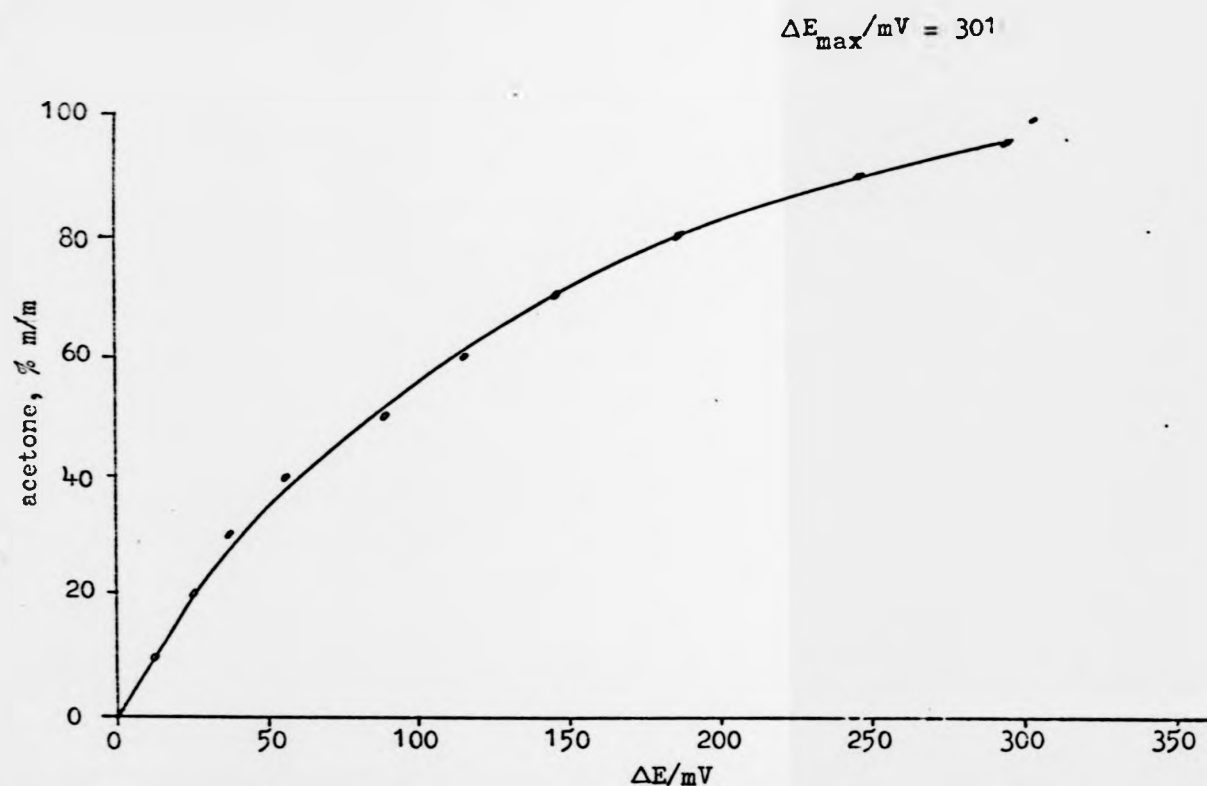


Fig. 90 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}$ —acetone( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M sodium chloride and various acetone concentrations, measured by using sodium-selective glass and SCE( $\text{LiCl}$ ) electrodes.

$$\Delta E_{\max}/mV = 106.6$$

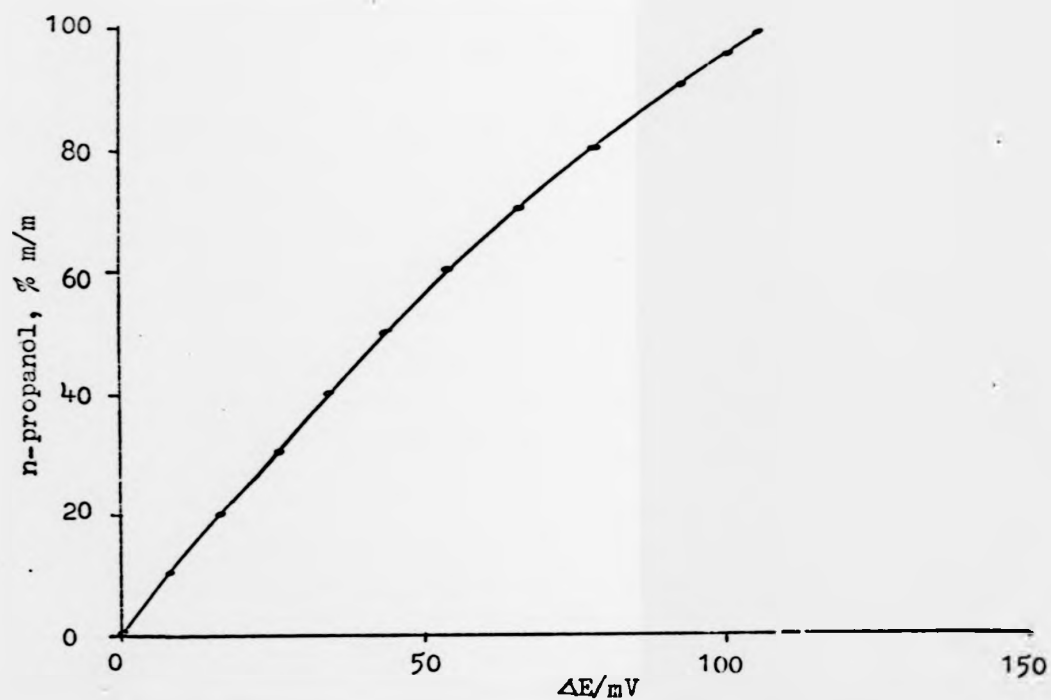


Fig. 91 Change in potential,  $\Delta E$ , for the system,  $\text{NaNO}_3$ --n-PrOH(MeOH), in solutions of  $10^{-3}$  M sodium nitrate and various n-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

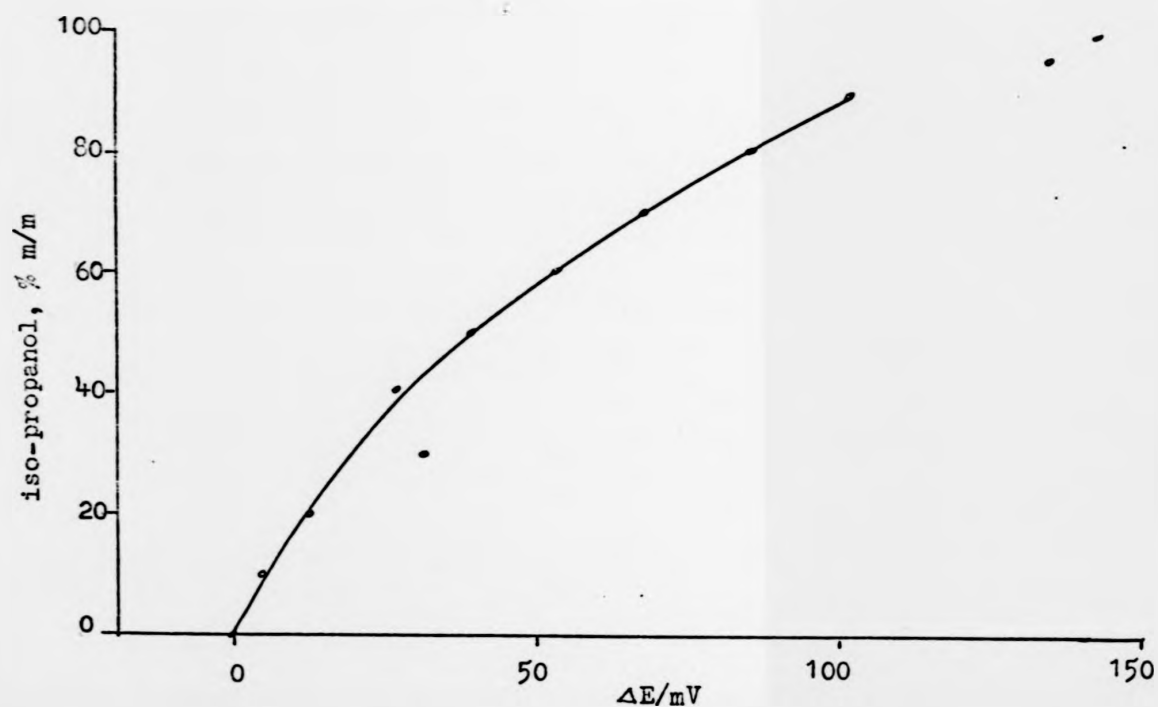


Fig. 92 Change in potential,  $\Delta E$ , for the system,  $\text{NaNO}_3$ -1-PrOH(MeOH), in solutions of  $10^{-3}$  M sodium nitrate and various iso-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

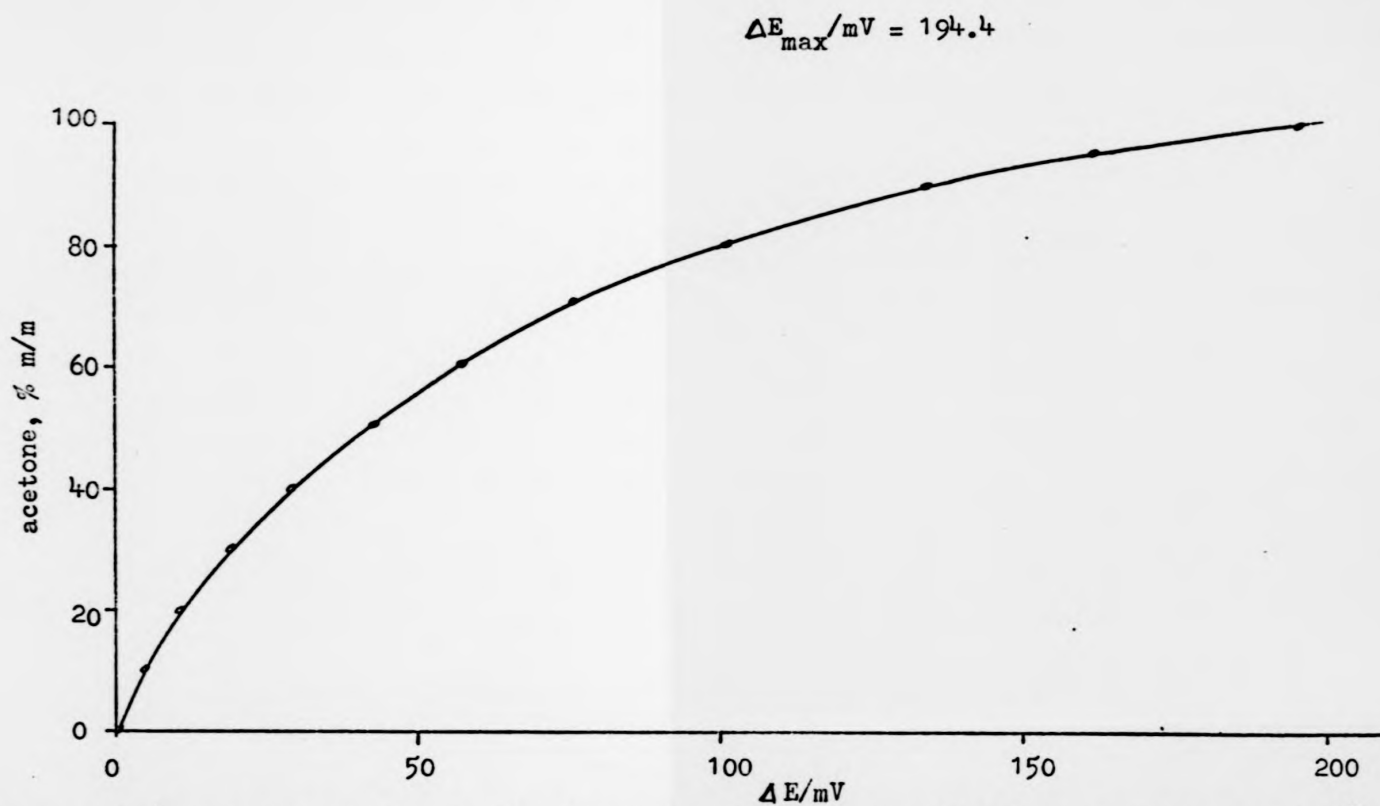


Fig. 93 Change in potential,  $\Delta E$ , for the system,  $\text{NaNO}_3$ -acetone (MeOH), in solutions of  $10^{-3}$  M sodium nitrate and various acetone concentrations, measured by using sodium-selective glass and SCE(LiCl) electrodes.

# 2.5.2 INDIRECT MEASUREMENTS

Table 96

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3\text{--MeOH(H}_2\text{O)}$ , in solutions  $10^{-3}\text{ M}$ ,  $10^{-4}\text{ M}$  and  $10^{-5}\text{ M}$  in sodium nitrate and of various methanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes

% m/E methanol	Potential/mV			Electrode slope /mV per decade	LLLRR	$E^0/\text{mV}$
	$10^{-3}\text{ MNa}^+$	$10^{-4}\text{ MNa}^+$	$10^{-5}\text{ MNa}^+$			
0	-43.7	-98.2	-142.6	54.5	$5 \times 10^{-5}$	119.8
20	-25.0	-79.2	-122.5	54.2	$5 \times 10^{-5}$	137.6
40	-2.2	-55.4	-95.4	53.0	$5 \times 10^{-5}$	156.8
60	18.2	-38.0	-81.6	54.2	$5 \times 10^{-5}$	180.8
80	45.3	-9.5	-45.5	53.8	$6 \times 10^{-5}$	207.2
90	61.2	7.1	-29.5	54.1	$6 \times 10^{-5}$	223.5
999	73.8	18.6	-16.1	53.2	$6 \times 10^{-5}$	233.4
$\Delta E_{\text{max}}/\text{mV}$	117.5	116.8	126.5			



Table 97

Change in potential (obtained by the 'indirect method') for the system, NaCl--EtOH(H<sub>2</sub>O), in solutions 10<sup>-3</sup> M, 10<sup>-4</sup> M and 10<sup>-5</sup> M in sodium chloride and of various ethanol concentrations, measured by using sodium-selective glass and silver-silver chloride (single-junction) electrodes

% m/m ethanol	Potential/mV			Electrode slope / mV decade	LLLR
	10 <sup>-3</sup> MNa <sup>+</sup>	10 <sup>-4</sup> MNa <sup>+</sup>	10 <sup>-5</sup> MNa <sup>+</sup>		
0	168	112	69	56.0	6 X 10 <sup>-5</sup>
10	177	120	78	57.0	6 X 10 <sup>-5</sup>
20	188	134	88	55.0	6 X 10 <sup>-5</sup>
30	199	144	97	55.0	6 X 10 <sup>-5</sup>
40	205	100	101	55.0	6 X 10 <sup>-5</sup>
50	213	158	105	55.0	6 X 10 <sup>-5</sup>
60	224	167	130	56.0	6 X 10 <sup>-5</sup>
70	234	176	129	56.0	6 X 10 <sup>-5</sup>
80	255	199	152	56.0	6 X 10 <sup>-5</sup>
90	277	225	181	61.0	6 X 10 <sup>-5</sup>
95	289	238	201	51.0	6 X 10 <sup>-5</sup>
99	298	248	210	50.0	6 X 10 <sup>-5</sup>
$\Delta E_{\text{max/mV}}$	130	136	141		

Table 98

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --n-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}\text{M}$ ,  $10^{-4}\text{M}$  and  $10^{-5}\text{M}$  in sodium nitrate and of various n-propanol concentrations measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0/\text{mV}$
	$10^{-3}\text{MNa}^+$	$10^{-4}\text{MNa}^+$	$10^{-5}\text{MNa}^+$			
0	-70.4	-130.2	-184.3	60.8	$2 \times 10^{-5}$	112.0
20	-31.1	185.4	-126.2	54.3	$6 \times 10^{-5}$	131.8
40	-21.0	-74.0	-110.8	53.0	$6 \times 10^{-5}$	138.0
60	-2.7	-57.5	-90.6	54.0	$6 \times 10^{-5}$	159.3
80	34.2	-18.9	-49.4	53.1	$6 \times 10^{-5}$	193.5
90	77.5	29.6	4.1	48.0	$6 \times 10^{-5}$	221.5
99	134.9	95.8	75.4	39.1	$6 \times 10^{-5}$	252.2
$\Delta E_{\text{max}}/\text{mV}$	205.3	226.0	259.7			

Table 99

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$  --i-PrOH( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various isopropanol concentrations, measured by using sodium-selective glass and silver-silver chloride (single-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode slope /mV per decade	LLRR	$E^0/\text{mV}$
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	-70.4	-130.2	-184.3	59.8	$2 \times 10^{-5}$	109.0
20	-36.6	-94.5	-139.7	58.0	$6 \times 10^{-5}$	137.4
40	-20.2	-74.2	-111.4	55.0	$6 \times 10^{-5}$	144.8
60	0.0	-55.4	-95.0	55.4	$6 \times 10^{-5}$	166.2
80	39.4	-15.0	-50.6	54.4	$6 \times 10^{-5}$	202.9
90	79.9	31.0	-2.2	49.0	$6 \times 10^{-5}$	226.9
99	139.7	100.8	74.6	38.9	$4 \times 10^{-5}$	256.4
$\Delta E_{\text{max}}/\text{mV}$	210.1	231.0	258.9			

Table 100

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --acetone( $\text{H}_2\text{O}$ ), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various acetone concentrations, measured by using sodium-selective glass and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0$ /mV
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	-57.4	-129.2	-179.7	71.8	$6 \times 10^{-5}$	158.0 (143.0)
20	-14.2	-84.9	-136.7	70.5	$6 \times 10^{-5}$	197.3 (164.1)
40	25.6	-39.9	-92.4	65.5	$6 \times 10^{-5}$	222.1 (163.5)
60	77.4	16.6	-31.4	61.0	$6 \times 10^{-5}$	260.4 (170.2)
80	145.2	88.4	38.4	56.0	$2 \times 10^{-5}$	313.2 (183.3)
90	196.2	146.1	95.2	50.5	$1 \times 10^{-5}$	347.7 (188.8)
99	268.3	229.8	194.6	38.0	$1 \times 10^{-5}$	382.3 (167.1)
$\Delta E_{\text{max}}/\text{mV}$	325.7	359.0	374.3			

( ) \*  $E^0$  Normalised w.r.t. silver-silver chloride (double-junction).

Table 101

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --n-PrOH(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various n-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-unction) electrodes

% m/m n-propanol	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0$ /mV
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	53.0	-2.3	-32.3	55.3	$6 \times 10^{-5}$	218.9
20	70.9	17.9	-12.9	51.0	$6 \times 10^{-5}$	223.9
40	90.8	38.3	7.2	51.5	$6 \times 10^{-5}$	245.3
60	115.2	60.6	30.7	53.5	$6 \times 10^{-5}$	275.7
80	140.9	89.1	60.8	51.0	$6 \times 10^{-5}$	293.9
90	159.9	110.7	81.7	49.2	$6 \times 10^{-5}$	307.5
99	169.6	125.3	100.8	44.3	$6 \times 10^{-5}$	301.5
$\Delta E_{\text{max}}/\text{mV}$	116.6	127.6	133.1			

Table 102

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --  $\text{i-PrCH(MeOH)}$ , in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various isopropanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes

% m/m isopropanol	Potential/mV			Electrode Slope /mV per decade	LLIRR	$E^0$ /mV
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	53.0	-2.3	-32.3	55.3	$6 \times 10^{-5}$	218.9
20	87.2	36.0	10.7	50.0	$6 \times 10^{-5}$	237.2
40	109.0	55.3	21.8	52.0	$6 \times 10^{-5}$	266.5
60	131.4	79.5	47.0	52.0	$6 \times 10^{-5}$	287.4
80	162.4	113.6	80.4	49.0	$6 \times 10^{-5}$	316.1
90	180.5	135.3	102.2	45.2	$6 \times 10^{-5}$	316.1
99	196.3	154.6	121.6	41.7	$6 \times 10^{-5}$	321.4
$\Delta E_{\text{max}}/\text{mV}$	143.3	156.9	153.9			

Table 103

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --acetone(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various acetone concentrations, measured by using sodium-selective glass and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLRR	$E^0$ /mV
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	158.7	97.9	49.6	63.0	$6 \times 10^{-5}$	347.7 (266.8)*
20	169.8	106.9	57.6	61.0	$6 \times 10^{-5}$	352.8 (258.0)
40	194.3	133.9	93.2	60.4	$6 \times 10^{-5}$	375.5 (267.1)
60	206.9	138.6	78.2	58.3	$6 \times 10^{-5}$	411.8 (286.3)
80	254.8	195.0	144.5	59.8	$6 \times 10^{-5}$	434.2 (286.1)
90	282.0	224.1	172.6	58.0	$6 \times 10^{-5}$	456.0 (268.4)
99	333.7	290.5	257.3	42.2	$6 \times 10^{-5}$	460.3 (241.0)
$\Delta E_{\text{max}}/\text{mV}$	175.0	192.6	207.7			

( )\*  $E^0$  Normalised w.r.t. silver-silver chloride (double-junction).

Table 103

Change in potential (obtained by the 'indirect method') for the system,  $\text{NaNO}_3$ --acetone(MeOH), in solutions  $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in sodium nitrate and of various acetone concentrations, measured by using sodium-selective glass and SCE(LiCl) electrodes

% m/m acetone	Potential/mV			Electrode slope /mV per decade	LLLR	$E^0$ /mV
	$10^{-3}$ MNa <sup>+</sup>	$10^{-4}$ MNa <sup>+</sup>	$10^{-5}$ MNa <sup>+</sup>			
0	158.7	97.9	49.6	63.0	$6 \times 10^{-5}$	347.7 (266.8) <sup>+</sup>
20	169.8	106.9	57.6	61.0	$6 \times 10^{-5}$	352.8 (258.0)
40	194.3	133.9	93.2	60.4	$6 \times 10^{-5}$	375.5 (267.1)
60	206.9	138.6	78.2	58.3	$6 \times 10^{-5}$	411.8 (286.3)
80	254.8	195.0	144.5	59.8	$6 \times 10^{-5}$	434.2 (286.1)
90	282.0	224.1	172.6	58.0	$6 \times 10^{-5}$	456.0 (268.4)
99	333.7	290.5	257.3	42.2	$6 \times 10^{-5}$	460.3 (241.0)
$\Delta E_{\text{max}}/\text{mV}$	175.0	192.6	207.7			

( ) \*  $E^0$  Normalised w.r.t. silver-silver chloride (double-junction).



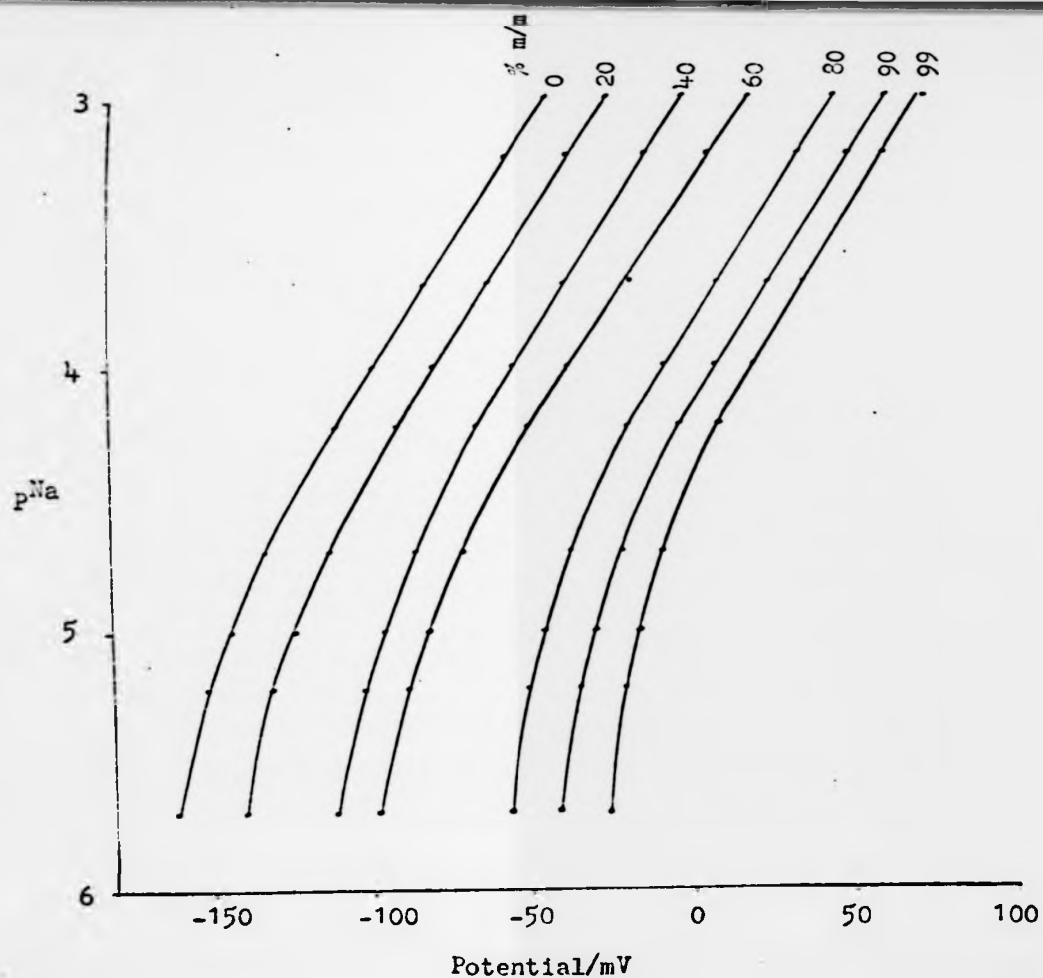


Fig. 94 Electrode calibration graphs for the system,  $NaNO_3$ - $MeOH(H_2O)$ , in solutions of constant methanol concentration and various sodium nitrate concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

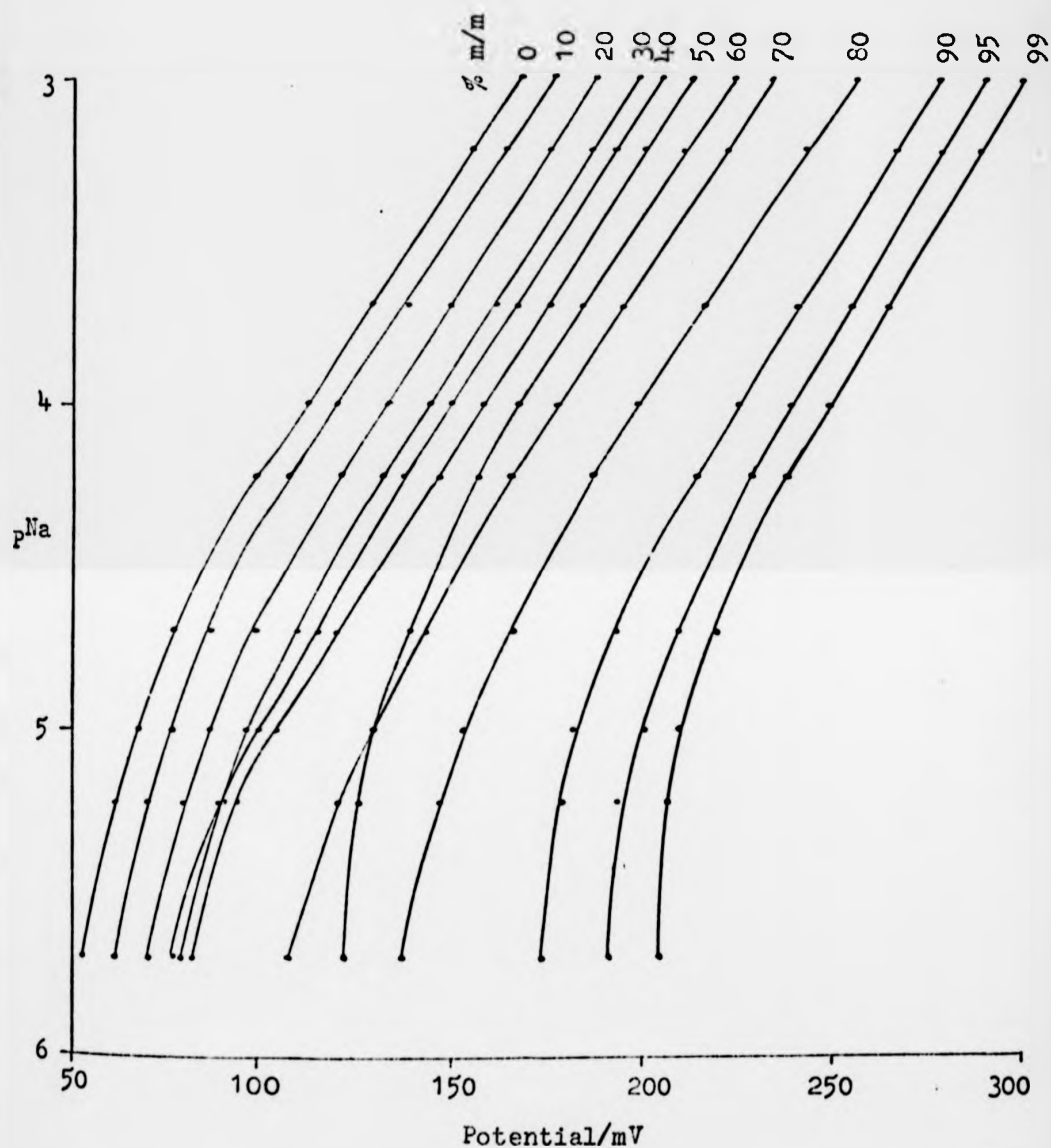


Fig. 95 Electrode calibration graphs for the system,  $\text{NaCl--EtOH(H}_2\text{O)}$ , in solutions of constant ethanol concentration and various sodium chloride concentrations, measured by using sodium-selective glass and silver-silver chloride (single-junction) electrodes.

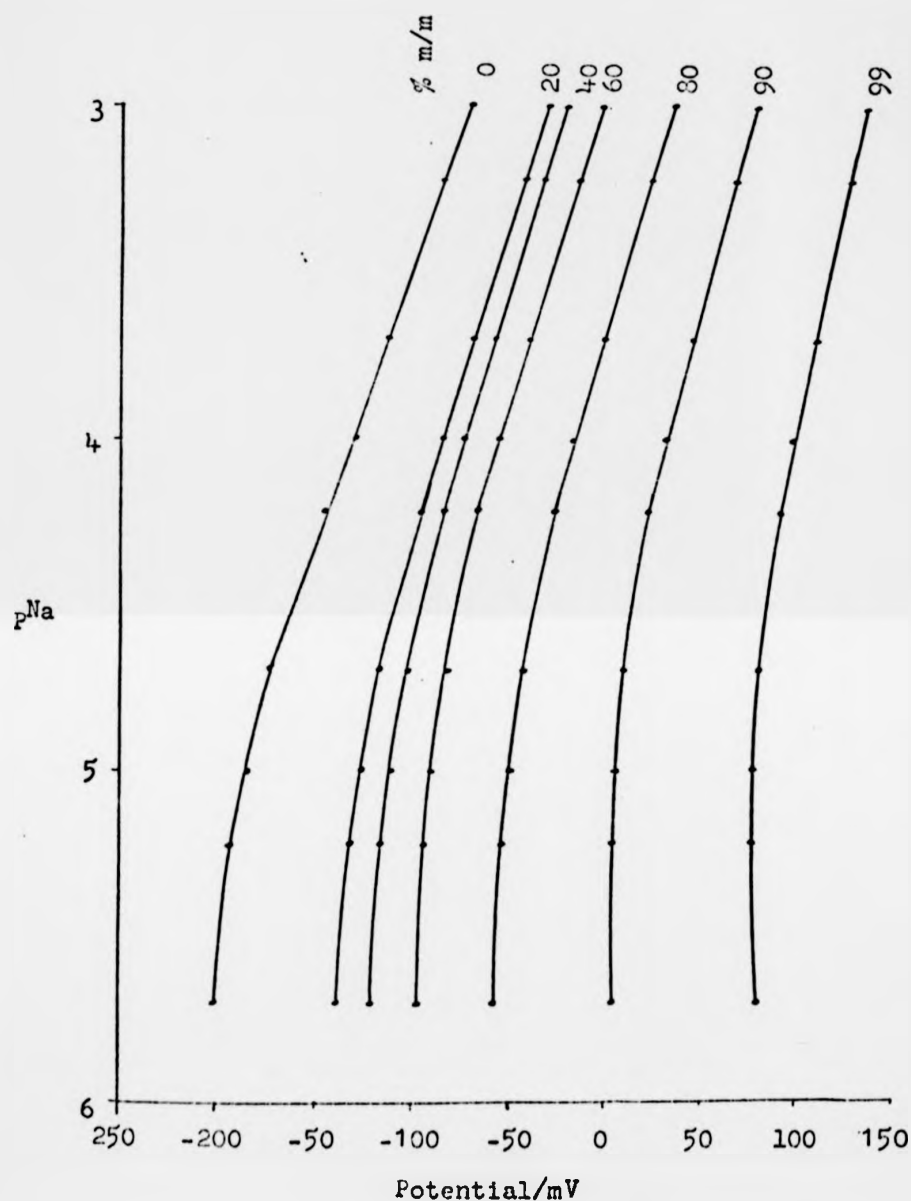


Fig.96 Electrode calibration graphs for the system,  $\text{NaNO}_3$ -n-PrOH( $\text{H}_2\text{O}$ ), in solutions of constant n-propanol concentration and various sodium nitrate concentrations, measured by using Sodium-selective glass and silver-silver chloride (double-junction) electrodes.

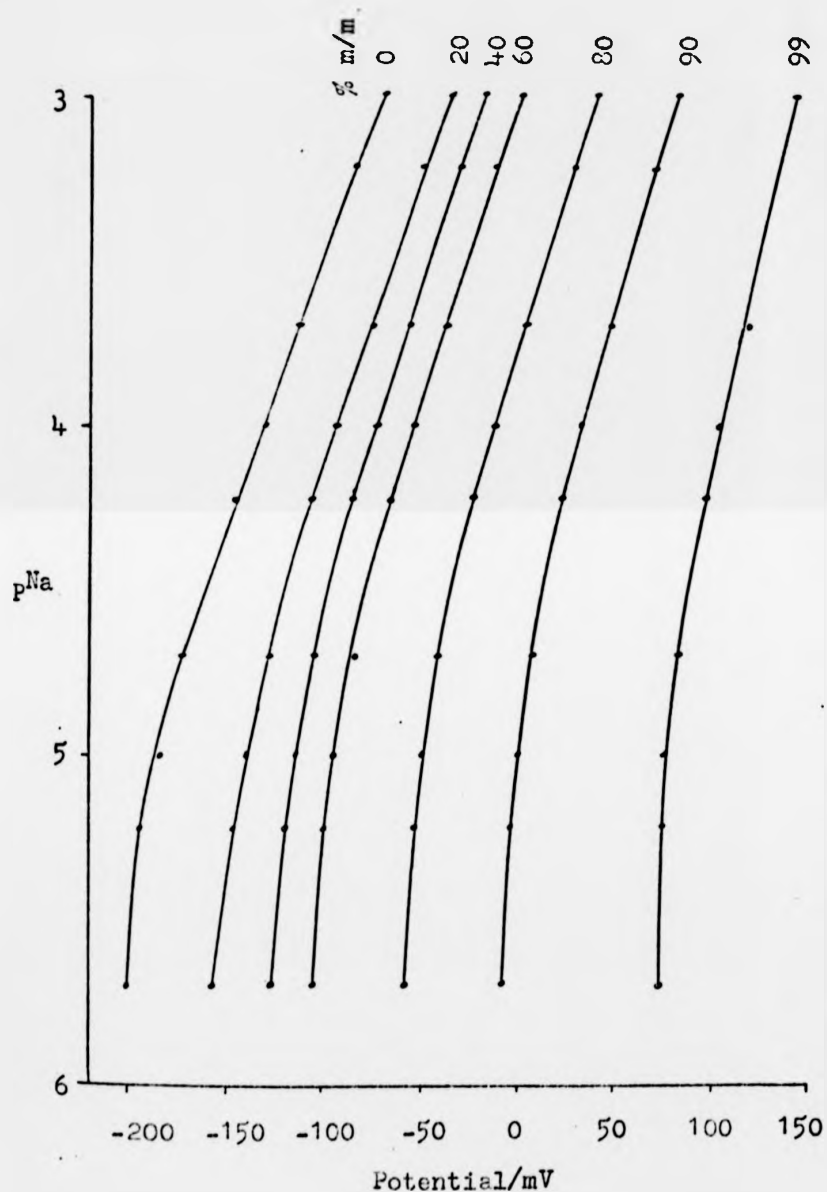


Fig.97 Electrode calibration graphs for the system,  $NaNO_3$ --1-PrOH( $H_2O$ ), in solutions of constant isopropanol concentration and various sodium nitrate concentrations, measured by using silver-silver chloride (double-junction) electrodes

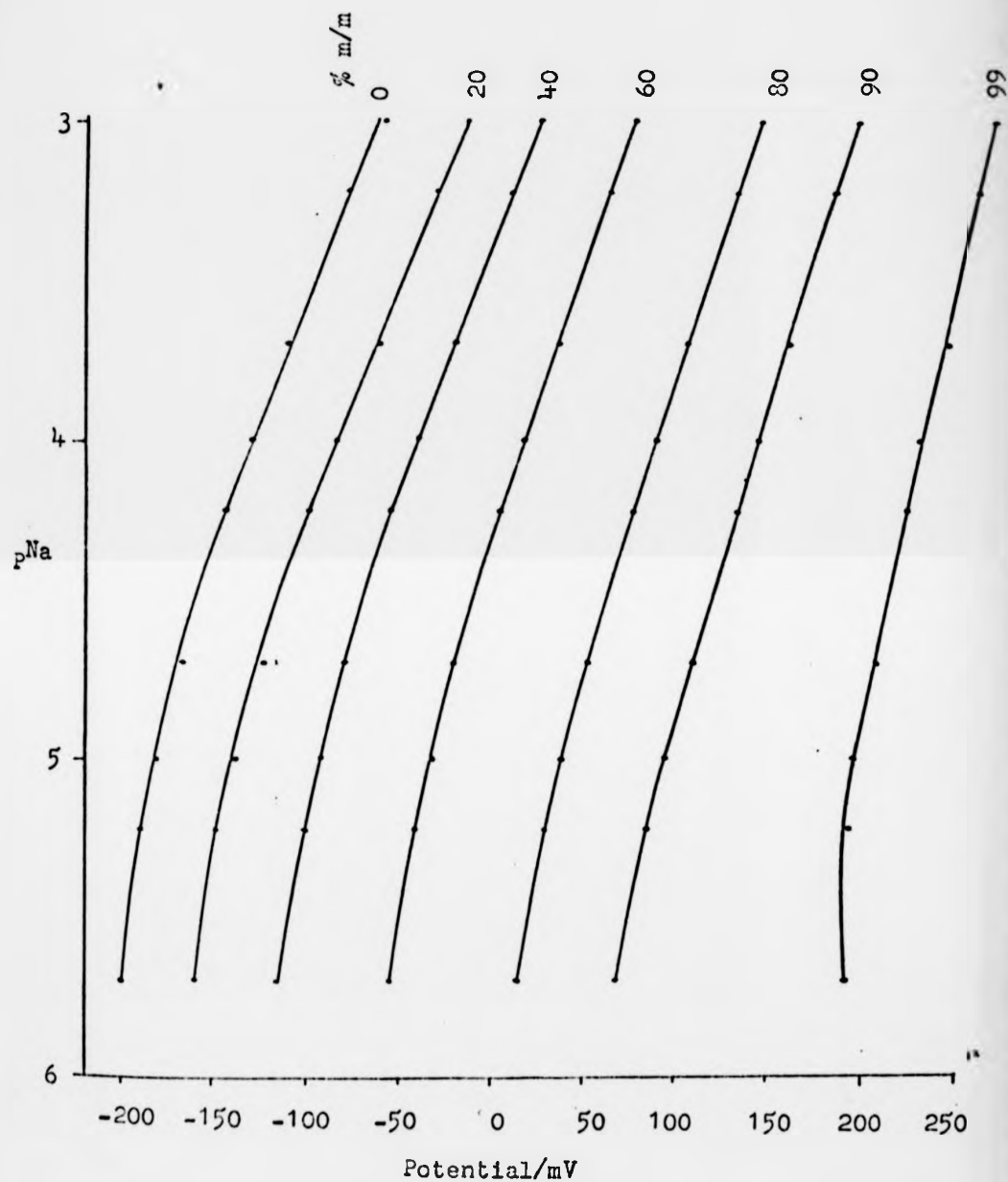


Fig. 98 Electrode calibration graphs for the system,  $\text{NaNO}_3$ -acetone( $\text{H}_2\text{O}$ ), in solutions of constant acetone concentration and various sodium nitrate concentrations, measured by using sodium-selective glass and SCE( $\text{LiCl}$ ) electrodes.

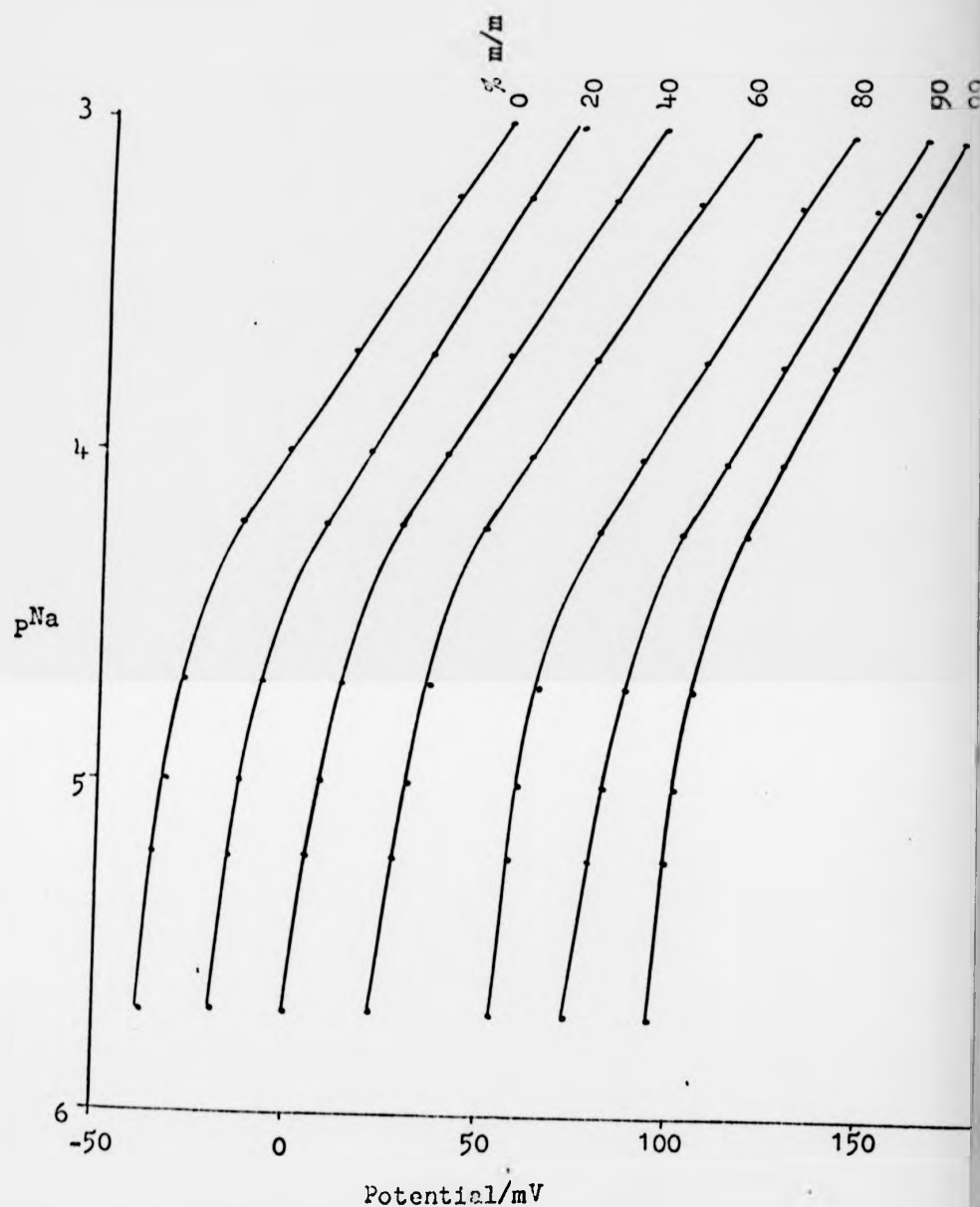


Fig. 99 Electrode calibration graphs for the system,  $NaNO_3$ -n-PrOH(MeOH), in solutions of constant n-propanol concentration and various sodium nitrate concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

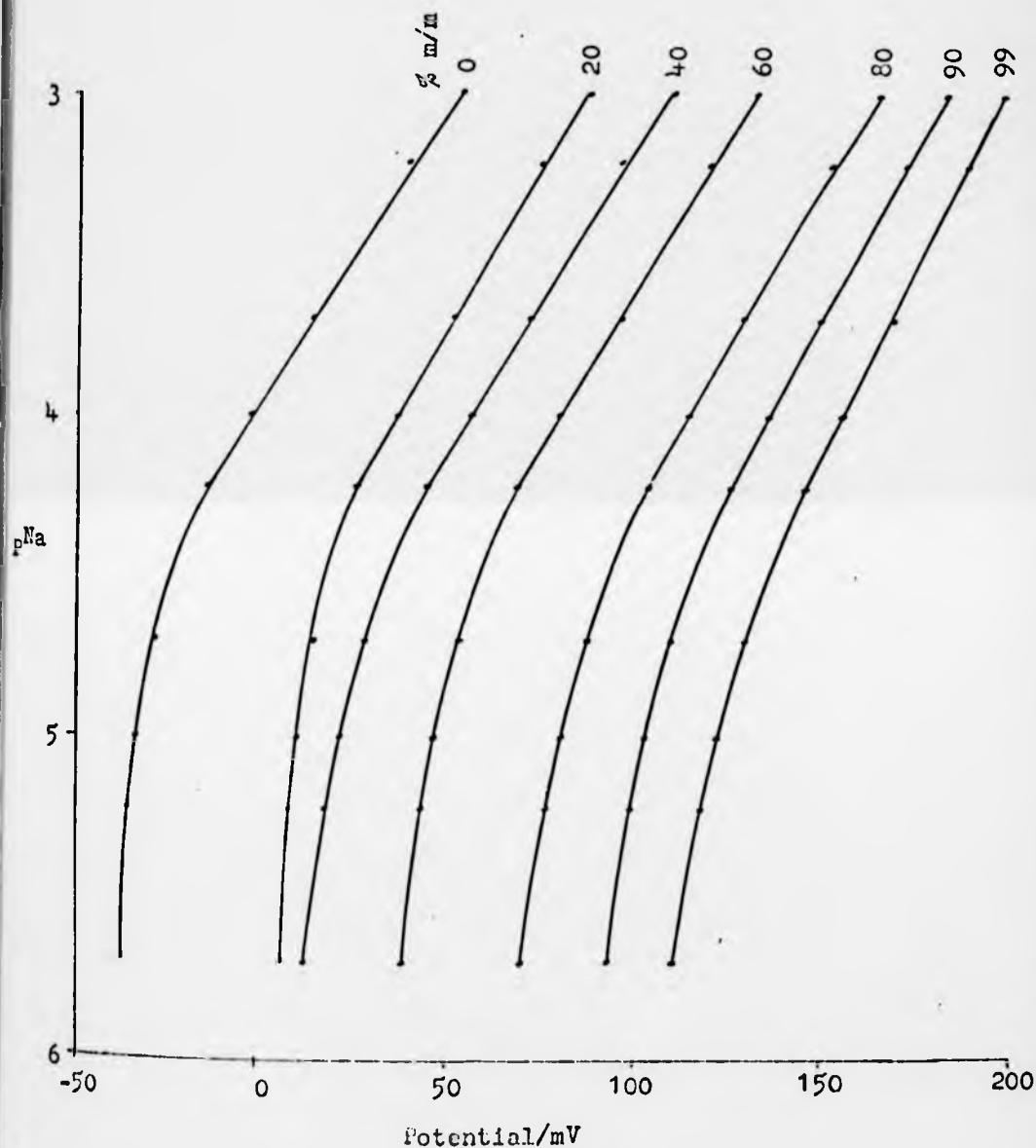


Fig.100 Electrode calibration graphs for the system,  $NaNO_3$ --1-PrOH(MeOH), in solutions of constant iso-propanol concentration and various sodium nitrate concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

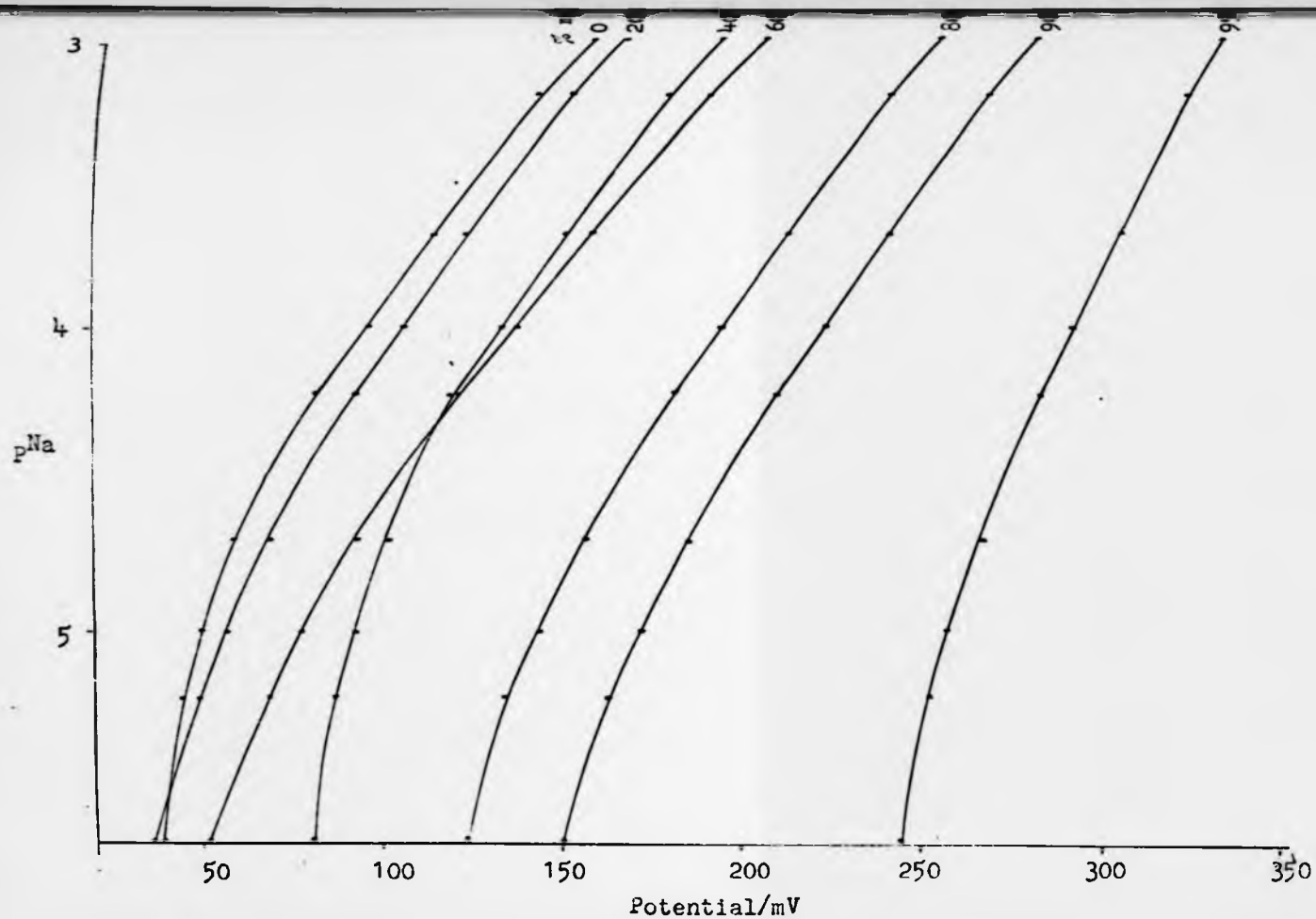


Fig.101 Electrode calibration graphs for the system,  $NaNO_3$ --acetone(MeOH), in solutions of constant acetone concentration and various sodium nitrate concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.



### 2.5.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTS

Table 104

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system  $\text{NaNO}_3$  - n-PrOH( $\text{H}_2\text{O}$ ) and  $\text{NaNO}_3$  - n-PrOH(MeOH), in  $10^{-3}$  M solutions of sodium nitrate for various n-propanol concentrations measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/\text{mV}$ ( $\text{H}_2\text{O}$ )		$\Delta\Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV}$ (MeOH)		$\Delta\Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	11.8	39.3	-27.5	13.9	17.0	-3.1
40	25.5	49.4	-23.9	29.7	37.8	-8.1
60	47.1	67.7	-20.6	48.3	62.2	-13.9
80	95.1	104.2	-9.1	76.1	87.9	-11.8
90	144.5	147.9	-3.4	91.1	106.9	-15.8
99	220.5	205.3	15.2	106.6	116.6	-10.0

Table 105

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the systems,  $\text{NaNO}_3$  - i-PrOH( $\text{H}_2\text{O}$ ) and  $\text{NaNO}_3$  - i-PrOH(MeOH), in  $10^{-3}$  M solutions of sodium nitrate for various iso-propanol concentrations, measured by using sodium-selective glass and silver-silver chloride (double-junction) electrodes.

iso-propanol % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ (MeOH)
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	9.2	33.8	-24.6	12.7	34.2	-21.5
40	21.2	50.2	-29.0	26.7	56.0	-29.3
60	43.1	70.4	-27.3	53.5	78.4	-24.9
80	91.6	109.8	-18.2	85.0	109.4	-24.4
90	141.5	150.3	-8.8	100.9	127.5	-26.6
99	223.0	210	13.0	142.2	143.3	-1.1

Table 106

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{NaNO}_3$ -acetone( $\text{H}_2\text{O}$ ) and  $\text{NaNO}_3$ -acetone( $\text{MeOH}$ ), in  $10^{-3}$  M solutions of sodium nitrate for various acetone concentrations measured by using sodium-selective glass and SCE( $\text{LiCl}$ ) electrodes.

acetone % m/m	$\Delta E/\text{mV} (\text{H}_2\text{O})$		$\Delta \Delta E$ ( $\text{H}_2\text{O}$ )	$\Delta E/\text{mV} (\text{MeOH})$		$\Delta \Delta E$ ( $\text{MeOH}$ )
	Direct	Indirect		Direct	Indirect	
0	0	0	0	0	0	0
20	24.9	43.3	-18.3	10.1	11.1	-1.0
40	56.1	83.0	-26.9	28.8	35.6	-6.8
60	115.7	134.8	-19.1	57.9	48.2	9.7
80	185.9	202.6	-16.7	100.8	96.1	4.7
90	244.6	253.6	-9.0	133.3	123.3	10.0
99	302.6	325.7	-23.1	193.4	175.0	19.4

2.6      HYDROGEN ION

2.6.1      Direct Measurements

2.6.2      Indirect Measurements

2.6.3      Comparison of Direct and Indirect Measurements.

2.6.1 DIRECT MEASUREMENTS

Table 102

Comparison of changes in potential,  $\Delta E$ , for a given system (pH-glass/silver-silver chloride d/i,  $10^{-3}$  M perchloric acid) and various solvent concentrations in different solvent-water mixtures.

Solvent % m/m	$\Delta E/mV$			
	MeOH	n-PrOH	i-PrOH	acetone
0	0 (214.3)	0 (219.8)	0 (217.9)	0 (252.2)
10	3.6	1.2	2.7	9.4
20	4.4	-0.9	0.7	17.3
30	4.0	-5.1	-4.1	23.8
40	2.7	-6.5	-8.1	31.5
50	2.7	-7.9	-11.3	47.7
60	4.5	-7.6	-12.6	62.8
70	9.2	-6.0	-10.8	84.2
80	21.1	-0.1	-5.6	118.4
90	49.9	17.6	10.5	183.5
95	78.0	39.4	32.4	262.7
99	119.8	81.0	76.9	422.1

\* SCE(LiCl) reference electrode was used.

Table 108

Comparison of changes in potential,  $\Delta E$ , for a given cell system (pH-glass/silver-silver chloride d/i,  $10^{-3}$  M perchloric acid) and various solvent concentrations in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$		
	n-PrOH	1-PrOH	acetone
0	0(371.3)	0(370.6)	0(466.1)
10	0.6	2.4	-16.6
20	0.5	3.5	-12.1
30	-0.4	4.5	-2.2
40	-1.6	5.6	10.9
50	-3.5	7.4	31.9
60	-5.5	6.9	53.9
70	-9.3	5.7	82.0
80	-14.4	4.4	124.9
90	-21.1	1.5	194.0
95	-	1.0	270.0
99	-29.2	-2.8	388.0

\* SCE(LiCl) reference electrode was used.

Table 108

Comparison of changes in potential,  $\Delta E$ , for a given cell system (pH-glass/silver-silver chloride d/i,  $10^{-3}$  M perchloric acid) and various solvent concentrations in different solvent-methanol mixtures.

Solvent % m/m	$\Delta E/mV$		
	n-PrOH	i-PrOH	acetone
0	0 (371.3)	0 (370.6)	0 (466.1)
10	0.6	2.4	-16.6
20	0.5	3.5	-12.1
30	-0.4	4.5	-2.2
40	-1.6	5.6	10.9
50	-3.5	7.4	31.9
60	-5.5	6.9	53.9
70	-9.3	5.7	82.0
80	-14.4	4.4	124.9
90	-21.1	1.5	194.0
95	-	1.0	270.0
99	-29.2	-2.8	388.0

\* SCE(LiCl) reference electrode was used.

$$\Delta E_{\max}/mV = 120$$

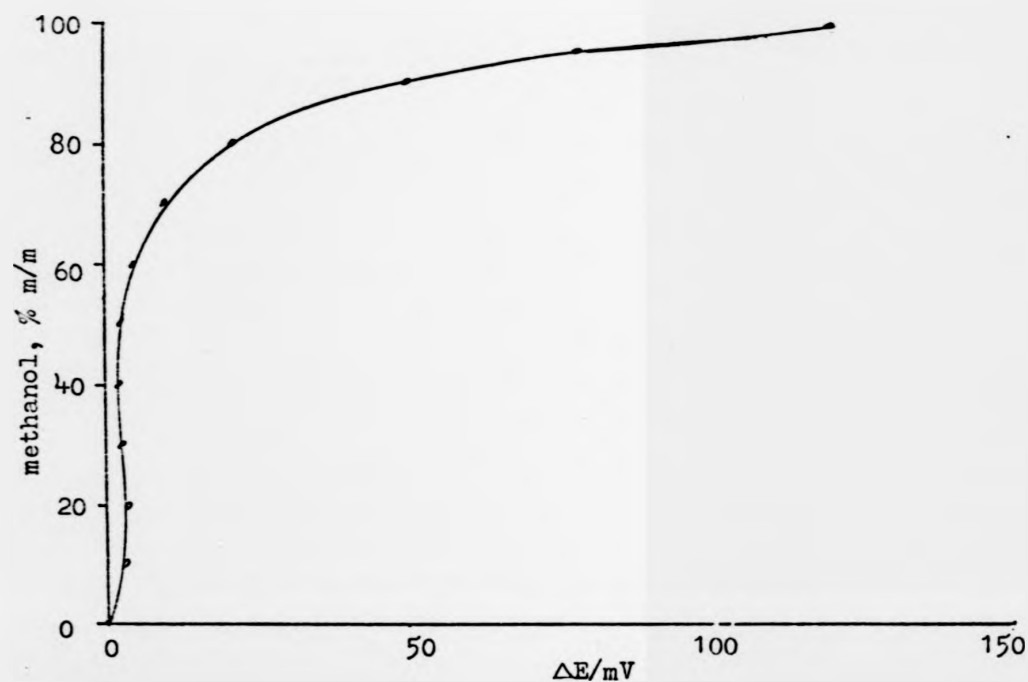


Fig.102 Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4\text{--MeOH(H}_2\text{O)}$ , in solutions of  $10^{-3}$  M perchloric acid and various methanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.



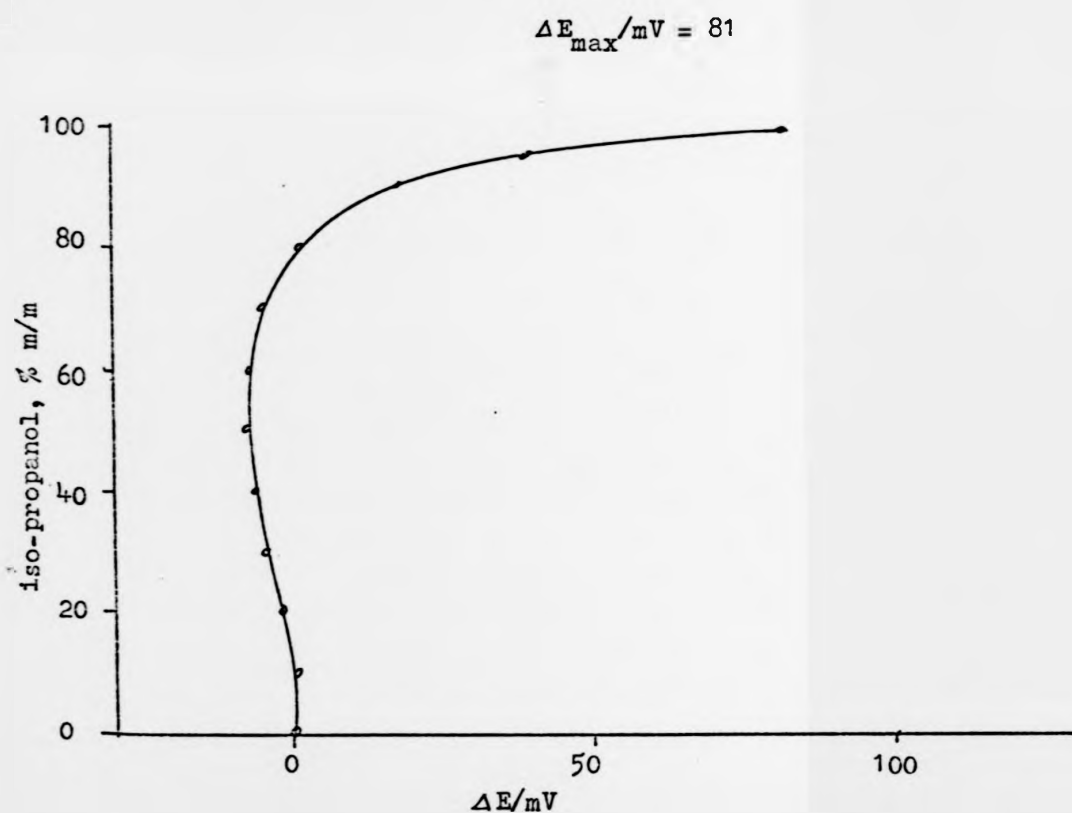


Fig.103 Change in-potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ -n-PrOH( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M perchloric acid and various n-propanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/mV = 76$$

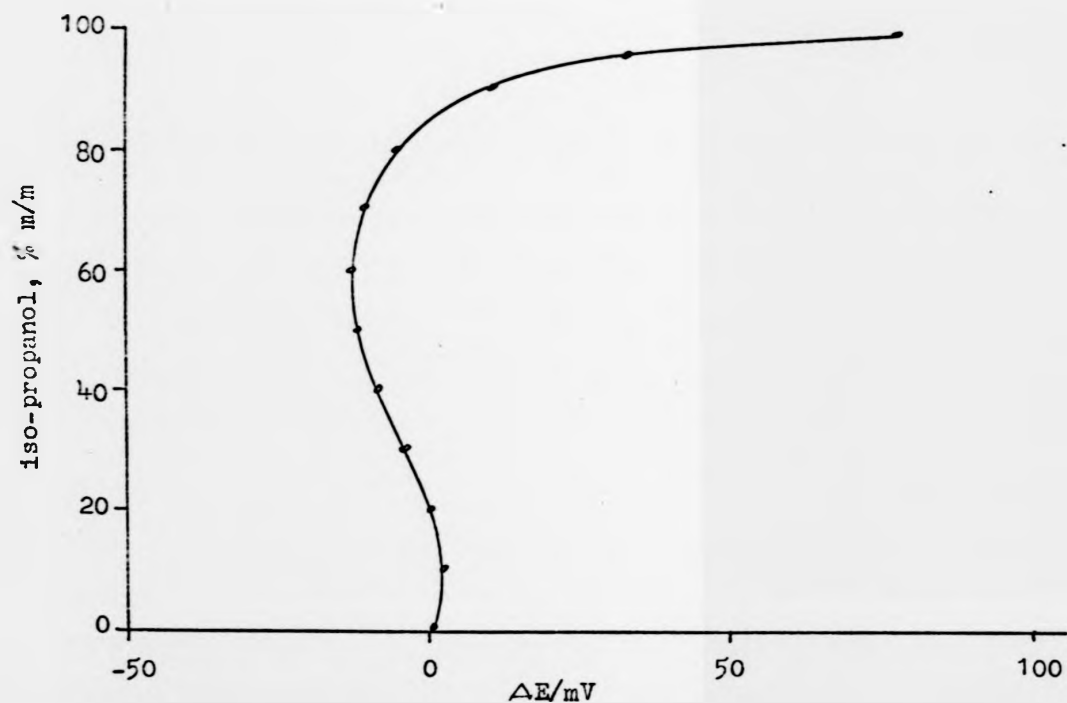


Fig. 10<sup>4</sup> Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ -i-PrOH( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M perchloric acid and various iso-propanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 4.22$$

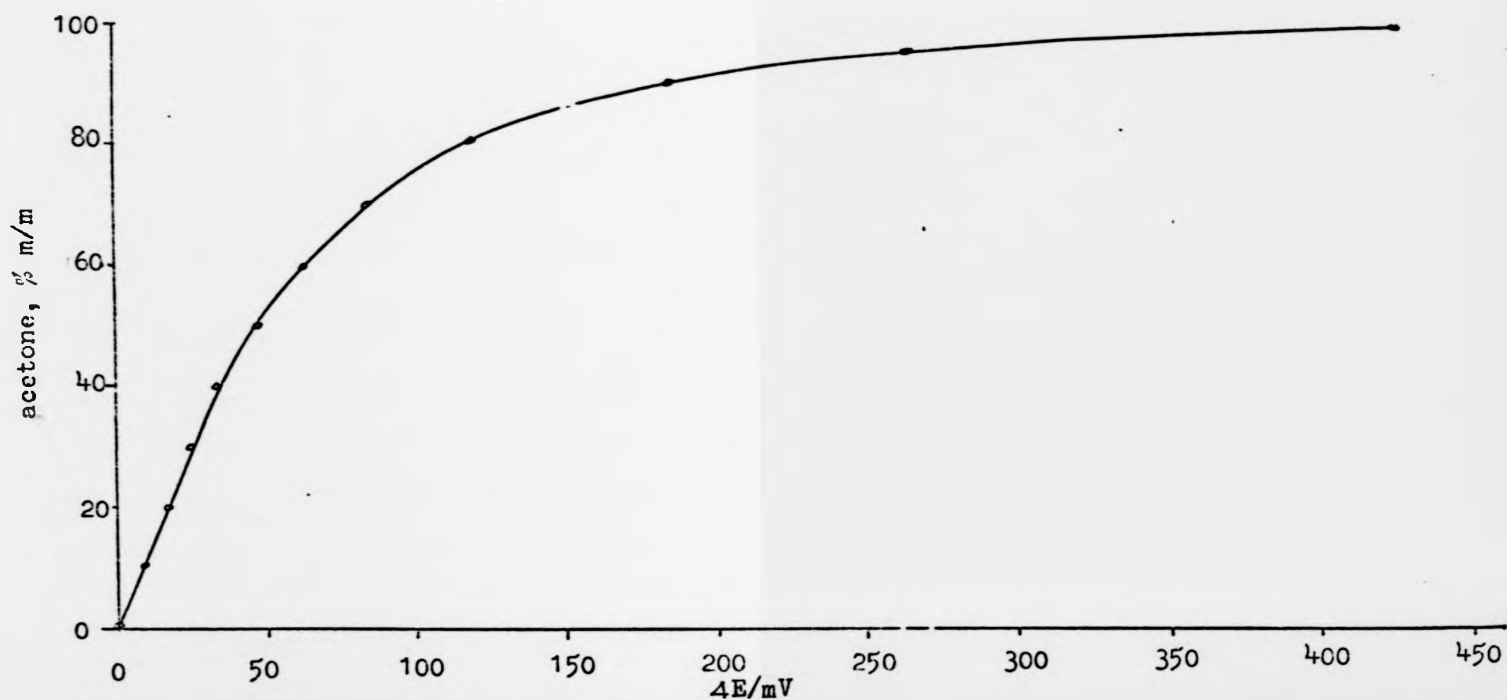


Fig.105 Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ -acetone( $\text{H}_2\text{O}$ ), in solutions of  $10^{-3}$  M perchloric acid and various acetone concentrations, measured by using pH glass and SCE( $\text{LiCl}$ ) electrodes.

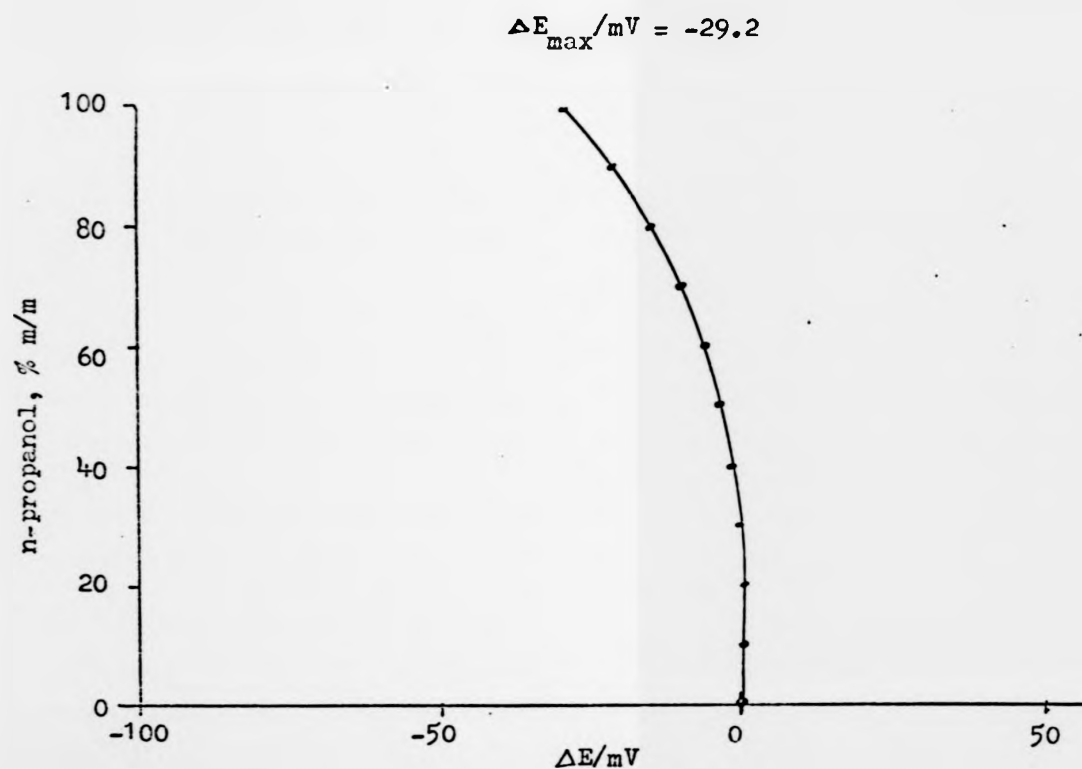


Fig.106 Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ — $n\text{-PrOH}(\text{MeOH})$ , in solutions, of  $10^{-3}$  M perchloric acid and various  $n$ -propanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

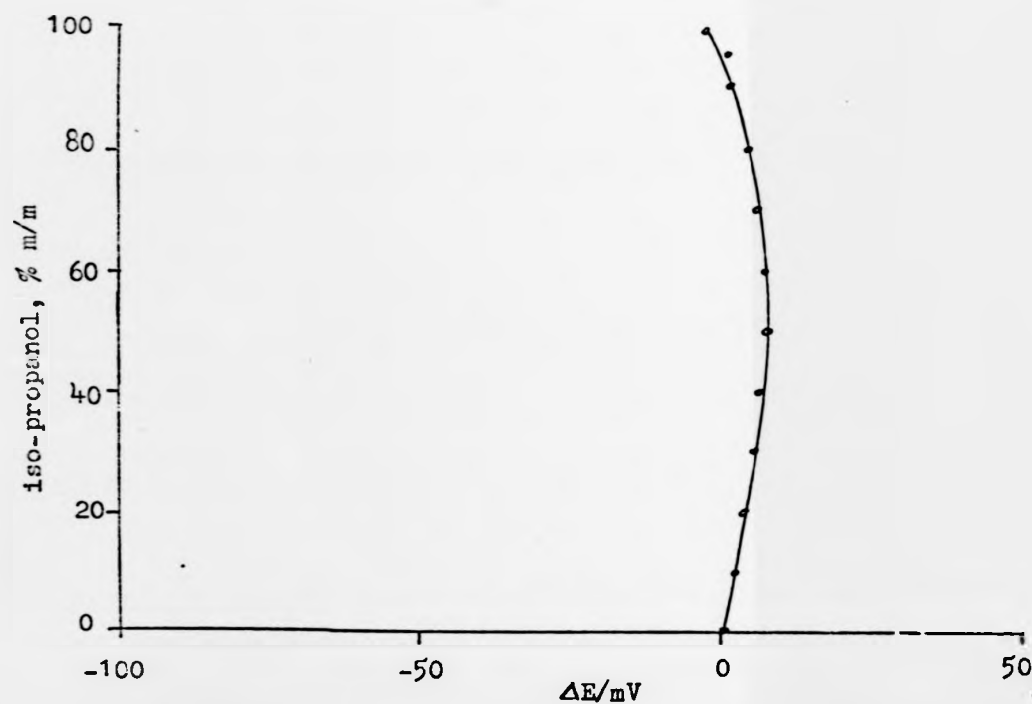


Fig.107 Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ -i-PrOH(MeOH), in solutions of  $10^{-3}$  M perchloric acid and various iso-propanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 388$$

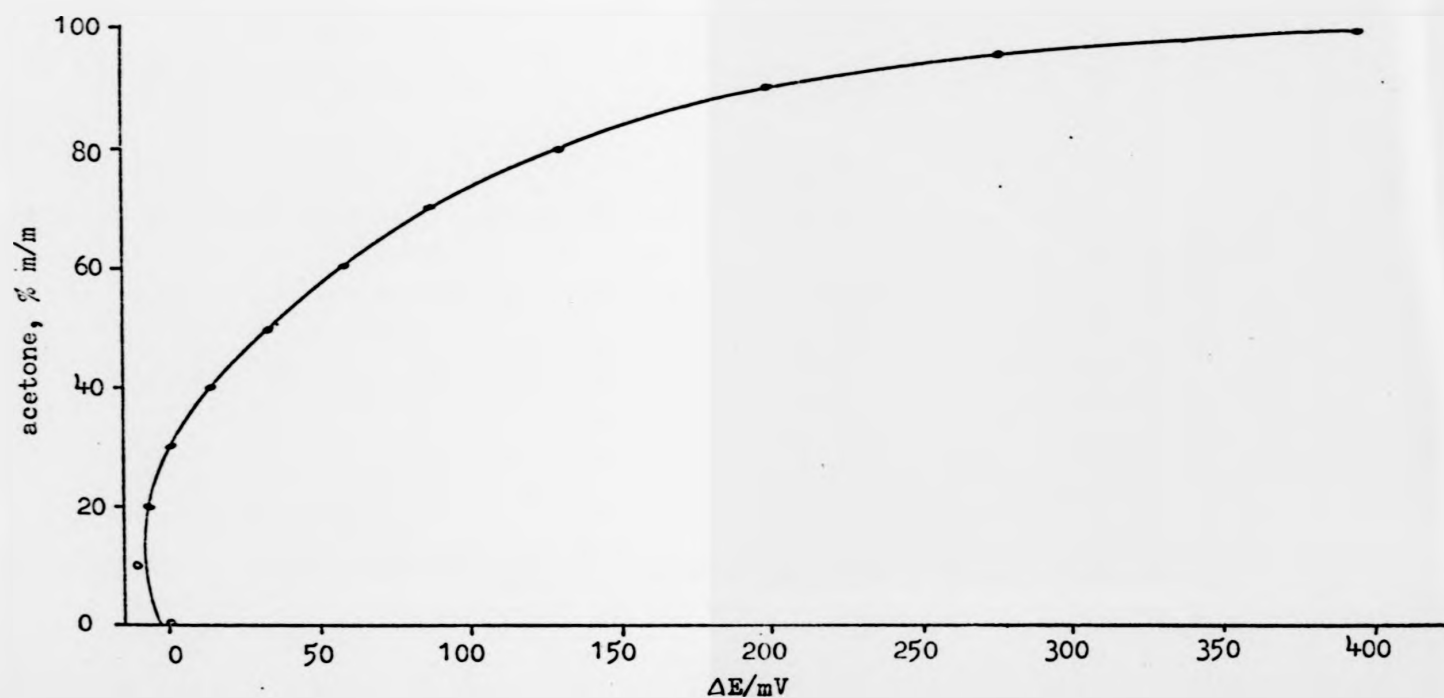


Fig.108 Change in potential,  $\Delta E$ , for the system,  $\text{HClO}_4$ —acetone(MeOH), in solutions of  $10^{-3}$  M perchloric acid and various acetone concentrations, measured by using pH glass and SCE(LiCl) electrodes.

2.6.2 INDIRECT MEASUREMENTSTable 109

Change in potential (obtained by 'indirect method')  
for the system,  $\text{HClO}_4$ --n-PrOH (MeOH), in solutions  
 $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in perchloric acid, and  
of various n-propanol concentrations, measured by  
using pH-glass and silver-silver chloride (double-  
junction) electrodes

% m/m n-propanol	Potential/mV		
	$10^{-3}$ MH <sup>+</sup>	$10^{-4}$ MH <sup>+</sup>	$10^{-5}$ MH <sup>+</sup>
0	362.3	292.9	-10.0
20	370.2	299.2	-19.0
40	374.1	303.4	-42.2
60	377.2	305.8	-69.6
80	379.0	303.4	-99.0
90	378.7	301.8	-114.4
99	377.7	298.5	-88.0
$\Delta E/\text{mV}$	15.4	5.5	-78.0

Table 110

Change in potential (obtained by 'indirect method')  
for the system,  $\text{HClO}_4$  --i-PrOH(MeCH), in solutions  
 $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in perchloric acid and of  
various isopropanol concentrations, measured by using  
pH-glass and silver-silver chloride (double-unction)  
electrodes

% m/m isopropanol	Potential/mV		
	$10^{-3}$ M $\text{H}^+$	$10^{-4}$ M $\text{H}^+$	$10^{-5}$ M $\text{H}^+$
0	362.3	292.9	-10
20	370.4	301.3	3.6
40	373.5	306.6	13.8
60	374.3	308.8	07.5
80	374.3	311.7	22.3
90	370.3	306.9	7.9
99	362.9	094.2	9.6
$\Delta E/\text{mV}$	0.6	1.3	19.6



Table 111

Change in potential (obtained by 'indirect method')  
for the system,  $\text{HClO}_4$ --acetone(MeOH), in solutions  
 $10^{-3}$  M,  $10^{-4}$  M and  $10^{-5}$  M in perchloric acid and of  
various acetone concentrations, measured by using  
pH-glass and SCE(LiCl) electrodes

% m/m acetone	Potential/mV		
	$10^{-3}$ MH <sup>+</sup>	$10^{-4}$ MH <sup>+</sup>	$10^{-5}$ MH <sup>+</sup>
0	463.5	385.2	80.3
20	455.5	386.2	88.2
40	477.0	407.1	109.4
60	502.0	435.6	129.7
80	580.0	517.8	236.4
90	638.3	579.3	301.8
99	757.4	710.9	(325.6)
$\Delta E_{\text{max/mV}}$	293.9	325.7	(245)

( )\*: Unstable

2.6.3 COMPARISON OF DIRECT AND INDIRECT MEASUREMENTSTable 112

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{HClO}_4$  n-PrOH(MeOH), in  $10^{-3}$  M solutions of perchloric acid for various n-propanol concentrations, measured using pH glass and silver-silver chloride (double-junction) electrodes.

n-propanol % m/m	$\Delta E/\text{mV}$ (MeOH)		$\Delta\Delta E/\text{mV}$ (MeOH)
	Direct	Indirect	
0	0	0	0
20	0.5	7.9	-7.4
40	-1.6	11.8	-13.4
60	-5.5	14.9	-20.4
80	-14.4	16.7	-31.1
90	-21.1	16.4	-37.5
99	-29.2	15.4	-44.6

Table 113

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{HClO}_4$ -1-PrOH(MeOH), in  $10^{-3}$  M solutions of perchloric acid for various methanol concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

iso-propanol % m/m	$\Delta E/\text{mV}$ (MeOH)		$\Delta\Delta E/\text{mV}$ (MeOH)
	Direct	Indirect	
0	0	0	0
20	3.5	8.1	-4.6
40	5.6	11.2	-5.6
60	6.9	12.0	-5.1
80	7.4	12.0	-4.6
90	1.5	8.0	-6.5
99	-2.8	0.6	-3.4

Table 114

Comparison of changes in potential obtained by 'direct' and 'indirect' measurements for the system,  $\text{HClO}_4$ -acetone(MeOH), in  $10^{-3}$  M solutions of perchloric acid for various acetone concentrations, measured by using pH glass and SCE(LiCl) electrodes.

acetone % m/m	$\Delta E/\text{mV}$ (MeOH)		$\Delta\Delta E/\text{mV}$ (MeOH)
	Direct	Indirect	
0	0	0	0
20	-12.1	-8.0	-4.1
40	10.1	13.5	-3.4
60	53.9	38.5	15.4
80	124.9	116.5	8.4
90	194.0	174.8	19.2
99	388.0	293.9	94.1

Slope Angle		Factor of Safety
Horizontal	Vertical	
0	0	0
1:1	1:1	1.00
1:2	1:2	1.15
1:3	1:3	1.30
1:4	1:4	1.45
1:5	1:5	1.60
1:6	1:6	1.75
1:8	1:8	2.00

## 2.7 POTENTIAL STABILITY STUDY

Table 115

Stability of potentials for the system,  $\text{Pb}(\text{ClO}_4)_2$ -- $\text{EtOH}(\text{H}_2\text{O})$ , using lead sulphide and silver-silver chloride (double-junction) electrodes

Time/min	Potential/mV (60% m/m ethanol)			Potential/mV (99% m/m ethanol)		
	$10^{-5} \text{ MPb}^{2+}$	$1.4 \times 10^{-5} \text{ MPb}^{2+}$	$10^{-4} \text{ MPb}^{2+}$	$10^{-5} \text{ MPb}^{2+}$	$1.4 \times 10^{-5} \text{ MPb}^{2+}$	$10^{-4} \text{ MPb}^{2+}$
0	-196.3	-190.2	-162.1	-245.6	-244.3	-186.8
2	-190.9	-190.4	-162.0	-238.6	-230.8	-185.0
4	-196.1	-190.2	-161.8	-247.6	-229.9	-181.4
6	-196.1	-190.2	-161.8	-249.2	-229.0	-181.4
8	-190.9	-190.2	-161.8	-244.6	-229.9	-186.0
10	-190.0	-190.2	-161.8	-256.4	-229.0	-189.0
14	-196.3	-190.2	-161.8	-256.4	-234.9	-191.3
18	-196.5	-190.4	-161.8	-257.3	-234.9	-193.1
24	-196.5	-190.4	-162.0	-256.4	-239.8	-193.3
30	-196.5	-190.4	-161.9	-260.4	-239.8	-197.1
36	-196.5	-190.4	-162.1	-265.8		-199.4
42	-196.5	-190.6	-162.1	-268.1		-201.2
48	-196.6	-190.6	-162.1	-275.6		
54	-196.6	-190.6	-162.0	-274.7		
60	-196.6	-190.6	-162.0	-273.8		
66	-196.7	-190.7				
72	-196.9	-190.7				
78	-197.0					
82	-197.0					

Table 116

Stability of potentials for the system,  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH(MeOH), using lead sulphide and silver-silver chloride (double-junction) electrodes

Time/min	Potential/mV (60% m/m n-propanol)			Potential/mV (99% m/m n-propanol)		
	$10^{-5} \text{ MPb}^{2+}$	$2 \times 10^{-5} \text{ MPb}^{2+}$	$10^{-4} \text{ MPb}^{2+}$	$10^{-5} \text{ MPb}^{2+}$	$2 \times 10^{-5} \text{ MPb}^{2+}$	$10^{-4} \text{ MPb}^{2+}$
0	-183.7	-173.2	-85.2	-180.0	-138.2	-4.3
2	-182.8	-166.5	-79.4	-174.6	-133.2	-3.4
4	-182.5	-166.5	-78.5	-172.8	-132.4	-2.9
6	-183.7	-166.8	-78.9	-172.4	-132.4	-2.7
8	-189.9	-167.6	-79.2	-172.4	-132.4	-2.8
10	-190.9	-167.6	-79.4	-172.4	-132.4	-2.9
14	-193.1	-166.8	-78.5	-172.8	-133.0	-2.8
18	-195.8	-166.8	-79.1	-173.7	-133.7	-3.0
24	-199.0	-167.7	-81.6	-175.5	-135.1	-3.4
30	-199.3	-167.7	-82.1	-176.4	-135.9	-3.6
36	-202.6	-168.4	-80.9	-177.1		-4.1
42	-203.3	-168.7	-80.7	-177.8		-4.3
46	-203.3	-167.6	-81.4			-4.9
54	-203.3		-81.6			-5.4
60			-81.6			-5.7
66			-82.0			-6.1
72			-81.6			-6.5
78			-82.0			-6.9
84			-82.0			-7.4
90			-82.8			-7.4
92			-82.8			

Table 117

Stability of potentials for the system,  $\text{AgNO}_3$ --n-PrOH( $\text{H}_2\text{O}$ ), using silver chloride and silver-silver chloride (double-unction) electrodes

Time/min	Potential/mV (60% m/m n-propanol)			Potential/mV (99% m/m n-propanol)		
	$5 \times 10^{-6} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$5 \times 10^{-6} \text{ MAg}^+$	$1 \times 10^{-5} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$
0	94.0	156.5	315.4	70.2	110.9	400.2
2	94.0	183.5	316.7	75.0	113.1	401.3
4	94.0	197.5	317.2	79.2	144.6	401.7
6	94.5	207.4	317.5	82.6	157.5	401.9
8	94.9	213.2	317.6	85.3	167.5	401.9
10	95.0	217.7	317.6	87.3	179.3	401.9
14	95.6	222.9	317.6	91.4	196.2	402.0
18	95.6	224.8	317.6	93.0	210.8	402.0
24	95.8	226.4	317.6	96.8	241.0	401.8
30	95.8	227.3	317.6	96.8	241.0	401.8
36	96.0	227.4	317.6	98.1	251.5	401.8
42	96.0	227.3	317.6	99.0	258.2	401.6
48	96.0	227.1	317.6	99.3	264.9	
52	96.0	227.1	317.4	99.7	267.9	
58		226.2	317.4	100.2	271.3	
64			317.3	100.8	274.9	
70			317.2	100.8	274.9	
72			317.2	100.8	274.9	
74			317.1		274.9	
80					275.0	
90					275.7	
94					275.5	
98					275.0	
102					275.0	
104					275.0	



Table 118

Stability of potentials for the system,  $\text{AgNO}_3$ --1-PrOH( $\text{H}_2\text{O}$ ), using silver chloride and silver-silver  
(double-junction) electrodes

Time/min	Potential/mV (60% m/m isopropanol)			Potential/mV (99% m/m isopropanol)		
	$5 \times 10^{-6} \text{ MAg}^+$	$1 \times 10^{-5} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$5 \times 10^{-6} \text{ MAg}^+$	$10^{-5} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$
0	154.1	219.4	302.7	66.0	92.2	367.4
2	169.9	227.5	305.4	63.5	119.2	385.0
4	176.0	229.2	305.5	63.7	140.8	385.4
6	181.9	230.6	306.0	64.8	157.0	385.8
8	184.9	230.8	306.0	65.4	169.5	385.8
10	188.2	230.8	306.0	66.4	183.5	385.9
14	191.5	231.0	306.0	68.4	201.0	386.0
18	193.7	231.1	306.0	70.3	214.5	386.0
24	195.5	231.1	306.0	71.7	229.1	386.0
30	195.4	231.1	306.4	72.6	239.4	386.0
36	197.1	231.1		73.5	246.5	
42	197.5	231.1		73.8	251.6	
48	197.5	231.1		74.5	255.1	
54	197.6	231.1		75.0	256.7	
60	197.8			75.3	258.2	
65	198.3			75.9	258.5	
70	198.3			75.9	258.5	
75	198.7			76.0	258.6	

Table 119

Stability of potentials, for the system  $\text{AgNO}_3$ -- $\text{EtOH}(\text{H}_2\text{O})$  using  
silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ )

electrodes

Time/min	Potential/mV (80% ethanol)		Potential/mV (90% ethanol)	
	$10^{-4} \text{M Ag}^+$	$10^{-3} \text{M Ag}^+$	$10^{-4} \text{M Ag}^+$	$10^{-3} \text{M Ag}^+$
0	13.6	94.0	34.9	90.5
2	14.6	94.2	34.4	91.2
4	15.1	94.6	33.3	91.2
6	16.3	95.0	32.6	91.3
8	19.0	95.6	31.8	91.7
10	21.2	95.8	31.6	91.8
14	26.2	96.6	31.2	92.3
18	28.5	97.3	31.2	92.7
24	32.8	98.0	31.2	93.5
30	35.8	98.9	31.2	94.1
36	37.2	98.9	31.2	94.2
42	36.2	98.7	31.4	94.2
52	37.2		31.4	94.2
62			34.4	
72			36.2	
82			37.6	

Table 120

Stability of potentials for the system  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH( $\text{H}_2\text{O}$ ),  
 using lead sulphide and silver-silver chloride (double-  
 junction) electrodes

Time/min	Potential/mV (80% n-propanol)		Potential/mV (90% n-propanol)	
	$10^{-4}$ MPb $^{2+}$	$10^{-3}$ MPb $^{2+}$	$10^{-4}$ MPb $^{2+}$	$10^{-3}$ MPb $^{+}$
0	-156.9	-127.4	-110.3	-89.7
2	-157.1	-122.3	-110.7	-89.7
4	-157.2	-127.3	-111.5	-89.7
6	-157.2	-127.4	-111.8	-89.8
8	-157.2	-122.4	-112.3	-89.8
10	-157.2	-127.4	-111.6	-89.8
14	-157.2	-127.4	-113.6	-89.8
18	-157.4	-127.4	-114.5	-89.8
24	-157.4	-127.4	-115.2	-89.8
30	-157.4	-127.4	-116.0	-89.8
36	-157.4		-116.8	
42	-157.4		-117.5	
48			-119.5	
52			-119.4	

Table 121

Stability of potentials for the system,  $\text{AgNO}_3$ --acetone(MeOH),  
using silver chloride and mercury-mercurous sulphate  
(1M  $\text{Na}_2\text{SO}_4$ ) electrodes

Time/min	Potential/mV (80% acetone)		Potential/mV (90% acetone)	
	$10^{-4} \text{ MAg}^+$	$10^{-3} \text{ MAg}^+$	$10^{-4} \text{ MAg}^+$	$10^{-3} \text{ MAg}^+$
0	150.2	186.9	154.3	197.8
2	149.9	186.9	+149.3	196.9
4	149.5	186.9	146.6	196.0
6	149.2	185.9	144.8	195.1
8	149.0	186.7	143.7	194.1
10	148.4	186.7	142.6	193.3
14	148.4	186.4	141.7	190.6
18	148.2	186.4	141.2	186.3
24	148.2	186.4	141.2	157.7
30	148.2	186.4	143.2	- *
36			148.0	-
42			153.6	-
48			164.8	-
52			166.3	-
58			165.4	43.4
62			163.6	48.4
72			162.2	50.6
76				53.3
72				56.6

-\* Potential off chart paper.

Table 122

Stability of potentials for the system,  $\text{KF--1,4-dioxan(H}_2\text{O)}$ ,  
using lanthanum fluoride and silver-silver chloride (double-  
junction) electrodes

Time/min	Potential/mV(60% 1,4-dioxan)		Potential/mV(90% 1,4-dioxan)	
	$10^{-4} \text{ MF}^-$	$10^{-3} \text{ MF}^-$	$10^{-4} \text{ MF}^-$	$10^{-3} \text{ MF}^-$
0	-101.9	-151.6	-238.1	-287.1
2	-104.3	-162.1	-242.0	-287.0
4	-105.1	-162.1	-242.9	-286.9
6	-105.4	-162.1	-243.0	-286.9
8	-105.3	-162.2	-243.0	-286.7
10	-105.4	-162.2	-243.0	-286.7
14	-105.4	-162.2	-242.6	-286.6
18	-105.4	-162.2	-240.5	-286.6
24	-105.4	-162.2	-240.5	-286.6
30	-105.4	-162.2	-239.2	-286.6
36		-162.2	-236.9	-286.5
42			-236.9	-286.5
48			-235.8	
54			-234.9	
60			-234.1	
66			-233.6	
72			-233.1	

Table 123

Stability of potentials for the system,  $\text{Pb}(\text{ClO}_4)_2$ --acetone( $\text{H}_2\text{O}$ ),  
using lead sulphide and SCE(LiCl) electrodes

Time/min	Potential/mV (90% acetone)		Potential/mV (99% acetone)	
	$10^{-4}$ MPb <sup>+</sup>	$10^{-3}$ MPb <sup>+</sup>	$10^{-4}$ MPb <sup>+</sup>	$10^{-3}$ MPb <sup>+</sup>
0	33.5	53.5	181.7	170.9
2	34.9	53.7	184.3	170.9
4	35.8	53.7	186.8	170.9
6	36.2	53.7	187.8	170.9
8	36.6	53.7	187.9	171.0
10	36.6	53.5	189.2	171.2
14	36.6	53.5	190.3	171.2
18	36.4	53.5	190.7	171.2
24	36.0	53.5	190.9	171.2
30	36.3	53.5	190.9	171.2
36	34.4	53.5	190.7	171.2
42	33.3	53.5	190.6	171.2
48	31.9			
54	30.5			
60	29.7			

Table 124

Stability of potentials for the system,  $\text{Et}_4\text{NCl}$ --acetone( $\text{H}_2\text{O}$ ),  
using silver chloride and mercury-mercurous sulphate  
(1M  $\text{Na}_2\text{SO}_4$ ) electrodes

Time/min	Potential/mV (90% acetone)		Potential/mV (99% acetone)	
	$10^{-4}$ M $\text{Cl}^-$	$10^{-3}$ M $\text{Cl}^-$	$10^{-4}$ M $\text{Cl}^-$	$10^{-3}$ M $\text{Cl}^-$
0	-323.2	-377.5	-413.4	-483.4
2	-325.0	-376.8	-420.2	-481.6
4	-325.2	-377.5	-426.5	-481.6
6	-325.0	-378.1	-429.6	-481.6
8	-324.4	-378.4	-431.9	-481.0
10	-324.1	-378.6	-433.2	-481.0
14	-323.2	-379.0	-435.0	-481.0
18	-323.0	-379.6	-436.8	-481.4
24	-322.6	-380.2	-437.7	-481.2
30	-323.2	-381.2	-439.1	-481.2
36	-323.4	-381.2	-439.4	-481.0
42	-323.2			
48	-323.2			

Table 125

Stability of potentials for the system  $\text{NaNO}_3$ --acetone( $\text{H}_2\text{O}$ ),  
using sodium-selective glass and SCE( $\text{LiCl}$ ) electrodes

Time/min	Potential/mV (90% acetone)		Potential/mV (99% acetone)	
	$10^{-4}$ M $\text{Na}^+$	$10^{-3}$ M $\text{Na}^+$	$10^{-4}$ M $\text{Na}^+$	$10^{-3}$ M $\text{Na}^+$
0	66.6	150.5	221.5	278.3
2	73.8	152.4	244.9	299.0
4	78.4	153.5	252.1	299.5
6	81.9	154.4	256.3	300.1
8	84.1	154.7	259.0	300.4
10	86.4	154.3	261.1	300.8
14	88.5	156.1	264.1	301.5
18	91.8	156.8	265.9	301.8
24	93.6	157.7	267.7	302.2
30	95.4	158.2	269.2	302.2
36	97.2	158.0	207.1	
42	98.6		270.6	
48	99.5		270.9	
54	99.9			
60	99.8			



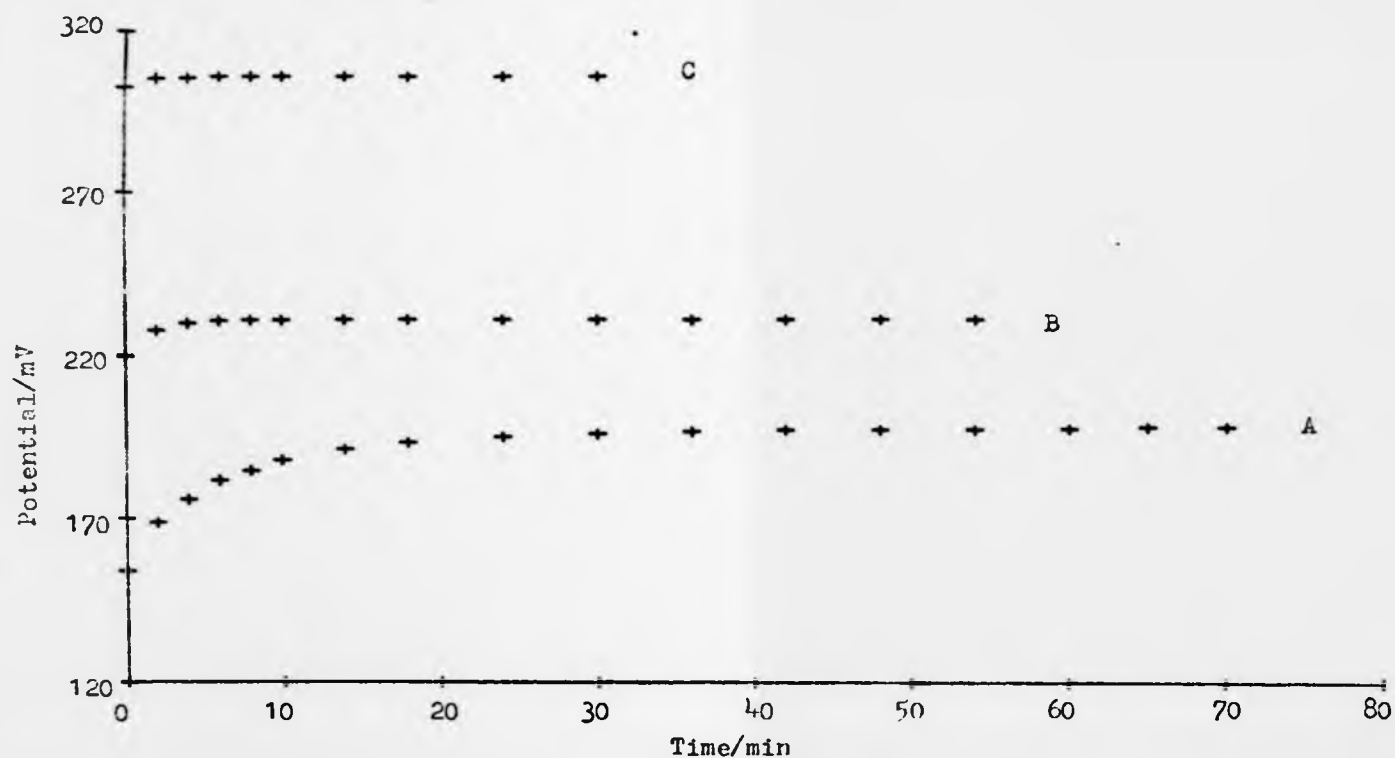


Fig 109. Graph of time versus potential for the system,  $\text{AgNO}_3$ -1-PrOH( $\text{H}_2\text{O}$ ), in 60% (m/m) isopropanol. Potential measured by using silver chloride and silver-silver chloride (double-junction) electrodes. Molarity of silver nitrate: A,  $5 \times 10^{-6}$  M; B,  $10^{-5}$  M; and C,  $10^{-4}$  M.

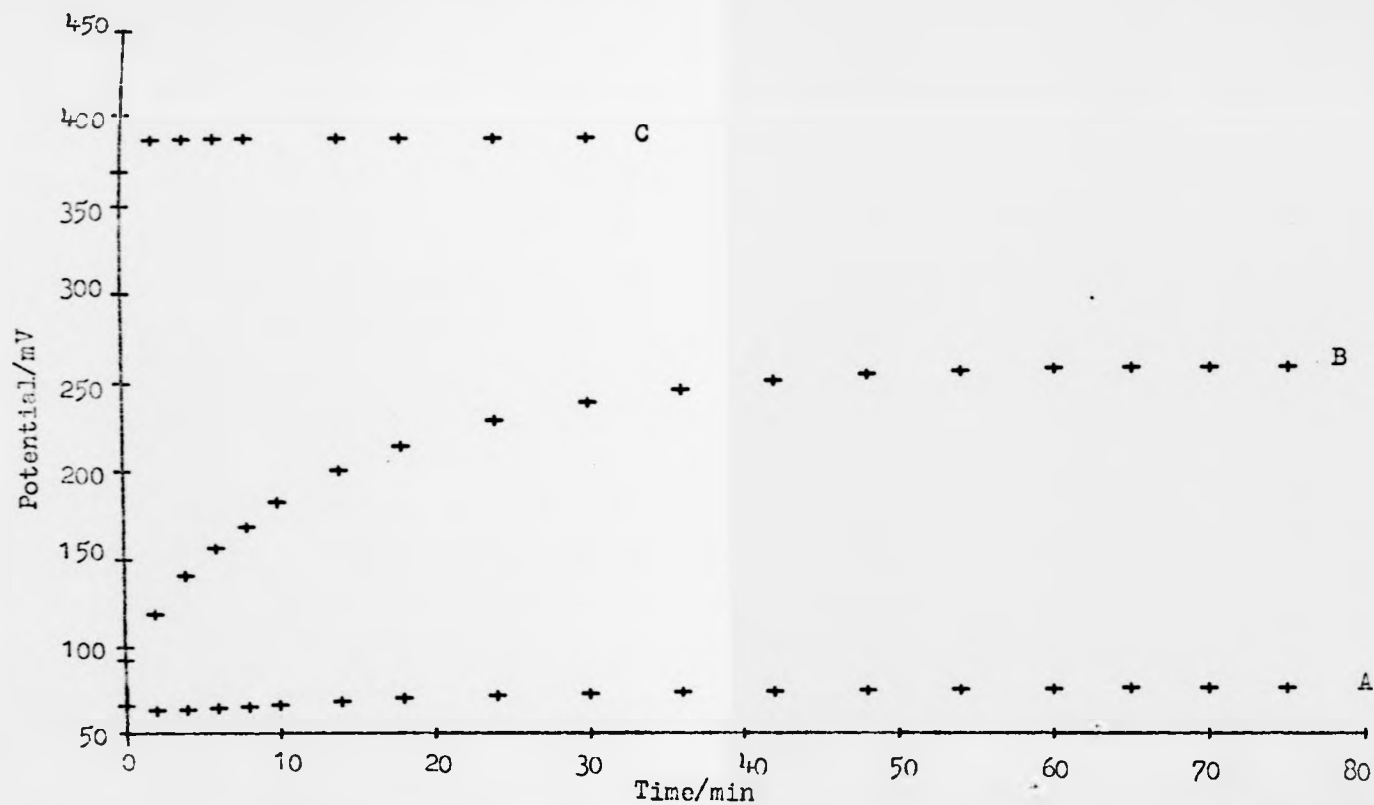


Fig 110. Graphs of time versus potential for the system,  $\text{AgNO}_3$ -- $i\text{-PrOH(H}_2\text{O)}$ , in 99% (m/m) isopropanol. Potential measured by using silver chloride and silver-silver chloride (double-junction) electrodes. Molarity of silver nitrate: A,  $5 \times 10^{-6}$  M; B,  $10^{-5}$  M; and C,  $10^{-4}$  M.

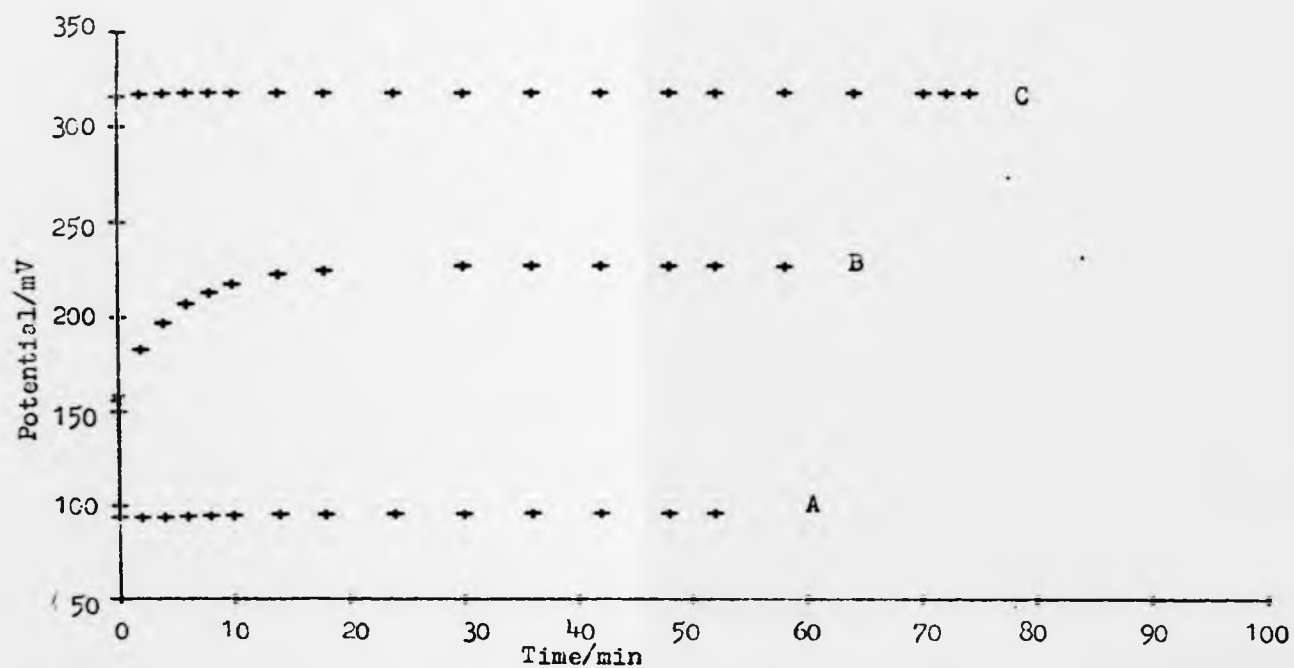


Fig 111. Graphs of time versus potential for the system,  $\text{AgNO}_3$ -- $\text{n-PrOH(H}_2\text{O)}$ , in 60% m/m) n-propanol. Potential measured by using silver chloride and silver-silver chloride electrodes. Molarity of silver nitrate A,  $5 \times 10^{-6}$  M; B,  $10^{-5}$  M; and C,  $10^{-4}$  M.

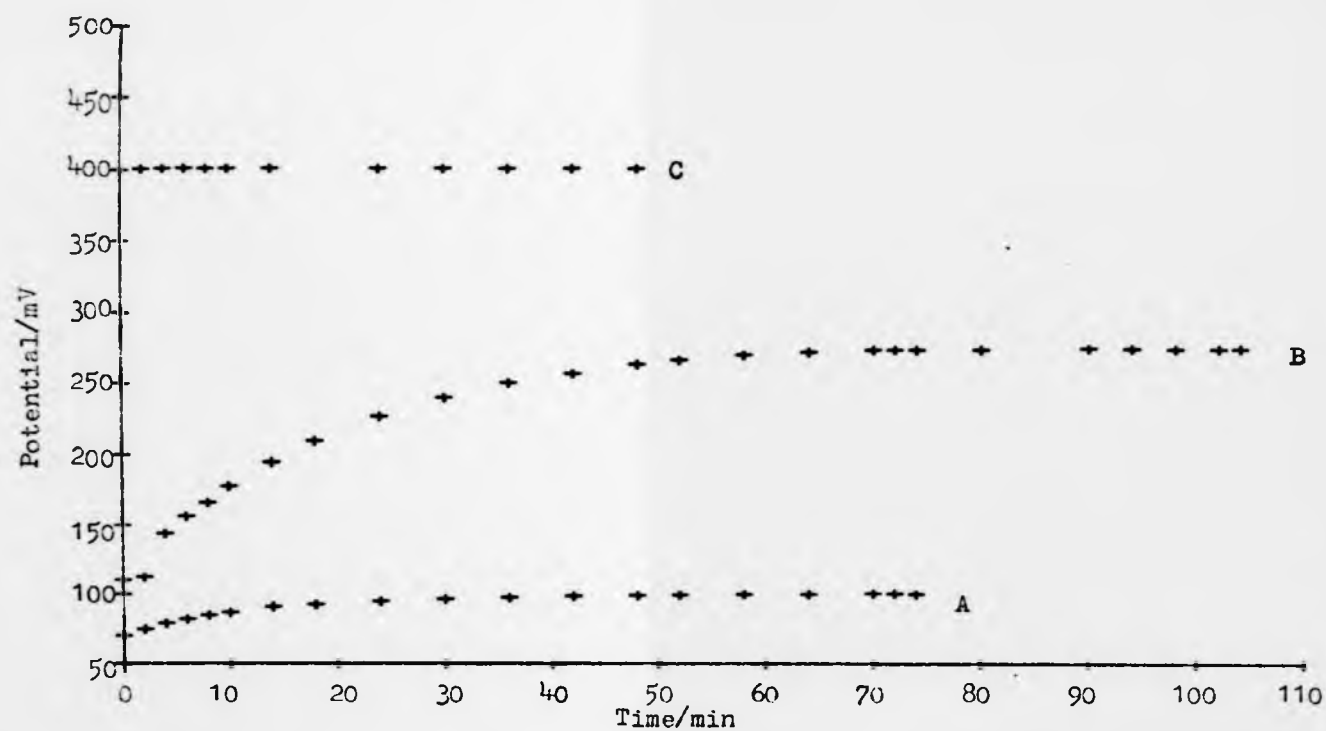


Fig 112. Graphs of time versus potential for the system,  $\text{AgNO}_3$ -- $n\text{-PrOH(H}_2\text{O)}$ , in 99% (m/m)  $n$ -propanol. Potential measured by using silver chloride and silver-silver chloride (double-junction) electrodes. Molarity of silver nitrate: A,  $5 \times 10^{-6}$  M; B,  $10^{-5}$  M; and C,  $10^{-4}$  M.

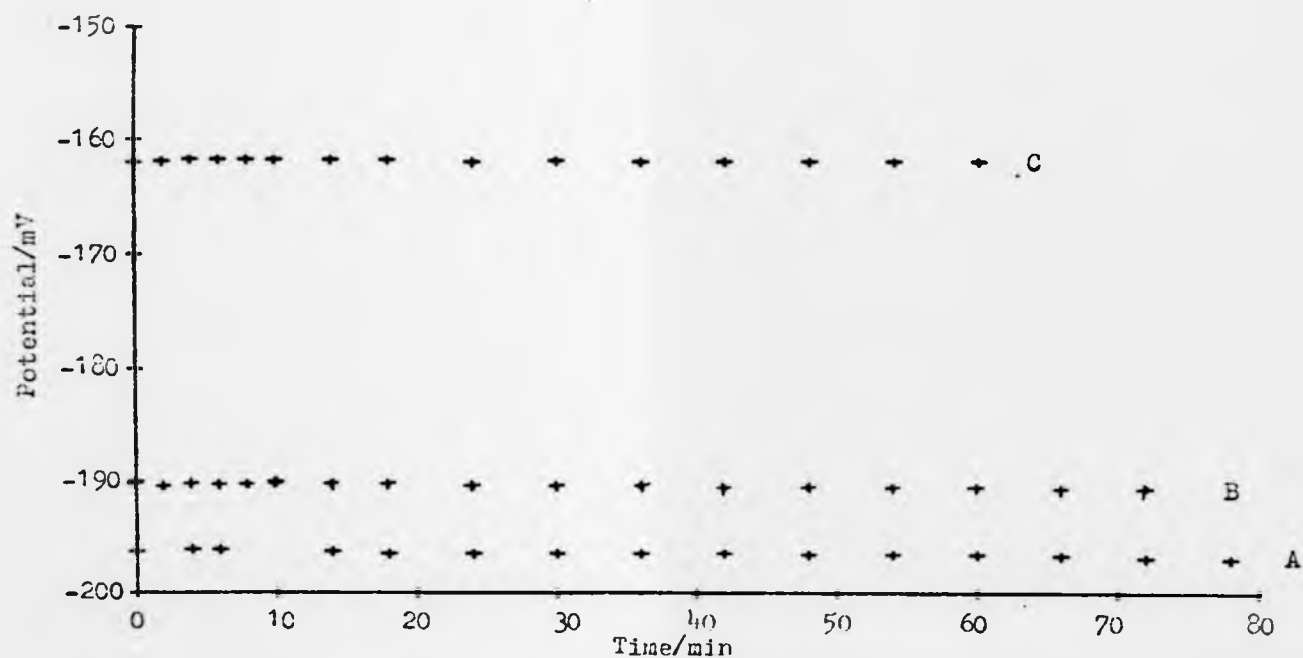


Fig 113. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ -- $\text{EtOH}(\text{H}_2\text{O})$ , in 60% (m/m) ethanol. Potential measured by using lead sulphide and silver-silver chloride (double-junction) electrodes. Molarity of lead perchlorate: A,  $10^{-5}$  M; B,  $1.4 \times 10^{-5}$  M; and C,  $10^{-4}$  M.

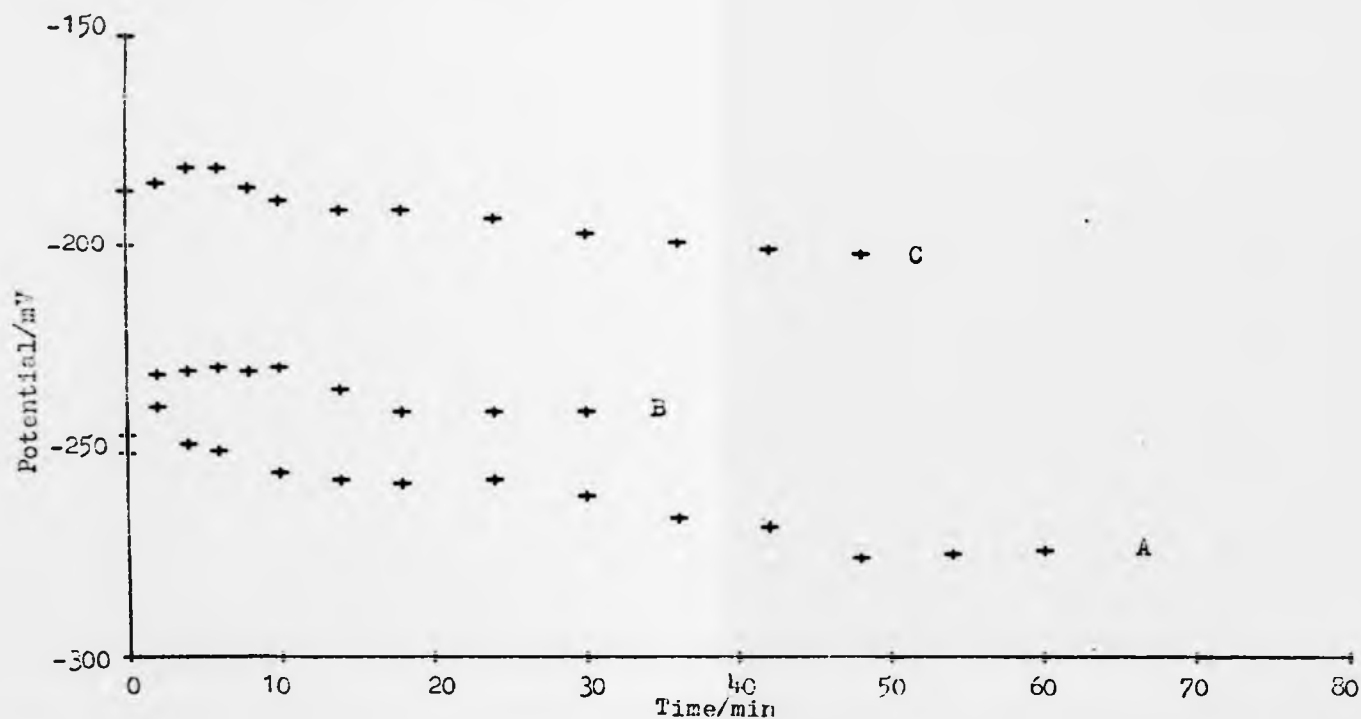


Fig 114. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ -- $\text{EtOH}(\text{H}_2\text{O})$ , in 99% (m/m) ethanol. Potential measured by using lead sulphide and silver-silver chloride (double-junction) electrodes. Molarity of lead perchlorate: A,  $10^{-5}$  M; B,  $1.4 \times 10^{-5}$  M. and C,  $10^{-4}$  M.

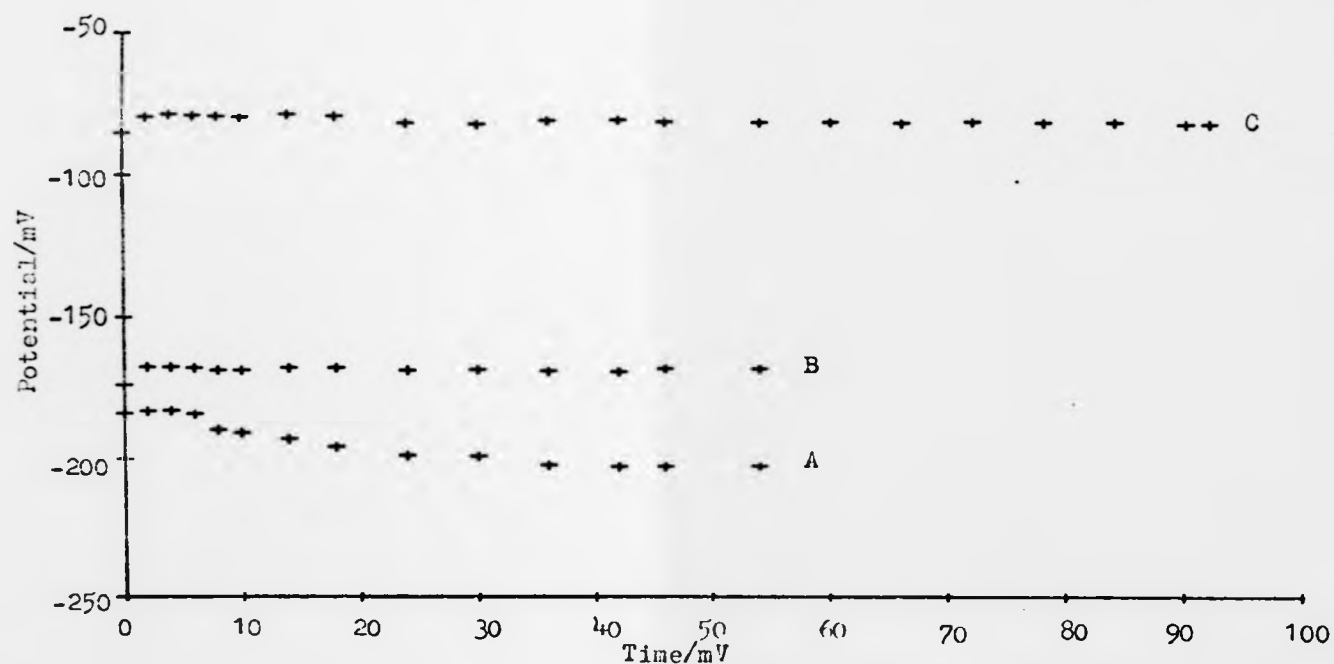


Fig 115. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH(MeOH), in 60% (m/m) n-propanol. Potential measured by using lead sulphide and silver-silver chloride (double-junction) electrodes. Molarity of lead perchlorate: A,  $10^{-5}$  M, B,  $2 \times 10^{-5}$  M; and C,  $10^{-4}$  M.

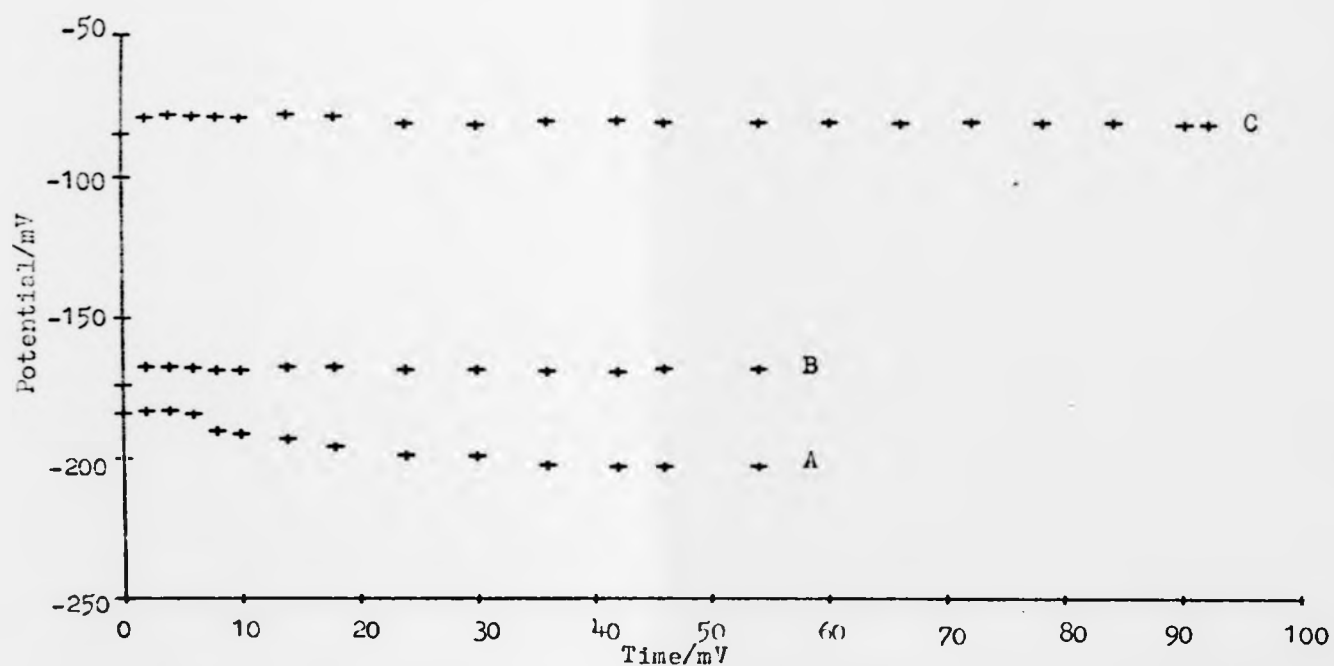


Fig 115. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH(MeOH), in 60% (m/m) n-propanol. Potential measured by using lead sulphide and silver-silver chloride (double-junction) electrodes. Molarity of lead perchlorate: A,  $10^{-5}$  M, B,  $2 \times 10^{-5}$  M; and C,  $10^{-4}$  M.



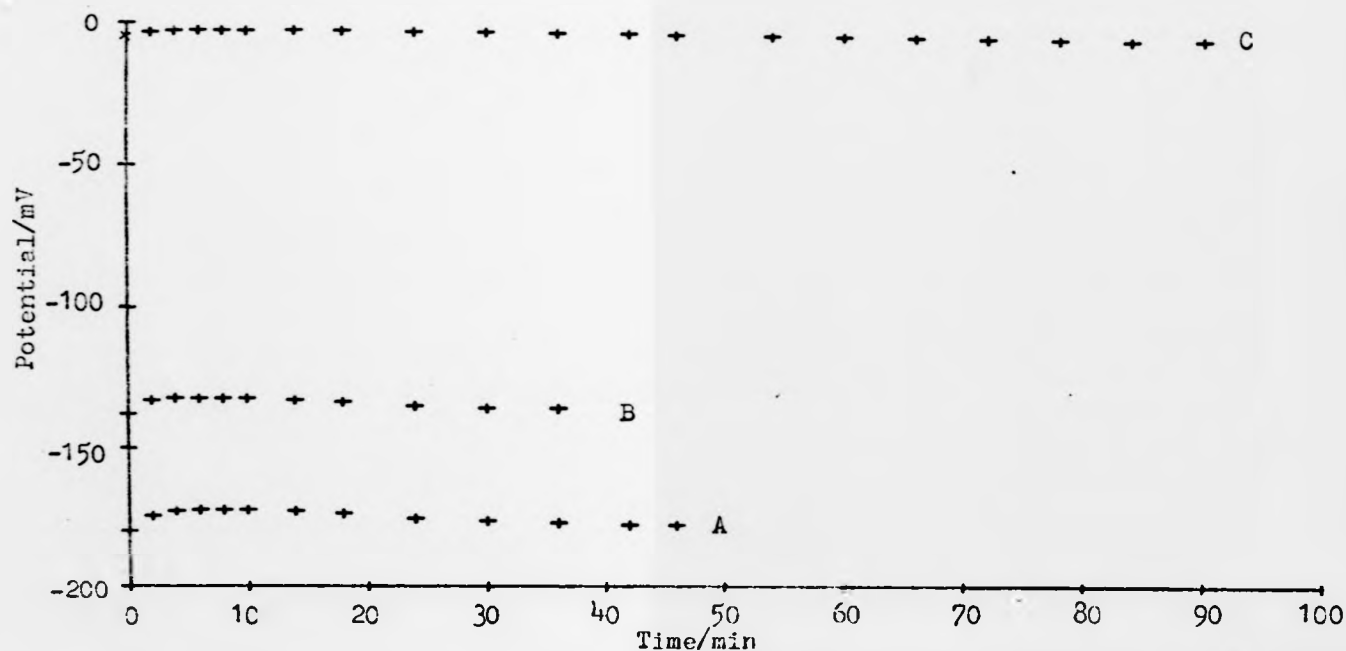


Fig 116. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH(MeOH), in 99% (m/m) n-propanol. Potential measured by using lead sulphide and silver-silver chloride (double-junction) electrodes. Molarity of lead perchlorate: A,  $10^{-5}$  M; B,  $2 \times 10^{-5}$  M; and C,  $10^{-4}$  M.

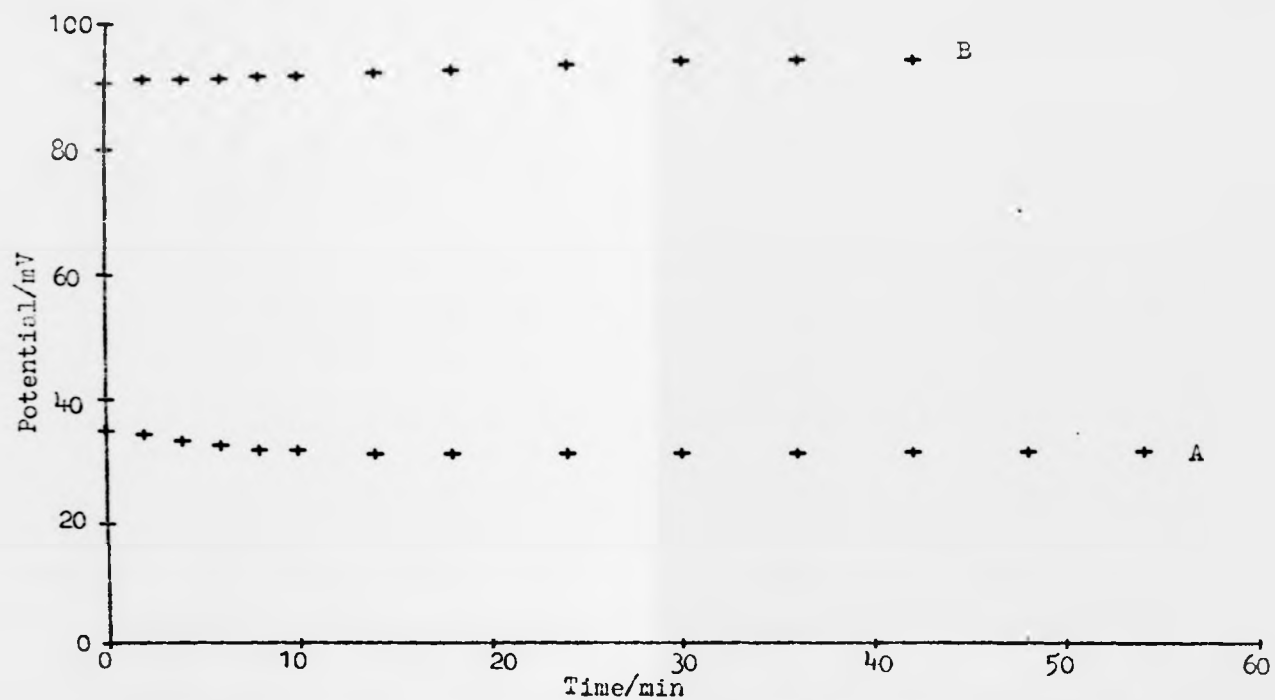


Fig 117. Graphs of time versus potential for the system,  $\text{AgNO}_3\text{-EtOH(H}_2\text{O)}$ , in 90% (m/m) ethanol. Potential measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes. Molarity of silver nitrate: A,  $10^{-4}$  M; and B,  $10^{-3}$  M.

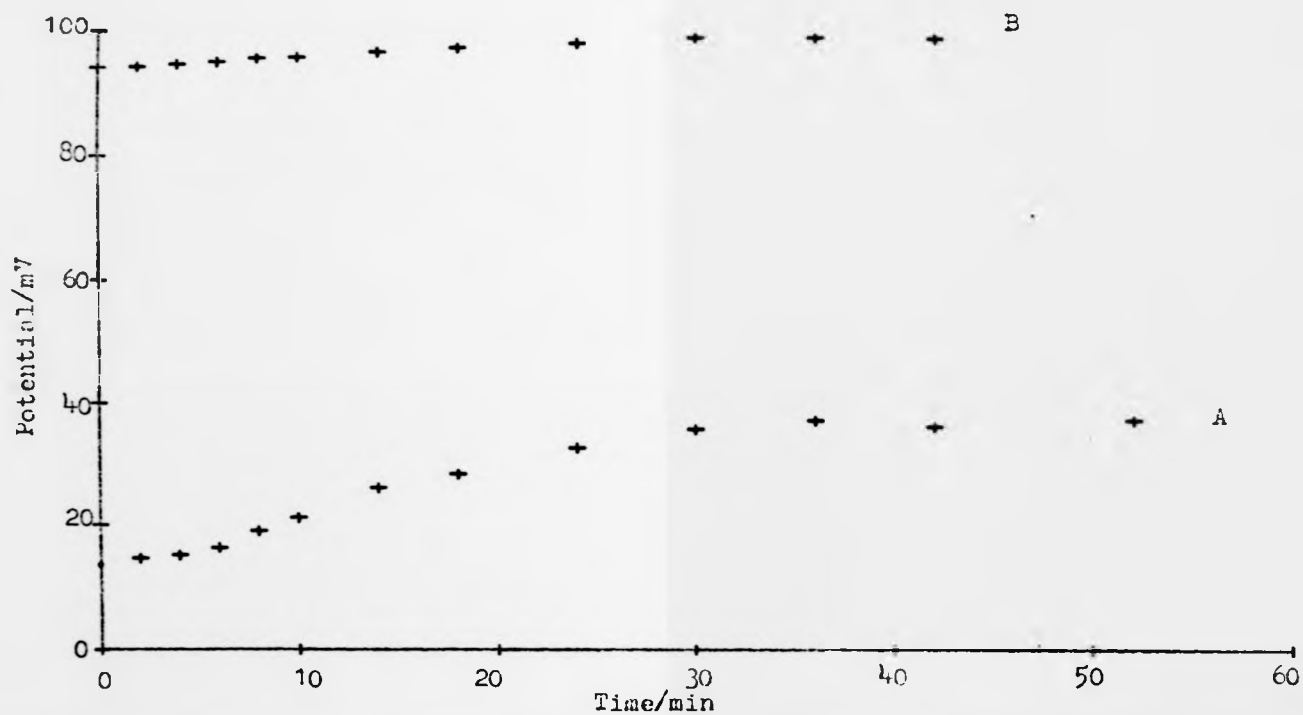


Fig 118. Graphs of time versus potential for the system,  $\text{AgNO}_3\text{--EtOH(H}_2\text{O)}$ , in 80% (m/m) ethanol. Potential measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes. Molarity of silver nitrate: A,  $10^{-4}$  M; and B,  $10^{-3}$  M.

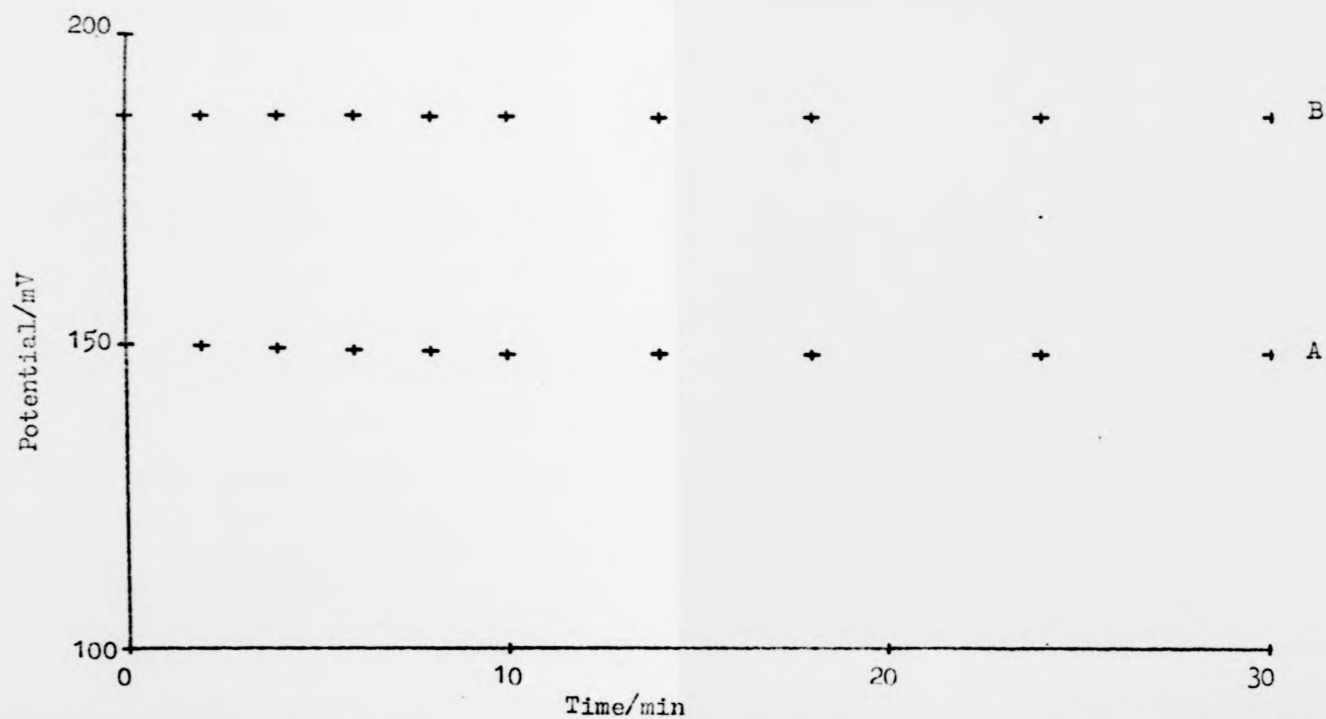


Fig 119. Graphs of time versus potential for the system,  $\text{AgNO}_3$ --acetone(MeOH), in 80% (m/m) acetone. Potential measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes. Molarity of silver nitrate: A,  $10^{-4}$  M; and B,  $10^{-3}$  M.

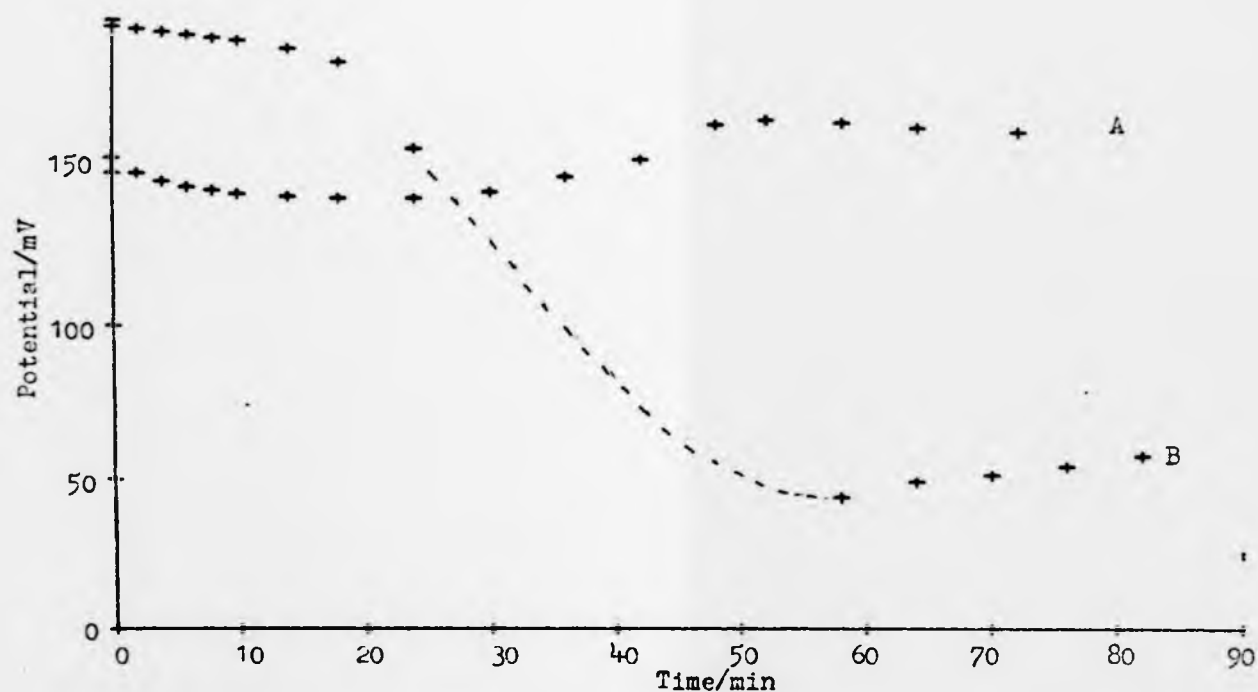


Fig 120. Graphs of time versus potential for the system,  $\text{AgNO}_3$ --acetone( $\text{MeOH}$ ), in 90% (m/m) acetone. Potential measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes. Molarity of silver nitrate:  $10^{-4}\text{ M}$ ; and B,  $10^{-3}\text{ M}$ .

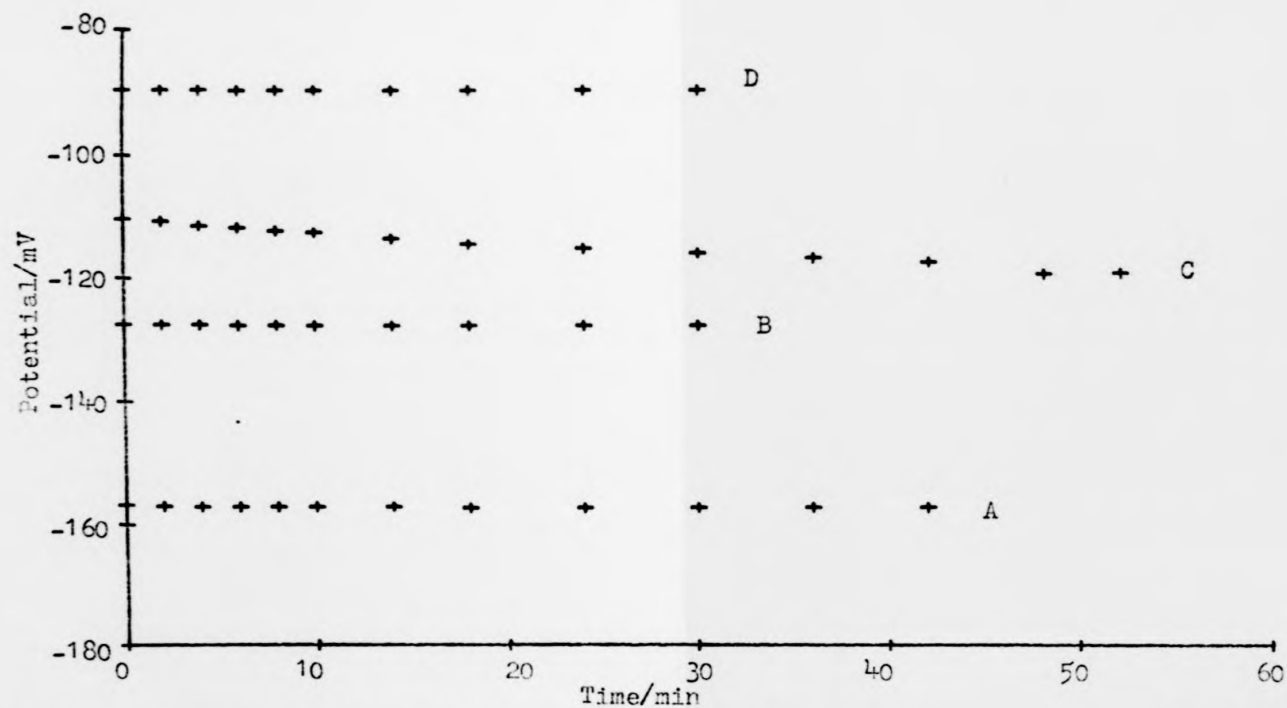


Fig 121. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ -- $n\text{-PrOH}(\text{H}_2\text{O})$ , in 80 and 90% (m/m)  $n$ -propanol. Potential measured by using lead sulphide and silver-silver chloride (d/j) electrodes. Molarity of lead perchlorate: A,  $10^{-4}$  M; B,  $10^{-3}$  M and C,  $10^{-4}$  M; D,  $10^{-3}$  M respectively.

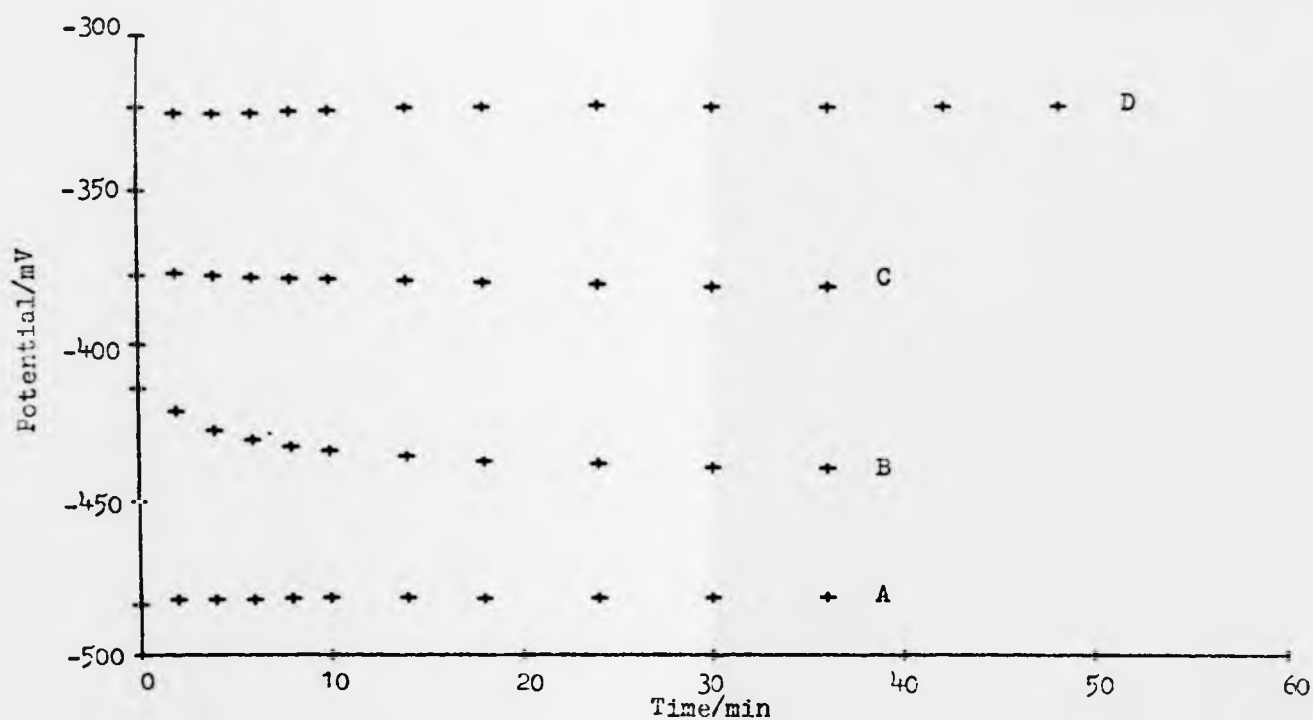


Fig 122. Graphs of time versus potential for the system,  $\text{Et}_4\text{NCl}$ --acetone( $\text{H}_2\text{O}$ ), in 90 and 99% (m/m) acetone. Potential measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes. Molarity of tetraethylammonium chloride: A,  $10^{-4}\text{ M}$ ; B,  $10^{-3}\text{ M}$ ; and C,  $10^{-4}\text{ M}$ ; D,  $10^{-3}\text{ M}$  respectively.

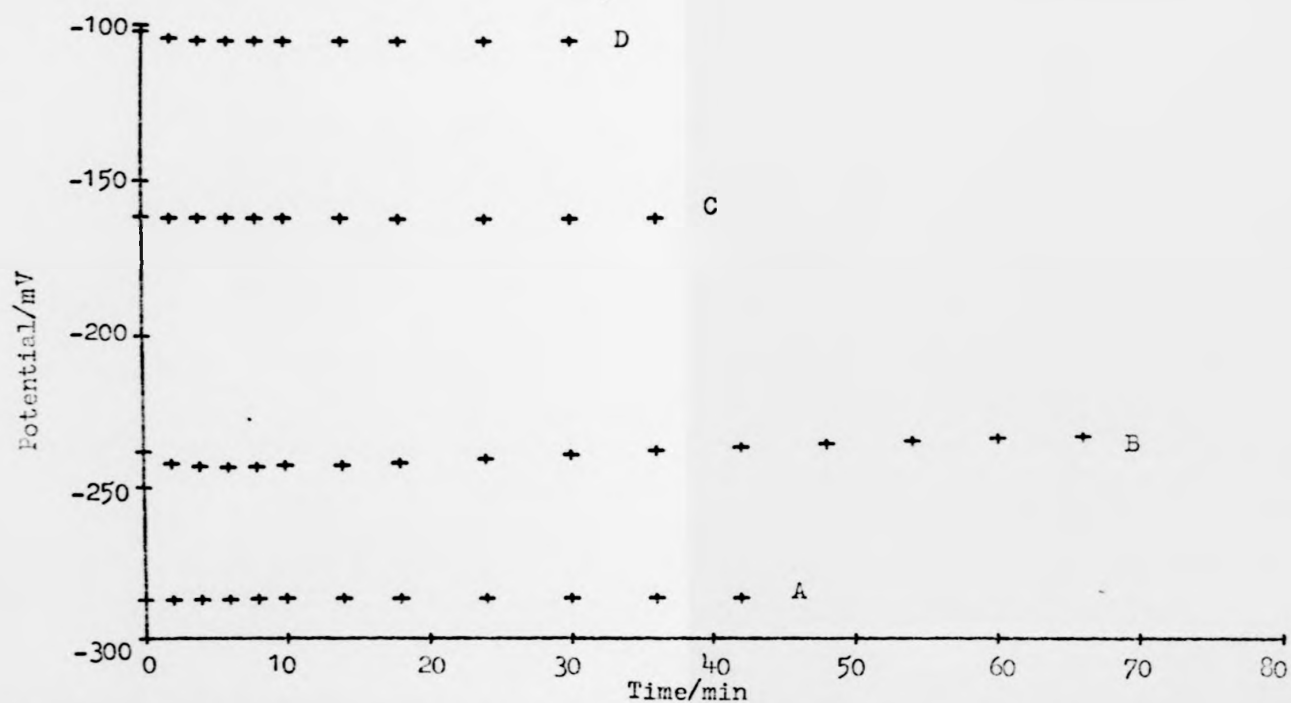


Fig 123. Graphs of time versus potential for the system, KF--1,4-dioxan( $H_2O$ ), in 60 and 90% (m/m) 1,4-dioxan. Potential measured by using lanthanum fluoride and silver-silver chloride (d/j) electrodes. Molarity of potassium fluoride: A,  $10^{-4}$  M; B,  $10^{-3}$  M and C,  $10^{-4}$  M; D,  $10^{-3}$  M respectively.



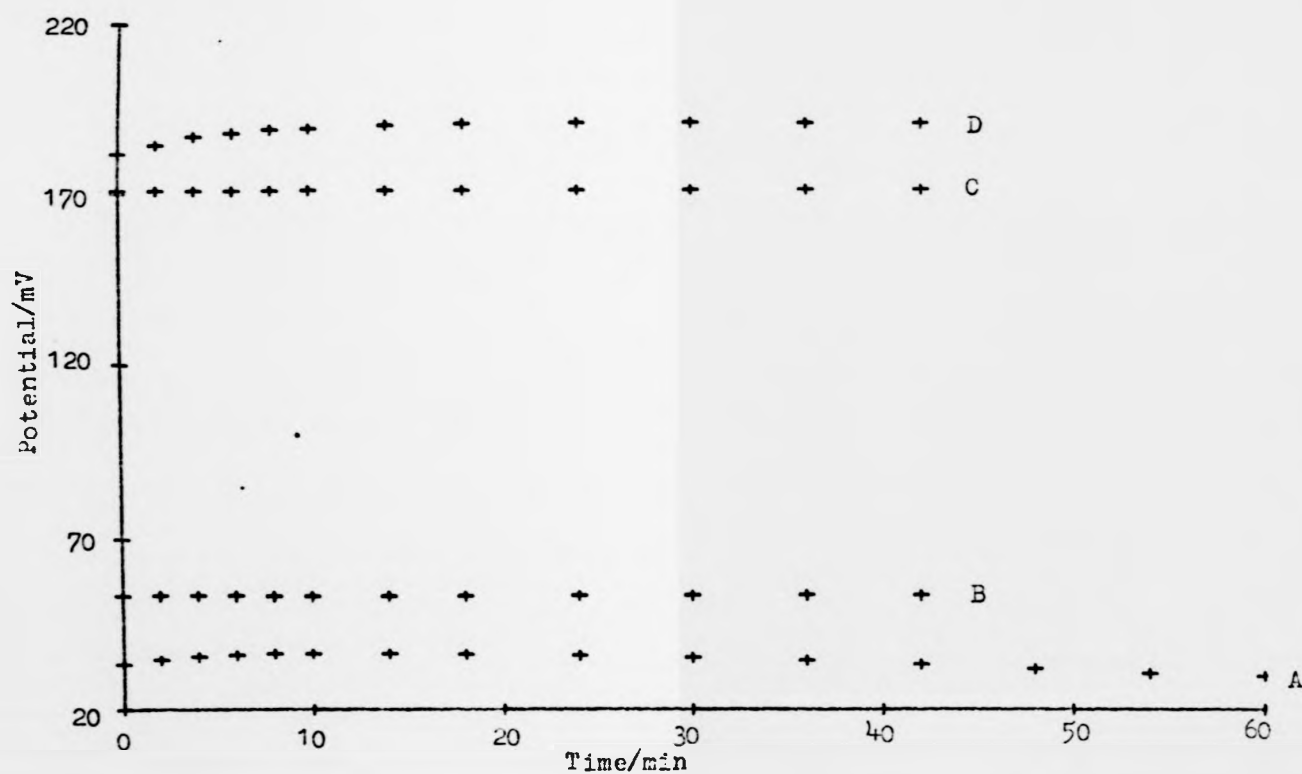


Fig 12<sup>4</sup>. Graphs of time versus potential for the system,  $\text{Pb}(\text{ClO}_4)_2$ -acetone( $\text{H}_2\text{O}$ ), in 90 and 99% (m/m) acetone. Potential measured by using lead sulphide and SCE(LiCl) electrodes. Molarity of lead perchlorate: A,  $10^{-4}$  M; B,  $10^{-3}$  M; and C,  $10^{-4}$  M; D,  $10^{-3}$  M respectively.

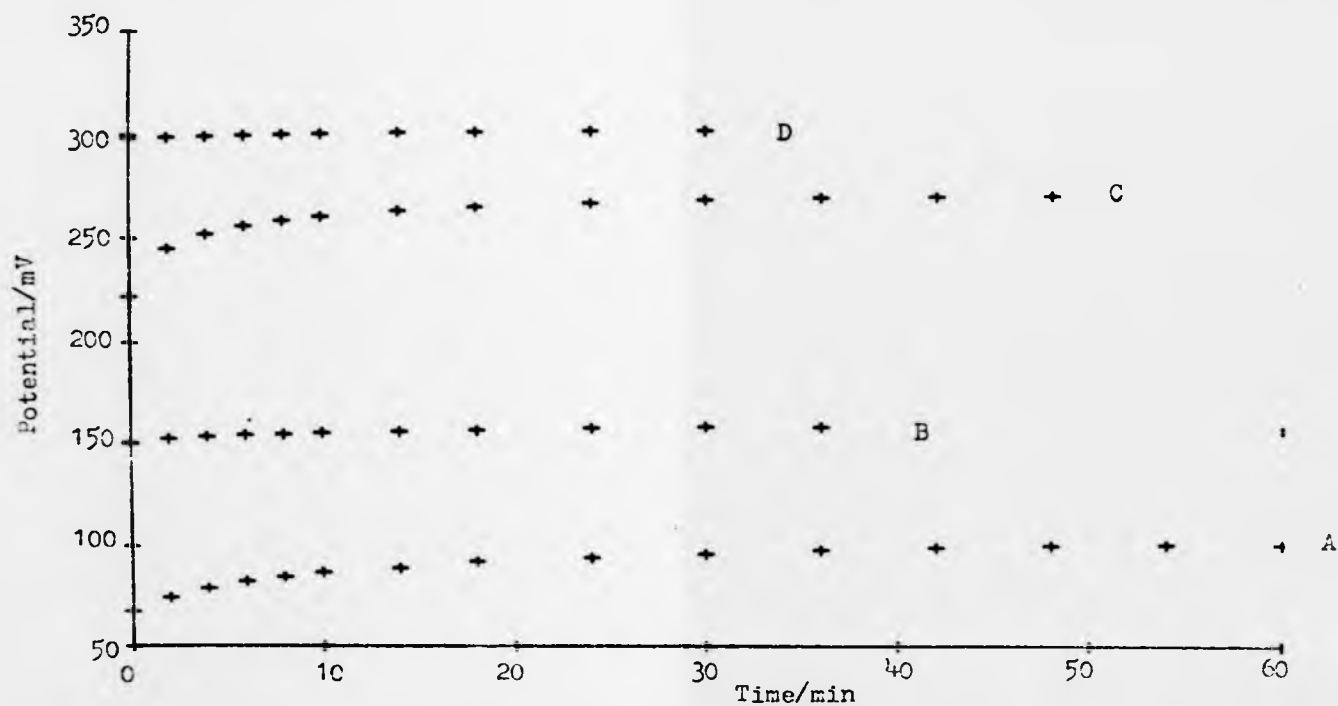


Fig 125. Graphs of time versus potential for the system,  $\text{NaNO}_3$ --acetone( $\text{H}_2\text{O}$ ) in 90 and 99% (m/m) acetone. Potential measured by using sodium-selective glass and SCE( $\text{LiCl}$ ) electrodes. Molarity of sodium nitrate: A,  $10^{-4}$  M; B,  $10^{-3}$  M and C,  $10^{-4}$  M; D,  $10^{-3}$  M respectively.

## DISCUSSION

### 3. DISCUSSION OF RESULTS

#### 3.1 EFFECT OF SOLVENT

The fact that solid-state membrane electrodes are compatible with nonaqueous solvents, permit their use in studies in aqueous-organic solvents media.

The variation of dielectric constant with different solvents and their mixtures is well known<sup>95</sup>. Since most organic solvents and their aqueous mixtures have lower dielectric constant than pure water, it is to be expected that the degree of association of ions of an electrolyte will be greater, and hence a decrease in activity of the ions in a medium of the former, as compared with the latter. This apart, ions are known to be solvated, the degree and the solvation number of which depend on the medium. Furthermore in mixed solvents, preferential solvation<sup>93,94</sup> of ions may occur, resulting in a net change of free energy (free energy of transfer), and hence a change in the associated potential.

Thus it is not surprising that solvents have a marked effect on the potentials of ion-selective electrodes.

For instance, in figs. (1-12 and 27-37), although the ions sensed by the electrodes were kept constant with respect to concentrations, changes in potentials,  $\Delta E$ s, were observed. While it is true that other factors, such as liquid junction

potential may contribute, the solvent effect (which can be attributed partly to the afore-mentioned factors and the development of an assymetry potential<sup>49</sup> across the electrode membrane arising from the different solvents on either side of it) is probably the overriding factor<sup>117</sup>.

### 3.2 INDICATOR IONS

#### 3.2.1 FLUORIDE ION

Previous investigations<sup>85,141</sup> in this department have been limited to around 0-90% m/m alcohol concentrations in a binary aqueous-alcohol solvent mixtures in the presence of a given constant concentration of fluoride ion. Thus the systematic change character of the associated cell potential,  $E$ , with variation in alcohol concentration was established.

The failure to attain higher alcohol concentrations was probably due to the limited solubility of sodium fluoride, particularly in the presence of a supporting electrolyte.

This present work is different from the previous work carried out in this department in that the investigations carried out are not confined to alcohol-water mixtures, but also include acetone-, 1,4-dioxan- and acetic acid-water mixtures. Also methanol-organic solvent mixtures were investigated, all of which were measured in the absence of a

supporting electrolyte. By substituting potassium fluoride for sodium fluoride, the systematic character of potential change,  $\Delta E$ , versus solvent concentration was extended to, 99% m/m organic solvent, and in the case of methanol, to 100% m/m.

The plots of  $\Delta E$ s versus solvent concentrations, indicating this systematic character are shown in figs. 1-7 and 8-13 (see tables 24 & 25). The deviations at higher solvent concentrations in figs. (3,9) and (7,13) can be explained as probably due to appreciable ionic association which will inevitably result, since the composition characters of the solvent mixtures approach those of the pure acetic acid and 1,4-dioxan (respectively), which have low dielectric constants.

A comparison of figs. (2a, 4a-6a) with figs. (2b, 4b-6b), obtained by using the same concentrations of potassium- and sodium fluoride, respectively, show that the use of the former instead of the latter is beneficial.

Since most direct potentiometry of fluoride in aqueous and in mixed aqueous-solvent, make use of sodium fluoride, no hesitation was made in using it in this investigation. The quest for an alternative fluoride salt stems from the fact and the observation that potassium fluoride is more soluble than sodium fluoride in methanol. Consequently the former was used

supporting electrolyte. By substituting potassium fluoride for sodium fluoride, the systematic character of potential change,  $\Delta E$ , versus solvent concentration was extended to, 99% m/m organic solvent, and in the case of methanol, to 100% m/m.

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for the methanol-organic solvent mixtures. However, the result obtained by its use in methanol-based system show that the deviation observed at higher solvent concentrations in the aqueous-based systems by using sodium fluoride, disappeared. Apparently this observation is not consistent with expectation, since the aqueous-based system would be expected to show less ionic association anomaly, than in methanol + the corresponding cosolvent. This is the exact opposite of what was observed. Consequently, it was considered necessary to repeat most of the measurements made in the aqueous-based system, using potassium fluoride instead. And thus the seeming inconsistency was accounted for.

Comparing  $\Delta E$ s for different alcohols (see table 24), it can be seen that there is a general tendency for increase in,  $\Delta E$ , magnitude-wise, in moving from methanol  $\rightarrow$  ethanol  $\rightarrow$  n-propanol  $\rightarrow$  iso-propanol. This is particularly obvious at higher alcohol concentrations. Since, this is the reverse order of the dielectric constant of the solvents, it is consistent with expectation, and also with the finding of Kakabadse et al<sup>85</sup>.

A comparison of the absolute potential,  $E$ , in the purely aqueous solution (0% m/m organic solvent in the aqueous-based system) shows consistent values within the experimental limitations involved, especially, when it is borne in mind that



the measurements were made at different times (up to a year, in some cases). The  $E_{\max} (-42.0) - E_{\min} (-37.1) = 4.9 \text{ mV}$  is well within the potential drift encountered in measurements associated with electrode potential. The contrasting value for acetone is as a result of different reference electrode used.

Except for acetic acid, all the solvents show a negative  $\Delta E$  character, and hence positive  $\Delta G$ , with increasing concentration of solvent. This is in agreement with the results obtained by previous workers<sup>85,141</sup>. The different  $\Delta E$  and hence  $\Delta G$  character shown by acetic acid is, perhaps, attributable to the positive shift of potential, which is well known<sup>20b</sup> to occur, as a result of protonation of fluoride ion in acid solutions.

Comparison of tables 24 and 25, shows that there is a similarity in  $\Delta E$  behaviour, when the water-based system is replaced by methanol-based system, but of smaller magnitude in the latter. If the  $10^{-4} \text{ M}$  potassium fluoride used in acetic acid-water system, is extrapolated to  $10^{-3} \text{ M}$ , then a comparable absolute potential,  $E$ , (for 0% m/m solvent) will be obtained in table 25, except for acetone where a different reference electrode is used. Again the different behaviour of acetic acid is seen in table 25 for the same reason, as

has been already discussed for table 24. The larger magnitudes of  $\Delta E$ s obtained in table 25 for methanol-acetic acid system, compared to those for the corresponding water analogues in table 24, is at variance with the magnitudes of  $\Delta E$ s in other systems. Since  $\Delta E$ s for water-based are generally larger than those for methanol-based systems. The anomaly is perhaps only apparent, rather than real, since acetic acid is expected to be a stronger acid in methanol than in water (methanol being more basic than water) and hence a readily easy protonation of fluoride ions.

This observation is consistent with the finding of Vesely and Stulik<sup>69</sup>, in their study of the effect of acidity on the response of the lanthanum fluoride electrode. According to these authors, potential response of this electrode is pH dependent, and shows potential hysteresis at both low and high pH, which increases its sensitivity at low fluoride activity. It is evident that the methanol/acetic acid medium has a relatively lower pH than the pure methanol medium and also the  $10^{-4}$  M KF used (in our case) is sufficiently low in activity to probably bring about the increase in sensitivity, and hence the relatively high values of  $\Delta E$ s observed in the medium of the former.

Figures 14-26 (see tables 26-38) show the calibration graphs for the lanthanum fluoride electrode, using potassium

fluoride (in some cases, sodium fluoride) for various water- and methanol-organic solvent systems.

Each figure shows a family of curves, which in nearly all indicate a negative shift in potential, which increases in magnitude as one moves from purely aqueous- or methanol solution to higher organic concentrations. Thus the curve for 50% m/m organic solvent lies wholly below and above those for 60% m/m and 40% m/m, respectively. Since all the curves are identical with respect to concentration range of indicator ion, it must be the solvent effect which operates.

Except for figures 15 and 16 (corresponding to Tables 27 & 28) which show near-Nernstian response slopes from 0-90% m/m ethanol and acetic acid in their mixed-water systems, virtually all others show sub-Nernstian slope response with a slight tendency to a decrease in value with higher solvent concentrations. Although it is not very clear why this is the case, intuitively the reference electrode used may probably be partly responsible. Since for the most of the measurements, silver-silver chloride (double-junction) electrode, having 0.1 M sodium nitrate in methanol as its outer filling solution was used. In this regard the non-equitransferent character of sodium nitrate is worth noting. Again electrode ageing, particularly when subjected to intense use in organic solvent may be another factor worthy of consideration. Also it is a

well known<sup>165,166</sup> fact that, supporting electrolyte (which is absent in our own case) improves response slope.

However, these arguments cannot be applied to the  $\text{AgNO}_3$ --solvent(base) system, which gave theoretical or slightly higher slope values (see section 3.2.3), inspite of using the same reference electrode. Furthermore, although supporting electrolyte are absent in figures 15 and 16, near-theoretical slopes were obtained.

From analytical view point, whether a calibration curve is Nernstian or sub-Nernstian is immaterial, linearity and reproducibility are by far a more crucial issue.

In tables 26-38, the lower limits of linear response range (LLRR) are indicated. For some of the investigated systems, this limit extends right to the lowest concentration measured. This quantity (LLRR) is similar to the lower limit of Nernstian response (LLNR) which is closely related to the lower limit of detection (LLD). Thus a lowering of LLRR would be expected with higher solvent concentrations, since solubility of lanthanum fluoride precipitate ( and presumably lanthanum fluoride single crystal) decreases<sup>49</sup>. This beneficial effect was not convincingly demonstrated, instead, in some cases (see tables 28,33 and 38) an opposite effect seemed to realized. However, the seeming contradiction is only apparent,

since the electrode responds to the thermodynamic activity and not the molar concentration of ions at its surface. The activity coefficient of fluoride ions in potassium fluoride (or sodium fluoride) is not constant, but decreases progressively from pure aqueous (or pure methanol) with increasing concentration of organic solvents in water or methanol + co-solvents.

The electrode 'standard' potential, expressed with respect to the silver-silver chloride (double-junction) and obtained by extrapolating the calibration curves to 1M potassium fluoride ( $\log_{10} a_{F^-}$  assumed zero), were found to show a decreasing trend with increasing organic solvent concentration except in methanol-acetic acid solvent mixture, where a reversed trend was shown.

The behaviour of Orion fluoride electrode in aqueous and aqueous-ethanol binary solvent mixture media was investigated by Lingane<sup>49</sup>. Using sodium fluoride, he obtained calibration data in purely aqueous and 60 Vol. % ethanol which showed a nearly parallel shift of about 100 mV to the more negative side for alcohol-water than for the purely aqueous fluoride solution. That his data did not reflect a lowering of the limit of detection of fluoride in 60 Vol. % ethanol as compared with the purely aqueous solution was attributed to the electrode responding to true thermodynamic activity and not the concentration of the fluoride ion.

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Although he used 60 Vol. % (instead of 60% m/m in our own case) our result is in good agreement with his result. Thus in figure 15 (see table 27) it can be seen that a parallel shift to a more negative side of 115 mV was obtained at 60% m/m ethanol as compared with purely aqueous fluoride solution.

The larger magnitude of  $\Delta E$  shift obtained in our case, could probably be due to different reference electrode used (SCE was used in his own case). Another possible contributing factor could be due to the supporting electrolyte of 0.1M sodium nitrate used in his own case (since activity coefficient decreases with increasing ionic strength and consequently a reduction in potential response, for a given concentration of a determinand). However, he failed to investigate what happens at higher water-alcohol mixtures. Judging by his experimental procedure, it is evident that a high background of 0.1M sodium nitrate as supporting electrolyte will further reduce the solubility of sodium fluoride (see figs. 2b and 15) and hence be restrictive on measurements at higher alcohol concentration.

The Russian workers<sup>142</sup> have investigated the behaviour of lanthanum fluoride electrode in various aqueous-organic solvent mixtures (see fig. 126 ).

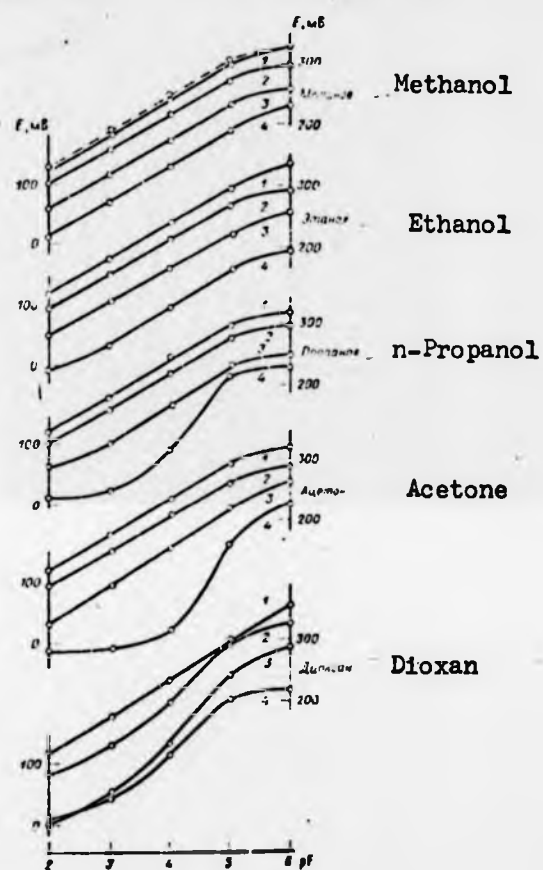


Рис. 1

Fig. 126 ( from ref. 142) Electrode calibration graphs for fluoride ion in various water-organic binary solvent mixtures.



Their assertion that the response time at  $10^{-4}$  -  $10^{-5}$  MF<sup>-</sup> is between 3-4 min and that it is independent of organic solvent is ambiguous! Could they be referring to organic solvent type or organic solvent concentration? In either case, this is contrary to our experience, since it was found that the response time vary to some degree with solvent type. Also, their claim that fluoride electrode potential response is invariant in the pH range 5-9 is somewhat strange! While the fluoride electrode is known to have its optimum pH range around the neutral pH<sup>18b</sup>, a pH of 9 is rather high and interference from hydroxide ions may be worthy of consideration.

Calibration graphs were made for methanol-, ethanol-, n-propanol-, acetone- and dioxan-water at 10, 30, 60 and 90% organic solvent. Whether volume or weight per cent was not stated. Presumably, their inability to go further than 90% organic solvent could be due to the limited solubility of sodium fluoride used. However, the failure to reference their measurements with purely aqueous solution of fluoride is a serious omission and could be misleading, as this is evident from some of our results (see table 34).

A comparison of our results (see figs. 14,15,17,19 and 20) with theirs (see fig. 126') shows that our results are better. For the methanol-, ethanol- and n-propanol-water mixtures, linear calibration curves were obtained from 0-99% m/m

alcohol concentrations. In fact linear calibration curve was obtained in pure methanol. The non-linear curves obtained for 95 and 99% m/m ethanol were re-investigated using potassium fluoride, which subsequently gave linear plots (see table 27). Furthermore the lower limit of their calibration curves occurred at around  $10^{-5} \text{ M F}^-$ , which in our own case was essentially  $2 \times 10^{-6} \text{ M F}^-$ .

In the case of water-acetone and dioxan-water mixtures, their calibration graphs were only linear up to 60 and 10%, respectively. Whereas, in our own case, linear calibration curves were obtained up to 90 and nearly 80% m/m respectively in the corresponding systems.

Their failure to achieve linearity in higher solvent concentration might be partly due to the reference electrode used (SCE with agar bridge in their case) and also the sodium fluoride used.

Comparison of measurements made by direct and indirect techniques are made at  $10^{-3} \text{ M}$  potassium fluoride (except where otherwise indicated)

For an ideal situation, readings obtained by the two methods should only show marginal variation (if at all, not indential). Although in several cases only marginal differences exist (  $\Delta\Delta E(\text{MeOH})$  in tables 39, 41 & 43 and  $\Delta\Delta E(\text{H}_2\text{O})$  )

in tables 40 & 41), for a large number of them, appreciable differences exist which are worth accounting for.

Apart from the water- and methanol-dioxan systems, which show very high  $\Delta\Delta E$ , both for water- and methanol-based systems (the reason probably being due to different reagent grades used), discrepancies between these two measurements are moderately small at low solvent concentration, but with a general tendency to increasing with increasing solvent concentration. The reasons for these discrepancies may be manifold:

(a) Apparently, the variation in the ambient air during the experimental condition (experiments were carried out at room temperature with temperature generally between 20-25°C) could have its contributing part. However, from table 21a ( $\Delta E$  for  $\Delta t = 5^\circ\text{C}$  is  $\sim 1$  mV); it is not very likely that this factor will contribute much. The small  $\Delta\Delta E(\text{MeOH})$  in table 39 can be virtually accounted for with this single parameter.

(b) There is a time lag interval between the measurement made by direct and indirect measurements. For instance, most of the indirect measurements were made more than six months after the direct measurements had been made. In this way, gradual drift which could be up to 0.6 mV/week<sup>164</sup>

could result in a cumulative drift of about  $\pm 15$  mV/ six months. Which in effect could lead to a discrepancy of 0-30 mV! If this is the case,  $\Delta\Delta E$ s in tables 39-42 can probably be accounted for in this way.

(c) Electrodes are exposed for a longer period in indirect measurements than they are in direct measurements and consequently potential equilibration is better favoured in the former than in the latter. As a result, a few millivolt difference may be shown in spite of the same concentration of indicator ion and solvent concentration in both cases. This factor may partially account for  $\Delta\Delta E(\text{MeOH})$ ,  $\Delta\Delta E(\text{H}_2\text{O})$  and  $\Delta\Delta E$ s in tables 39, 40 and 41 respectively.

(d) Dilution effect on solvent (not the dilution effect on concentration, since this will only result in a parallel and constant shift) especially at higher solvent concentration, where potential response change is very sensitive to solvent concentration change. This is inevitable because of the incremental addition of stock solutions which were prepared either in water or methanol for the water-based and methanol-based systems, respectively. For example an initial 99% m/m acetone in acetone-water mixture would have been reduced to about 96% m/m after 2.8 ml

aqueous stock solutions have been added. An estimate of  $\Delta E$  associated with dilution effect in figure 6a gives about 60 mV. But this dilution is not encountered in direct measurement. Similar dilution at 10% acetone, barely have any effect at all, and hence the increase in discrepancy with higher solvent concentration. This effect is perhaps significant for iso-propanol (table 42) and well pronounced for acetone ( $\Delta\Delta E(H_2O)$ ) and perhaps for dioxan (tables 43 and 44). However, as has been pointed out earlier, the large discrepancy in the case of dioxan, is perhaps, largely attributable to the difference in reagent grade used.

(e) Difference in reference electrode, and electrolyte type used have their contributing part. This is particularly, pertinent to  $\Delta\Delta E(H_2O)$  in table 39, when compared to its  $\Delta\Delta E(MeCH)$  counterpart.

### 3.2.2 CHLORIDE ION

Figures 27-31 and 32-37 (see tables 45 and 46) show the graphs of % m/m organic solvent in water- and methanol-organic solvent mixtures, respectively, for a given constant concentration of indicator ion. Again, as in the case of fluoride ion (see section 3.2.1), the striking feature is the systematic

potential response with increase in solvent concentration.

The similarity (but opposite trend, since

$\Delta G_t^{\circ}(X) = F\Delta E_t^{\circ}(X)$ , the apparent -ve sign missing in this equation is inherent in the definition of  $\Delta E_{(t)}(X)$ <sup>115</sup> shown by the observed results to that obtained by Wells<sup>115,124</sup> for the free energy of transfer  $\Delta G_t^{\circ}(Cl^-)$  from water into mixtures of water + co-solvent (from 0-60 wt% methanol, ethanol, acetone, isopropanol and dioxan), suggests that factors associated with free energy change (e.g. solvation) may have important contribution to the observed  $\Delta E$  in the aqueous-based systems, and hence, also in the methanol-based systems.

By using the equation:

$$\Delta G_t^{\circ} = 96.4 \{ E_m^{\circ}(\text{water}) - E_m^{\circ}(\text{solvent}) \} \text{ KJmole}^{-1} \dots\dots 3.1$$

(in ref. 115), we calculated  $\Delta G_t^{\circ}(Et_4NCl)$  from water to isopropanol-water mixtures using our  $E^{\circ}$  values at 0, 10, 20 and 40% m/m ( $E^{\circ}$ , being estimated at 10% from tables 45 and 50). These values are: 0.49, 1.52 and 3.15 for 10, 20 and 40% m/m isopropanol, respectively. Whereas the corresponding values obtained by Wells were 3.03, 7.5 and 11.0. Clearly the same trends are shown, but our values are consistently lower for the corresponding solvent concentrations. The discrepancy in magnitudes can be probably accounted for, if we take into consideration the fact that,

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$$\Delta G_t^0(\text{MX}) = \Delta G_t^0(\text{M}^+) + \Delta G_t^0(\text{X}^-) \dots\dots\dots 3.2 \text{ (in ref 170)}$$

Thus it can be seen that, while the  $\Delta G_t^0$ , calculated by Wells refer to chloride ion, it is  $\Delta G_t^0(\text{Et}_4\text{NCl})$  that was calculated in our own case. Another probable reason is that,  $\Delta G_t^0(\text{Cl}^-)$  were calculated from a cell without liquid junction, which is not the case in our s.

The data in tables 14 and 15 give a trend in the  $\Delta G_t^0(\text{Et}_4\text{NCl})$  from methanol to methanol + co-solvent, and are in good agreement with the relative magnitudes of  $\Delta E$ s in the corresponding mixed systems in our results.

The electrode calibration graphs for chloride ion are shown in figures 38-43 and 44-48 (see tables 47-57) for the water-based and methanol-based systems respectively. In figure 38, a systematic trend is shown for the  $\text{NaCl--EtOH(H}_2\text{O)}$  system from 0-95% m/m ethanol. The observed anomaly in the calibration curve at 99% m/m, probably arises as a result of appreciable ion-pair formation of the electrolyte ions. Measurements in other alcohol-water systems using tetraethylammonium chloride instead of sodium chloride suggest that the reason given above might be the case. The seeming contradiction between this explanation and the observation in figure 27, can be easily resolved, if it realized that  $10^{-3}$  M sodium chloride was used as the indicator ion in this figure, whereas measurements



were made between  $10^{-6}$  M and  $10^{-2}$  M sodium chloride in figure 38. Thus while ionic association may not be pronounced at  $10^{-3}$  M NaCl in 99% m/m, this may not be the case at  $10^{-2}$  M NaCl.

Also in figure 38, it can be seen that the calibration curves tend to converge at low- and diverge at high chloride concentrations. In other words the solvent effect is more pronounced at higher chloride concentration. From the practical point of view, the divergent end would be worthy of further consideration since it may be analytically beneficial for the determination of the solvents in their binary mixtures.

To some degree, the family of calibration curves shows similarity from one system to another. However, some diverge at the bottom end, a few show large anomaly at high solvent concentrations and others stay fairly parallel throughout.

In tables 47-57, three types of electrode slope behaviour are shown, namely: Nernstian; near-Nernstian and non-Nernstian. The first type is characterised by the acetone-water system (table 51) and to some extent (0-40% m/m) ethanol-water system (see table 47). The mixed acetic acid systems fall into the second type (see table 48 and 54). The third type (non-Nernstian) can be further subdivided into three types: (a) There are those that show marginal decrease with increase in solvent concentration, e.g. n-propanol-water and the mixed

isopropanol systems (tables 49,50 and 56). (b) There are also those that show considerable changes with increase in solvent concentration, e.g. ethanol-water system increases considerably between 50 and 99% m/m ethanol in table 47) whereas acetic acid show considerable decrease from 80-99% m/m, see table 48. (c) Finally, dioxan-water and n-propanol- and isopropanol-methanol show fairly steady electrode slope throughout (see table 52,53 and 55).

In general the slope values range from 45-60 mV/decade concentration for most of the systems. Our results show good agreement with that of the Russian workers<sup>161</sup>, with their s having slope values of 35-50 and 40-59 mV/decade in pure alcohol and aqueous-alcohol mixtures (respectively), despite the different cell systems used (see section 1.4.2.5. for the table showing the slope values).

Although, a general trend of LLLRR with increasing solvent concentration is lacking, there are certainly some lowering of LLLRR with solvent concentrations in some systems. For instance, while the LLLRR remain virtually the same in tables 50,51,53,54 and 55, tables 48,49 and 52 show a definite beneficial trend of LLLRR with increasing solvent concentrations, particularly in the case of dioxan-water system, where the LLLRR is lowered by the order of a decade concentration at 60 and 80% m/m dioxan in dioxan-water mixture, as compared to the

purely aqueous system. This lowering of LLLRR with solvent concentration is in agreement with the finding of Kakabadse et al.<sup>84,111</sup>. Using silver bromide (in the presence of 0.1M potassium nitrate) and silver chloride electrodes, these authors showed that there is a decrease of the order of a decade and half-a-decade (respectively) in LLLRR in the electrode calibration graphs of 80% V/V methanol (in water-methanol), as compared to purely aqueous solutions.

Tables 58-62 show a comparison of changes in potential measurements by 'direct' and 'indirect' methods. Table 59 shows more or less constant shifts of the order of 10 and 7 mV. for  $\Delta\Delta E(H_2O)$  and  $\Delta\Delta E(MeOH)$  respectively. This could probably be a reflection of the different degrees of equilibration attained in the indirect and the direct systems, and also the dilution effect of stock solutions in the former. The  $\Delta\Delta E$  values are only marginal in table 60, and thus showing reasonable agreement between the two sets of measurements involved.

Tables 47-57 show a decreasing trend in 'standard' electrode potential with increasing solvent concentrations.

### 3.2.3 SILVER ION

Figures 49-54 and 55-57 (see tables 63 and 64) show that the change in potential response as a function of % m/m solvent

concentration for water and methanol-organic solvent mixtures, respectively. Nearly all the graphs, except in mixed-acetone solvents (which are only systematic to 80% m/m), show systematic potential increase with concentration (0-99% m/m) of organic solvent.

In the case of methanol-organic solvent mixtures, except for the acetic acid-methanol system, linear calibration curves were obtained, though, with rather small magnitudes of  $\Delta E$ s.

The graphs obtained in the water-alcohol mixtures are similar to those obtained by Kakabadse et al<sup>85</sup>. However, whereas, 70 (0-80% m/m), 30 (0-80% m/m), 60 (0-100% m/m) and 12 (0-80% m/m) mV were obtained for the water-alcohol mixtures (alcohol = n-propanol, ethanol, methanol and iso-propanol, respectively). The obtained  $\Delta E$  values for the corresponding solvent type and concentrations are 70, 100, 180 and 50 mV, respectively. These values are much larger than their's. The reason might probably be due to the supporting electrolyte of 0.1M sodium nitrate in their case, which was absent in this determination. Another factor which might contribute is the difference in reference electrodes used, which are essentially mercury-mercurous sulphate, and less frequently silver-silver chloride double-junction in the present determination, but only the latter was used in their own case. Most importantly, the indicator electrodes were different:  $Ag_2S$  in ref. 85.

concentration for water and methanol-organic solvent mixtures, respectively. Nearly all the graphs, except in mixed-acetone solvents (which are only systematic to 80% m/m), show systematic potential increase with concentration (0-99% m/m) of organic solvent.

In the case of methanol-organic solvent mixtures, except for the acetic acid-methanol system, linear calibration curves were obtained, though, with rather small magnitudes of  $\Delta E$ s.

The graphs obtained in the water-alcohol mixtures are similar to those obtained by Kakabadse et al.<sup>85</sup>. However, whereas, 70 (0-80% m/m), 30 (0-80% m/m), 60 (0-100% m/m) and 12 (0-80% m/m) mV were obtained for the water-alcohol mixtures (alcohol = n-propanol, ethanol, methanol and iso-propanol, respectively). The obtained  $\Delta E$  values for the corresponding solvent type and concentrations are 70, 100, 180 and 50 mV, respectively. These values are much larger than their's. The reason might probably be due to the supporting electrolyte of 0.1M sodium nitrate in their case, which was absent in this determination. Another factor which might contribute is the difference in reference electrodes used, which are essentially mercury-mercurous sulphate, and less frequently silver-silver chloride double-junction in the present determination, but only the latter was used in their own case. Most importantly, the indicator electrodes were different:  $Ag_2S$  in ref. 85.

Figures 59-62 are the electrode calibration graphs of the direct potentiometry of silver in water-organic solvent mixture, while figures 63 & 64 refer to methanol-based systems, which show potential inversion at around  $p_{Ag}$  of 5. This is discussed in a latter section (3.3.3). Figure 59 shows similarity in character for the different calibration curves from 0-50% m/m ethanol. Above this concentration, there is a loss of linearity and hence the system becomes less useful electrochemically, as well as analytically. Similarly in figure 61, linearity is only shown for calibration curves up to 80 wt% acetone.

The calibration curves in acetone-methanol system indicate that the direct potentiometry of silver ion is possible in the system. In figure 64, there is a clear departure from linearity above 60% m/m acetone in acetone-methanol system. Non-reproducible curves were obtained for higher solvent concentration which were characterised by erratic potential rupture.

Tables 65-73 show the electrode slopes obtained for the calibration curves. Except tables 65 and 68, which show slightly low slope response, electrode slopes are generally slightly on the high side with values ranging from 62-69 mV/decade.

Previous determinations in this department<sup>84,85</sup> show slope values of (58-61.3) mV for methanol-water and

58-59.5 mV/decade for water alcohol (alcohol = methanol, ethanol, n-propanol, isopropanol) for 0-80% m/m alcohol concentrations. Clearly the electrode slopes obtained by them are better. However, it is evident from literature<sup>165,166</sup> that supporting electrolyte improves electrode slope. In this connection, it is not strange that they obtained better results, since 0.1M sodium nitrate was used as supporting electrolyte in their measurements.

Tables 74-77 give a comparison of potential measurements by 'direct' and 'indirect' techniques. The trends of  $\Delta\Delta E(\text{H}_2\text{O})$  and  $\Delta\Delta E(\text{MeOH})$  are similar to some extent to those already discussed.  $\Delta\Delta E$ s are generally smaller in magnitude than for fluoride and chloride systems, most especially  $\Delta\Delta E(\text{H}_2\text{O})$  for the acetone system (table 77). This is not too surprising, since  $\Delta E$ s for this system are generally smaller than those for the fluoride and chloride systems. The relatively high and anomalous values of  $\Delta\Delta E(\text{MeOH})$  in table 77 at 80 and 90% m/m are probably ascribable to the potential rupture observed for the associated system.

3.2.4. LEAD ION

Figures 65-69 and 70,72-74 (see tables 78 and 79) show systematic changes in potential,  $\Delta E$ , as a function of m/m per cent organic solvents in water- and methanol-organic solvent mixtures respectively.

Unlike in the case of fluoride and chloride ions which show systematic decrease in potentials with concentration, an opposite effect is obtained for lead ion as for silver ion. As has been pointed out in section 3.1, amongst several factors which could be responsible for this effect is the difference in free energy of transfer of ions between the purely aqueous (or methanol) solution and the different solvent-water (methanol) composition mixtures. The results show a +ve  $\Delta E$  and hence a -ve  $\Delta G^0_{(t)}$  with increasing solvent concentrations.

The change in potential is remarkably high in mixed-acetone systems ( $\Delta E = 427$  mV!) for the aqueous-based system. Perhaps this can be partly accounted for, considering the fact that the high +ve charge density of lead ion and the large nucleophilic character of acetone combine favourably for the preferential solvation by the latter of the aquo-complex ions.

Electrode calibration graphs of lead (II) in a series of water-organic solvents are shown in figures 76-81 (see tables 80-85). Similar measurements are shown in figures



82-85 for methanol-organic solvent mixtures (see tables 86-89).

The electrode response to lead in 20, 40, 60 and 80% m/m methanol is very similar to that in purely aqueous solution (see figure 76). Near-linear calibration curves are obtained for 90 and 99% m/m methanol.

The result obtained for the direct potentiometry of lead in methanol-water (fig. 76) show some agreement with that obtained by Rechnitz et al.<sup>140</sup>, using Orion double-junction electrode as reference. It is, however, at variance with their obtained result for the differential meter, when a glass electrode was used as a reference electrode. It is surprising that they expected the calibration curves to converge for different concentrations of methanol in the mixed solvents! Their failure to realise the solvent effect on the glass electrode, as well as, on the lead electrode might probably account for the reverse order of the calibration curve obtained by them (see fig. 127).

Table 126

Direct Potentiometry of Lead (II) in Water-Methanol systems, using Lead Sulphide and Sodium-Selective glass (as reference) electrodes in the presence of  $10^{-3}M$  sodium nitrate

% m/m Methanol	$\Delta E/mV$	Observed E at $10^{-3} M Pb^{2+}$	'Corrected' E for $10^{-3} M Pb^{2+}$
	$10^{-3} M Na^+$		
0	0	-194.7	-194.7 (+ $\epsilon$ )*
20	18.7	-181.2	-199.9
40	41.5	-169.0	-210.5
60	61.9	-154.6	-216.5
80	89.0	-131.2	-220.2

\*  $\epsilon$  is a constant shift ( $E_{PbS//sod. glass} - E_{PbS//D/j}$ )

In the table shown above, the 'corrected' column is obtained by combining the cells,  $PbS//D/j$  and sodium-sel. glass//D/j to obtain  $PbS//sod.-sel. glass$ . From this table, it can be seen that, E in the 'observed' column increases from 0-80% m/m methanol, whereas the reverse is the case in the corrected column, viz, E decreases with increasing concentration of methanol.

Figures 77, 78, 82 and 83 show potential inversion for the electrode calibration graphs of lead in various systems. This is discussed in a latter section (3.3.3).

The overall impression gained from these calibration curves is that the aqueous-based systems show similarity in behaviour up to moderately high organic solvent concentrations, but distinctly different from the aqueous character at very high solvent concentrations. The methanol-based systems, though show families of curves, are generally non-linear and exhibit a more complex nature.

The electrode slopes of the different systems are shown in tables 80-89. Electrode slopes are fairly high, in contrast to the rather low values obtained for the fluoride and the chloride electrodes.

The 'standard' electrode potentials show increasing trend with increasing solvent concentrations.

A comparison of changes in potential obtained by 'direct' and 'indirect' measurements show a similar trend to the fluoride system and thus the arguments applied to fluoride hold as well. The only exception is the dioxan system, where  $\Delta\Delta E$ s are relatively much lower than for the fluoride systems. The reason is probably due to the fact that analar grade 1,4-dioxan were used for both the direct

and indirect system, in contrast to the laboratory and analytical grades used for the fluoride.

### 3.2.5 SODIUM ION

Figures 86-90 (see table 94) show the systematic character of the plot of % m/m organic solvent, in a binary water-organic solvent mixtures as a function of changes in potential,  $\Delta E$ , for a given concentration of sodium ion. Similar behavioural patterns are shown for the methanol-based systems in figures 91-94 (see table 95).

The electrode calibration graphs for sodium ion are shown in figures 94-101 for water- and methanol-organic solvent mixtures. All the systems show remarkable similarity to one another, giving almost in all cases, distinct patterns of family of curves.

Electrode slopes are shown in tables 96-103. Except in the mixed acetone system where electrode slope show a rather slightly high value (super-Nernstian) at low solvent concentrations (see tables 100 and 103), electrode slopes are generally slightly lower than theoretical value, with a tendency to decreasing with increasing solvent concentrations.

Again, except in mixed water-acetone where there is a clear lowering of the LLLRR with increasing acetone concentrations, such a trend is not clearly shown for other systems. Rather the reverse is true: a slight increase in LLLRR with increasing solvent concentration.

The standard potentials were found to increase gradually with increasing solvent concentrations.

Tables 104-106 show a comparison of 'direct' and 'indirect' measurements. In contrast to the  $\Delta\Delta E$  values for fluoride and chloride ions, there seem to be more or less a constant shift, with some anomalies at higher solvent concentrations. The shift can probably be explained if it is borne in mind that the indirect measurements were made in the presence of  $10^{-3}$  M ammonia, which was not the case for the direct measurements. The trend for  $\Delta\Delta E(\text{MeOH})$  in table 106 is different from the rest. This is rather strange! It may probably be that, these measurements were made under different conditions (e.g., not basifying with ammonium hydroxide in the indirect measurements).

Potential drift is a known problem with virtually all the commercially available sodium electrode<sup>156</sup>. The experience gained in this work about this problem is not at variance with that of other authors who have reported on the problem.

Michael et al<sup>156</sup> reported the use of 2M Rubidium chloride as the outer filling solution of Orion double-junction electrode, which according to them, was found to be beneficial. We tried 50% V/V 0.1M Rubidium chloride in methanol as the outer filling solution, but the result obtained by its use was not better than when 0.1M potassium nitrate in methanol was used instead. Thus for most of the measurements made with the sodium electrode for sodium measurements, there was a waiting time of about 10 min. Even then, potential drift was not overcome within this waiting time. However, the results obtained do not reflect any serious error arising from this effect, since measurements are all affected (to a first approximation) to the same extent, provided this time is constant from one measurement to another.

The claim<sup>117</sup> that the potential response of glass electrodes which are not exclusively hydrated (e.g. Beckman No 39127) is largely independent of solvent composition for a variety of water and nonaqueous solvent is not supported by the experimental evidence in this work using a Beckman sodium-responsive glass electrode.

A comparison of the variation of  $\Delta E$ s, e.g. for silver and sodium ions in the water-solvent systems in tables 130<sup>134</sup> and 135<sup>135</sup> using the same reference electrode shows that the

corresponding  $\Delta E$ s for sodium ion are consistently larger than for silver ion. Evidently, one would expect the liquid junction potentials to be comparable for the two ions in a given mixed-solvent system (since the same reference electrodes are used). In which case, if it is assumed that the  $\Delta E$ s for the silver ions are entirely due to the liquid junction potential of the reference electrode (though not likely), the excess  $\Delta E$  of  $(233.6-110.7) 122.9$  mV (see table 135) obtained for sodium over silver ions cannot be accounted for in this way. It follows that the liquid junction potential can not be solely responsible for the  $\Delta E$  obtained for sodium ion. This is further supported by the evidence obtained in the methanol-based systems (see tables 139 and 140).

$\Delta E_{\text{max}}$ s in n-propanol- and isopropanol- methanol systems are 12.4 and -10.4 mV respectively, for silver ion, whereas the corresponding  $\Delta E$ s for sodium ions are 106.6 and 142.2 mV, using the same reference electrode. It can be seen therefore that the solvent effect does exist for the sodium-selective glass electrode used in our experiments.

#### HYDROGEN ION

Figures 102-105 and 106-108 (see tables 107 and 108) show the plot of the change in potential response as a function

of % m/m organic solvent mixtures.

It can be seen from figs. 102-105 that there is a relatively small potential response change from 0-80% m/m solvent concentration followed by a considerable potential response at higher solvent concentration.

This change is by far less pronounced in the methanol-organic solvent systems (figs. 106 & 107) except for the mixed acetone solvent (fig. 108) which is similar in character to its water analogue. Again the unusual behaviour is glaring, and the explanation might be similar to that given in section 3.2.4.

The results obtained in aqueous-organic systems show good agreement with those obtained previously in this department<sup>85</sup>.

Electrode calibration graphs for hydrogen ion in methanol-organic systems showed considerable complexity, and are therefore not given. However, potential response at  $10^{-3}M$ ,  $10^{-4}M$  and  $10^{-5}M$  perchloric acid are shown in tables 109-111 for methanol-organic systems.

Tables 112-114 show a comparison of potential measurements by 'direct' and 'indirect', technique. The trends of  $\Delta\Delta E$ s are similar to those already discussed.



### 3.3. GENERAL

#### 3.3.1 REFERENCE ELECTRODE

As has been discussed already in section 1.2, the choice of a suitable reference electrode for potential measurements in a given system can be of crucial importance, particularly when working in organic or aqueous-organic systems. This is obvious, because the presence of even small amount of water (diffused from the filling solution of the reference electrode) is likely to have a marked effect on the properties of electrolyte in organic media, e.g., on account of the preferred solvation of ions by water molecule, leading to increase in ionization<sup>81</sup>.

##### 3.3.1.1 SILVER SILVER CHLORIDE (ORION DOUBLE-JUNCTION)

The silver-silver chloride (double-junction) reference electrode was used for most of our investigations, except in acetone, where experience has shown that the plastic body of the electrode is attacked by it.

The advantage of this electrode in organic and aqueous-organic systems was demonstrated by Kakabadse et al.<sup>84,85</sup>, who used organic solvents as its outer filling solution. Hence it became the only irresistible choice, when working in organo-methanol systems.

Furthermore, the use of a double-junction with the modified solution would be expected to minimize the variation of liquid junction potential arising from the variation in the composition of the outer filling solution and solvent mixtures. This view is supported by some of our experimental results. From the small values of  $\Delta E$ s obtained for silver ion in the n-propanol- and isopropanol- methanol systems (see tables 130 and 140), it can be assumed that the contribution to  $\Delta E$  values by liquid junction potential is probably small.

The outer filling solution for the double junction was 0.1M sodium nitrate in methanol, except for measurements involving sodium ion, where 0.01M potassium nitrate in methanol was used.

Although the equitransferent requirement favours the use of potassium nitrate than sodium nitrate, it was not possible to prepare 0.1M potassium nitrate in methanol. A solution of 0.1M electrolyte was considered desirable because the strongest test solution used for most of our measurements was  $10^{-3}M$  in electrolyte. This would not be expected to alter the ionic strength of the outer filling solution assuming some diffusion of ions occur from the test solution to the outer compartment, and vice versa.

Furthermore, the use of a double-junction with the modified solution would be expected to minimize the variation of liquid junction potential arising from the variation in the composition of the outer filling solution and solvent mixtures. This view is supported by some of our experimental results. From the small values of  $\Delta E$ s obtained for silver ion in the n-propanol- and isopropanol- methanol systems (see tables 130 and 140), it can be assumed that the contribution to  $\Delta E$  values by liquid junction potential is probably small.

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3.3.1.2. SILVER-SILVER CHLORIDE (SINGLE-JUNCTION)

This reference electrode was only used before the double-junction reference electrode was available. The electrode was found to show good potential stability.

3.3.1.3 SATURATED CALOMEL ELECTRODE (LITHIUM CHLORIDE)  
"SCE(LiCl)"

Saturated Calomel Electrode (Lithium Chloride) was used as a reference electrode in aqueous acetone and methanol-acetone solvent mixtures.

The electrode was found to be rather unstable (i.e. appreciable fluctuation) at low organic solvent concentration in water-acetone mixture but, showed a gradual increase in stability with increasing organic solvent concentration. It was realised that chloride ion, diffusing into the test solution could interfere with low level chloride and silver determinations, thus mercury-mercurous sulphate electrode was used for their direct potentiometry. Because of the aqueous filling solution in the SCE(LiCl) electrode, trace water may be expected to diffuse into the test solution.

## 3.3.1.4

MERCURY-MERCUROUS SULPHATE REFERENCE ELECTRODE

The reason for using the mercury-mercurous sulphate electrode in acetone has been discussed. There was no special preference for its use in other systems, except for the fact that the measurement were made before the double-junction was available for use in this project. One advantage, however, was that it gave larger  $\Delta E$  values in  $\text{AgNO}_3$  solutions compared with a d/j reference electrode.

The electrode showed appreciable fluctuation and drift in a number of the systems investigated, especially, in the direct potentiometry of silver ion, where a palish red tinge was often observed on the porous plug after prolonged exposure of the electrode to silver solution. This was probably due to clogging of the porous plug by silver sulphate, which must have been formed in-situ at the interface of the test solution and the filling solution of the reference electrode. Attempts were made to minimize this effect by cleaning it with plastic abrasive from time to time, especially before commencement of new sets of determination.

## 3.3.1.5

CORRELATION OF DIFFERENT REFERENCE ELECTRODES  
WITH RESPECT TO DOUBLE-JUNCTION ELECTRODE

Table 127 indicates a correlation of different reference electrodes with respect to the double-junction electrode used.

From the results obtained, the presence of liquid-junction potential was evident, as can be seen from the variation of the potential measurements with increasing concentration of organic solvent. The variation observed could be a reflection of the differences in liquid-junction potential of the two reference electrodes involved.

At first, it may appear puzzling that there is a marked difference in potential between the silver-silver chloride (double-junction) and the single-junction, since only one standard potential of silver-silver chloride is available in literature. The big discrepancy (75 mV), is perhaps, only apparent rather than real, since the modified filling solution of the double-junction (0.1M sodium nitrate in methanol) gives rise to liquid-junction potential which contribute to the overall potential of the double-junction electrode. This discrepancy was further explored by using aqueous filling

instead of the modified solution in the outer chamber, which consequently reduced the discrepancy to 35 mV.

Furthermore, using two double-junction electrodes, both with aqueous filling, a discrepancy of 7 mV was obtained. Measuring the potential between the second double-junction reference electrode and the single-junction gave 43 mV.

Our findings lead us to the following conclusion:

- (1) A difference of 7 mV may be within the tolerance range of the standard potential of double-junction reference electrodes.
- (2) It is conceivable, that the gradual diffusion, though small, of the outer filling solution (0.1M sodium nitrate in methanol) into the inner chamber could cause irreversible adsorption of foreign organic molecules into the reference element, causing a change in the 'standard' potential of the electrode<sup>166</sup>.

instead of the modified solution in the outer chamber, which consequently reduced the discrepancy to 35 mV.

Furthermore, using two double-junction electrodes, both with aqueous filling, a discrepancy of 7 mV was obtained. Measuring the potential between the second double-junction reference electrode and the single-junction gave 43 mV.

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Correlation of reference electrodes with respect to silver-silver chloride (double-junction) electrode, in the presence of  $10^{-3}$  M potassium fluoride

Table 127 (a)

Methanol-Water

% m/m Methanol	Potential/mV		
	Single-junction	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )	SCE (LiCl)
0	73.8	-48.6	14.2
20	74.1	-40.1	24.4
40	72.2	-31.4	35.4
60	67.3	-25.0	50.3
80	62.8	-22.6	62.8
90	58.5	-31.5	70.1
95	56.3	-39.0	73.9
99	55.8	-41.5	76.9

Table 127 (b)

Ethanol-Water

% m/m Ethanol	Potential/mV	
	Single-junction	Hg, Hg <sub>2</sub> SO <sub>4</sub>
0	77.7	-44.8
20	78.5	-35.6
40	76.7	-29.4
60	74.1	-27.4
80	67.0	-36.3
90	64.9	-43.9
95	64.4	-46.8
99	61.7	-49.6

Table 127 (c)

Acetic acid-Water

% m/m Acetic acid	Potential/mV	
	Single-junction	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	77.7	-44.8
20	84.7	-53.8
40	90.7	-59.0
60	93.3	-64.8
90	94.6	-77.2
80	86.6	-80.6
95	80.5	-84.0
99	79.6	-87.2

Table 127 (d)

Acetone-Water

% m/m Acetone	Potential/mV	
	SCE(LiCl)	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	15.0	-38.8
10	24.2	-29.6
20	34.2	-22.5
40	57.6	-13.1
60	90.2	-1.8
80	129.9	-1.6
90	158.9	10.4
95	174.4	8.5
99	215.2	14.6

Table 127 (e)

Acetone-Methanol

% m/m Acetone	Potential/mV	
	SCE(LiCl)	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	80.9	-53.2
10	87.9	-47.0
20	94.8	-42.0
40	108.4	-34.4
60	125.5	-25.1
80	148.1	-14.1
90	167.1	-13.1
95	187.6	10.0
99	219.3	5.8

Table 127 (c)

Acetic acid-Water

% m/m Acetic acid	Potential/mV	
	Single-junction	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	77.7	-44.8
20	84.7	-53.8
40	90.7	-59.0
60	93.3	-64.8
90	94.6	-77.2
80	86.6	-80.6
95	80.5	-84.0
99	79.6	-87.2

Table 127 (d)

Acetone-Water

% m/m Acetone	Potential/mV	
	SCE(LiCl)	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	15.0	-38.8
10	24.2	-29.6
20	34.2	-22.5
40	57.6	-13.1
60	90.2	-1.8
80	129.9	-1.6
90	158.9	10.4
95	174.4	8.5
99	215.2	14.6

Table 127 (e)

Acetone-Methanol

% m/m Acetone	Potential/mV	
	SCE(LiCl)	Hg, Hg <sub>2</sub> SO <sub>4</sub> (1M Na <sub>2</sub> SO <sub>4</sub> )
0	80.9	-53.2
10	87.9	-47.0
20	94.8	-42.0
40	108.4	-34.4
60	125.5	-25.1
80	148.1	-14.1
90	167.1	-13.1
95	187.6	10.0
99	219.3	5.8

### 3.3.2. LOWER LIMIT OF LINEAR RESPONSE RANGE (LLRR)

Midgley<sup>160</sup> illustrated the shortcomings in the IUPAC'S definition of lower limit of detection. This view is also indirectly supported by Bailey (see section 1.8).

The former author presented a mathematical approach for the lower limit of detection (about 10 equations). Apart from involving cumbersome arithmetic, this approach makes use of some basic assumptions, which may not be valid in organo-aqueous or pure organic systems. For instance,  $\sigma_A$ ,  $\sigma_B$ , being errors associated with sample and blank readings, are assumed to be equal! Experience has shown that blank measurements are rarely reproducible- this is worse still in aqueous-organic or pure organic system.

In this work, a simple working definition has been adopted, viz, the "Lower Limit of Linear Response Range (LLRR)". This is defined as the lower limit of the point of departure from linearity for a plot of logarithm of  $a_x$  as a function of potential response. Infact, this point is identical with the lower limit of Nernstian Response (LLNR) for systems which obey Nernst equation closely. However, it differs from the latter in the sense that electrode may exhibit non-Nernstian behaviour, especially in nonaqueous systems.

While the proposed LLRR may seem to have no advantage over the existing definitions, it serves as a basis for

comparison of measurements, using similar cell systems.

Apart from isolated cases (e.g. tables 27, 47, 49, 52 & 73), there was no pronounced lowering of LLLRR with increasing solvent concentration. One possible limitation, is the measurement and evaluation procedure. Parameters which vary only slightly under different experimental conditions are best carried out and evaluated as much as possible in a reproducible manner. This is sometimes difficult to achieve.

Since in dilute aqueous solutions of monovalent electrolyte ( $10^{-5}$  M and less), activity can be assumed to be equal to concentration, a lowering of LLLRR would be expected with increasing solvent concentration for the inorganic-based electrodes (solubility of membrane is assumed to decrease). This was demonstrated by Kakabadse et al.<sup>84</sup>, (see section 3.2.2). At the same time, it is true that for a given electrolyte, activity coefficients vary from solvent to solvent and also vary from electrolyte to electrolyte for a given solvent. Thus there is probably no common border line, when activity and concentration can be regarded as being equal irrespective of solvent or electrolyte type. This probably further clarifies the lack of a general trend concerning LLLRR (from system to system) observed in our results.

### 3.3.3 POINT OF INVERSION (POI) STUDY

Figures 60,61,77,78 & 82 show clear points of inversion in the calibration graphs of the systems indicated. Potential measurements along the calibration graphs show reasonable initial equilibration over the usual time of measurements, followed by a prolonged potential drift about the point of inversion. Above and below the point of inversion, good equilibration was shown.

This strange behaviour was further investigated by chart-recording millivolt readings over a period of 30-60 min at 60% and 99% solvent, and measuring in each case, at indicator ion concentrations lying below, close to and above the POI: The results are shown in figures 109-116 (tables 115-118).

Three criteria were employed in the consideration of POI.

(i) Comparing  $E_s$  above POI - systems with higher solvent concentration are expected to show higher  $E$  throughout.

(ii) Comparing  $E_s$  close to POI - POI if present, should show nearly the same  $E$  value for both solvent concentrations, otherwise, higher solvent concentration should be at higher mV readings.

(iii) Comparing  $E_s$  below POI, here crossing over would be expected, viz, higher solvent becoming more negative.

The results of (i) - (iii) for each of the four POI

cases are shown in table 128

Table 128

System	Potential/mV					
	Below POI		POI		Above POI	
	60%	99%	60%	99%	60%	99%
$\text{Pb}(\text{ClO}_4)_2$ --EtOH( $\text{H}_2\text{O}$ )	-196.5	-260.4	-190.4	-239.8	-161.9	-197.1
$\text{Pb}(\text{ClO}_4)_2$ --n-PrOH(MeOH)	-199.3	-176.4	-167.7	-135.9	-82.1	-3.6
$\text{AgNO}_3$ --n-PrOH( $\text{H}_2\text{O}$ )	95.8	96.8	227.3	241.0	317.6	401.8
$\text{AgNO}_3$ --i-PrOH( $\text{H}_2\text{O}$ )	195.4	72.6	231.1	239.4	306.4	386.0

From the table above it can be seen that it is only the  $\text{AgNO}_3$ --i-PrOH( $\text{H}_2\text{O}$ ) which showed a PCI in potential stability study. One possible reason for the difference in behaviour shown in these results and that shown in the electrode calibration graphs may be due to the fact that the condition of measurement are not exactly identical.

It is worth pointing out that this strange behaviour was observed for silver and lead ions in alcohols (especially propanols when using heterogeneous membrane electrodes ( $\text{PbS}/\text{Ag}_2\text{S}$  and  $\text{AgCl}/\text{Ag}_2\text{S}$ ). Possibly the contributions of  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  ions arising from the finite solubility of these membranes may interfere with added  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  respectively at low level concentrations of these ions.

The sort of interference by the former ions could be envisaged as a form of inertia, suppressing the initial response of the determinand ions. As more and more determinand ions are added, this inertia is gradually overcome. This might be expected to apply to chloride as well, since the same electrode was used for it as for the silver ion, but there is no reason why this should be so, since  $S^{2-}$  does not interfere with  $Cl^{-}$  determination.

Furthermore, inadequate electrode conditioning (since this tends to show a levelling effect of potential response at low concentrations) might be thought to give rise to this POI anomaly, but this argument can easily be dispelled on the ground that it will only affect the first and perhaps the second calibration graphs with others unaffected because of the conditioning brought about in the course of measurements with time.



### 3.3.4 NON-NERNSTIAN ELECTRODE SLOPES

Tables 47 and 48 show the variation of electrode slopes with solvent concentrations in water-ethanol and water-acetic acid solvent mixtures, respectively. In the latter table, the gradual decrease of slope response with increasing solvent concentration is consistent with the decrease in dielectric constant, and hence decrease in activity coefficient. However, the remarkable increase in electrode slopes with increasing solvent concentrations in the former does not fit a simple explanation. Judging by the dielectric constant of the mixed solvent, one would expect a decrease in electrode slope. On the other hand, the assumption that electrode membrane might contribute substantial chloride ion through dissolution is inconsistent with the lowering of the lower limit of detection which are usually attributed to decrease in solubility of electrode membrane in higher organic solvent concentrations<sup>49</sup>. Apparently, perhaps, the only reasonable alternative left is to assume that the reference electrode, for some reasons, misbehaved under this particular circumstance. But, again, this will be very suprising indeed since the same reference electrode was used in figs. 42 and 48!

Several workers have reported<sup>161-165</sup> non-Nernstian slope response, but, perhaps, there hasn't been as such (if any at all), radical approach to probe its possible theoretical origin.

Thus it is the aim of the author to explore an approach into the non-Nernstian behaviour of the systems investigated, and to propose qualitative arguments of interpreting this behaviour.

Consider the Nernst equation of the form:

$$E = E^{\circ} \pm \frac{2.303RT}{nF} \log_{10} \gamma_X [X] + E_j \dots\dots (3.1)$$

where  $E_j$  is the liquid junction potential.

A function,  $\psi$  can be defined, such that ,

$$E_j = \frac{2.303RT}{nF} \log_{10} \psi \dots\dots\dots (3.2)$$

subst. (3.2) into (3.1), we obtain:

$$\begin{aligned} E &= E^{\circ} \pm \frac{2.303RT}{nF} \left\{ \log_{10} \gamma_X [X] + \log_{10} \psi \right\} \\ &= E \pm \frac{2.303RT}{nF} \log_{10} \gamma_X \psi[X] \dots\dots\dots (3.3) \end{aligned}$$

Suppose we define,  $\sigma$ , as an "association factor" which can be envisaged as involving a number of parameters: ion-pairing, adsorption and desorption of determinand ions at the vessel wall, particularly, in the absence of supporting electrolyte. Obviously  $\sigma$  will depend on the nature as well, as the concentrations of the electrolyte. Also it will depend on the solvent types and the compositions involved.

Thus a further modification can be made to take care of  $\sigma$ .

$$E = E^0 \pm \frac{2.303RT}{nF} \log_{10} \gamma_X \Psi[X] \dots\dots\dots (3.4)$$

It can therefore be seen that the electrode slope of a system which obeys equation (3.4) will depend on  $\sigma$ ,  $\gamma_X$  and  $\Psi(E_j, \sigma)$

Expanding this equation, we obtain,

$$E = E^0 \pm \frac{2.303RT}{nF} \left\{ \log_{10} \gamma_X + \log_{10} \Psi + \log_{10} [X] \right\} \dots\dots (3.4a)$$

From the above equation, the following deductions can be made (assuming a constant temperature).

(a) A plot of  $E$  versus  $\log_{10} [X]$  will be linear only if  $\sigma$ ,  $\Psi$  and  $\gamma_X$  assume constant values.

(b) When  $\Psi$  is constant, non-linear plot will be a result of variation in  $\gamma_X$ .

(c) If  $E_j$  is constant, non-linearity is a result of variation of either  $\Psi(\sigma)$  or  $\gamma_X$  or probably both.

(d) If  $\Psi(E_j)$  and  $\gamma_X$  can be assumed constant, non-linearity may be attributed to  $\sigma$ .

(e) The magnitude of the slope factor, either for the linear plot or the non-linear plot (tangential slope) will depend on the values assumed by  $\sigma$ ,  $\Psi$  and  $\gamma_X$ .

Applying the above modified equation to our systems, say, X-n-propanol (base solvent) systems, it can be seen that

the KF-n-propanol (base solvent) systems (see tables 29 & 35) show only little variation in the slope factor from 0-99% m/m n-propanol, and hence  $\psi(E_j)$ ,  $\gamma_X$  and  $\sigma$  can be assumed approximately constant despite the variation in solvent and electrolyte concentrations.

In the case of the  $\text{Et}_4\text{NCl}$ --n-propanol (base solvent) systems (see tables 49 and 55), electrode slopes, apart from being generally low (perhaps due to membrane ageing<sup>84</sup>), show a slight reduction in value in higher solvent concentration. Evidently since the same reference electrode was used as in the case of the fluoride-based system, the effect could not have possibly been due to  $\psi(E_j)$ . If it is assumed that  $\gamma_X$  does not change appreciably (since fairly low concentration of electrolyte is involved), then the observed effect can be attributed to the  $\sigma$  factor.

For the  $\text{AgNO}_3$ --n-propanol (base solvent) systems (see tables 66 and 71), it can be seen that electrode slopes in table 66 are fairly constant in contrast to slope values in table 71, which show a decreasing slope trend with increasing n-propanol concentrations. By a similar argument to that already adduced for the chloride-based system, the effect shown in the latter table can be associated with  $\sigma$ . Similarly, the case of  $\text{NaNO}_3$ --n-propanol (base solvent) (see tables 98 and 101) can be attributed to  $\sigma$  effect.

A very different picture emerges in the system,  $\text{Pb}(\text{ClO}_4)_2$ --n-PrOH (MeOH): 40(78); 60(75); 80(90); 90(116) and 99(129). In the preceding figures, tangential slopes are shown in bracket for the non-linear plots at a given concentration points ( $10^{-4}$  M  $\text{Pb}(\text{ClO}_4)_2$ ) for 40-99% m/m n-propanol.

Also, for a given n-propanol concentration, the tangential slope increases with decreasing electrolyte concentrations. Thus at 80% n-PrOH, we have: 14, 90 and 126 mV/decade at  $10^{-3}$ ,  $10^{-4}$  and  $10^{-5}$  M  $\text{Pb}^{2+}$ , respectively. Obviously  $\Psi(E_j)$  can be assumed constant for a given curve. Also, if it is assumed that either  $\sigma$ , or  $\gamma_X$  or possibly both vary, one would expect a negative contribution of slope from  $\gamma_X$  with increase in concentration of electrolyte, since  $\gamma_X < 1$  implies that  $\log_{10} \gamma_X$  is -ve and hence  $\frac{2.303RT}{nF} \log_{10} \gamma_X$ . Furthermore, if we assume that  $\sigma$  increases with increase in concentration of electrolyte (as implied from its definition), then  $\frac{2.303RT}{\sigma nF}$  will decrease with increasing  $\sigma$ . Both of the above considerations fit the observed trend of tangential slopes.

Also in table 86, for a given concentration of the electrolyte (say  $10^{-5}$  M), the tangential slopes can be seen to be increasing with increasing solvent concentrations. Evidently at such a low electrolyte concentration, one would expect minimal contribution from  $\gamma_X$ , and hence the effect can be assumed to be virtually due to  $\sigma$ .

Thus, the two informative scans which can be applied to electrode slopes are: (a) horizontal scan: keeping concentration of ion, X, constant and varying solvent concentration; and (b) vertical/diagonal scan: keeping solvent concentration constant ( $E_j = \text{constant}$ ) and varying X ion concentration.

A further important contribution to the cell potential can result from a time-variable potential ( $E_{\text{var.}}$ ) at high solvent concentration. For this reason, eleven systems were submitted to potential measurements over prolonged periods of time (30-60 min). Four of these systems have been discussed in the section dealing with Point of Inversion. Findings on the following seven systems, some of which are characterised by unusual sub-Nernstian slopes, are presented below (see tables 119-125).

Table 129

System	Electrode Slope/mV per decade			
	$10^{-3} - 10^{-4}$ M electrolyte			
	60	80	90	99(% solvent)
Pb(ClO <sub>4</sub> ) <sub>2</sub> --acetone(H <sub>2</sub> O)			23.8	-19.4
AgNO <sub>3</sub> --EtOH(H <sub>2</sub> O)		61.5	56.6	
AgNO <sub>3</sub> --acetone(MeOH)		38.2	105.6	
NaNO <sub>3</sub> --acetone(H <sub>2</sub> O)			58.2	31.4
KF--dioxan(H <sub>2</sub> O)	-56.8		-53.4	
Et <sub>4</sub> NCl--acetone(H <sub>2</sub> O)			-58.0	-41.6
Pb(ClO <sub>4</sub> ) <sub>2</sub> --n-PrOH(H <sub>2</sub> O)		30	29.6	

From this table, it can be seen that, non-Nernstian electrode slope behaviour is more pronounced at 99% m/m solvent than for other solvent concentrations.

A comparison of some of these values ('equilibrium' slope) with the obtained electrode slopes from the calibration graphs, e.g., 50.1 and 38.5 mV/decade at 90 and 99% m/m solvent (table 100) respectively, being obtained in the later for the system,  $\text{NaNO}_3$ -acetone( $\text{H}_2\text{O}$ ), shows that a substantial improvement of electrode slope could be achieved over prolonged period of measurements. A similar improvement, though non-Nernstian, for the system,  $\text{Et}_4\text{NCl}$ -acetone( $\text{H}_2\text{O}$ ), where -41.6 was obtained at 99% m/m solvent in the former, as compared with -32.5 mV/decade obtained from the calibration graph (table 51 ).

The case of  $\text{AgNO}_3$ -acetone( $\text{MeOH}$ ) is one of a clear anomaly. Electrode slopes from the calibration graphs are, -3.3 and 20.2 mV/decade (table 73). The sets of electrode slopes from both results show very poor agreement, with either, being far from Nernstian behaviour.

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3.3.5 DIFFERENT CELL SYSTEMS IN DIFFERENT SOLVENT SYSTEMSTABLES (130 - 142)

Using silver- and metal halide electrodes, Bishop et al<sup>167</sup>. attributed the remarkably high values of  $\Delta E$ s in mixed acetone solvents to the poisoning effect of acetone. This effect was thought to arise from appreciable adsorption of acetone onto the electrodes.

However, although remarkable high  $\Delta E$  values were obtained for mixed acetone systems in our experiments, there was no ground for us to support this view. For instance, high  $\Delta E$  values have been obtained by independent methods, viz, direct and indirect measurements, and were found to conform. 'Poisoning' would be expected to give rise to erratic results!

Furthermore when isopropanol is compared with other alcohols, it is seen that its  $\Delta E$  values are higher. An attempt to explain this observed behaviour suggests that an intrinsic chemical property is probably involved in the case of the high  $\Delta E$  values for acetone.

It has been shown<sup>114</sup> that acetone and isopropanol owe their high values of  $-\Delta G_t^0(H^+)$  (and hence their ability to replace water molecules in the aquo-proton  $(H_2O)_4(H^+)$  to the high electron density on the basic oxygen atom produced by the inductive effect of the methyl groups.

Similarly the  $-\Delta G_t^0(M^+)$  found in methanol + water mixture were ascribed<sup>124</sup> largely to the replacement of an  $H_2O$  contiguous with  $M^+$  by a  $CH_3OH$  molecule with the negative end of the dipole in both  $CH_3OH$  and  $H_2O$  oriented towards  $M^+$ . The increased dipole forces arising from the electron releasing inductive effect of the methyl groups result in a loss of free energy of transfer on transferring  $M^+$  from water into the mixture. On account of increased charge density,  $-\Delta G_t^0(M^+)$  would be expected to become larger with decreasing size of  $M^+$ . Thus the higher values for  $-\Delta G_t^0(M^+)$  for simple  $M^+$  in acetone + water compared with methanol + water is thought to arise from the greater tendency for acetone to replace the oriented  $H_2O$  contiguous with  $M^+$  with large cation dipole forces.

Applying this to our case for the positive ions studied, the order of decreasing ionic radii is,  $Ag^+ > Pb^{2+} > Na^+$ . One would expect  $Ag^+$  to show the least  $-\Delta G_t^0(M^+)$  and hence also the least  $\Delta E$  values, with the  $Pb^{2+}$  ion next on account of its size. However, the situation is not all that simple, since on account of charge density one would expect  $Pb^{2+}$  to have greater associated  $\Delta E$  than  $Na^+$ .

In accordance with this expectation, the  $\Delta E$ s are least for  $Ag^+$ , amongst the three ions, whereas  $\Delta E$ s show neck-and-neck values for  $Na^+$  and  $Pb^{2+}$ , in some cases  $\Delta E$  observed for  $Pb^{2+}$

is greater than for  $\text{Na}^+$  and vice versa (see Tables 134-136 and 139-141). Tables 139-141 show that a similar inference could be made for methanol-based systems, except in isopropanol/methanol system, for  $\text{Ag}^+$  which show -ve  $\Delta E$  values.

It is important to point out, especially where different reference electrodes are used, that deductions can only be made with caution, since this may have their own effect on the magnitude of  $\Delta E$ s observed.

A similar, but, opposite argument can be applied to the fluoride and the chloride ions. On account of the smaller ionic size of the fluoride ion, a greater degree of preferred solvation (viz, hydrogen bonding) will be expected for water in mixed solvents (where the cosolvent is aprotic or less protic than water). Consequently  $\Delta G_t^0(\text{Halide})$  would be +ve and hence -ve  $\Delta E$  values. The results obtained show good agreement with this expectation. Again, it is, however important that comparison should only be made with caution where different reference electrodes are used.

From an overall consideration of the  $\Delta E$ s for a given cell system in different mixed systems, it can be seen that the magnitude of  $\Delta E(|\Delta E|)$  increases in the order: methanol < ethanol < n-propanol < iso-propanol < acetone for the water-solvent systems. A similar trend holds for the methanol-solvent

system: ethanol < n-propanol < iso-propanol < acetone.

This order can probably be partially accounted for in term of varying degrees of preferential solvation of ions in the mixed solvents, which probably follow the same order for cations, for a given base solvent. Since,  $\Delta E$  is -ve for anions, a reverse order for cation is expected( i.e., least preferred solvation where the magnitude of  $\Delta E$  is largest).

system: ethanol < n-propanol < iso-propanol < acetone.

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Table 130

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various ethanol concentrations in binary ethanol-water mixtures.

ethanol % m/m	$\Delta E/mV$				
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (NaCl)	AgCl//D/j Ag (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(10 <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaCl)
0	0(-37.4)	0	0	0	0
10	-14.3	-14	-1	-5	11
20	-29.6	-27	-1	-3	23
30	-46.6	-38	1	-2	34
40	-64.2	-51	3	0	41
50	-86.6	-70	7	0	48
60	-106.1	-86	11	4	63
70	-128.1	-99	17	30	78
80	-150.7	-108	47	27	100
90	-175.1	-130	64	39	136
95	-187.5	-146	68	66	152
99	-195.0	-166	76	99	166

Table 131

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various acetic acid concentrations in binary acetic acid-water mixtures.

acetic acid % m/m	$\Delta E/mV$		
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )
0	0 (-37.1)	0	0
10	53.9	-7	4
20	63.4	-13	10
30	70.8	-19	16
40	75.9	-22	24
50	81.0	-39	27
60	89.4	-51	51
70	98.3	-64	59
80	108.9	-81	73
90	113.7	-112	105
95	106.3	-139	138
99	94.3	-149	168

Table 132

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems,  
in solutions of  $10^{-3}$  M electrolyte and of various acetic acid concentrations  
in binary acetic acid-methanol mixtures.

acetic acid % m/m	$\Delta E/mV$			
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (PbAc <sub>2</sub> )
0	0(-106.9)	0(88.1)	0(400.5)	0(187.4)
10	147.4	3.5	9.8	14.8
20	175.0	-0.1	16.1	25.9
30	195.0	-2.9	23.8	38.7
40	212.5	-6.5	32.4	51.3
50	227.2	-9.1	41.4	64.4
60	240.6	-14.7	53.6	78.3
70	252.3	-22.6	68.3	96.3
80	257.6	-33.4	85.5	114.0
90	253.3	-57.1	105.7	131.7
95	250.6	-76.2	114.9	139.0
99	246.2	-94.3	122.0	149.4



Table 133

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various methanol concentrations in binary methanol-water mixtures.

methanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NC1)	AgCl/Hg, Hg <sub>2</sub> SO <sub>4</sub> Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaNO <sub>3</sub> )	pH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-40.7)	0(121.4)	0	0(205.7)	0(25.6)	0(214.3)
10	-10.9	-4.4	15	8.0	5.4	3.6
20	-23.4	-10.4	28	14.5	9.4	4.4
30	-36.0	-17.0	41	21.1	15.0	4.0
40	-48.4	-24.8	55	27.7	22.5	2.7
50	-63.5	-35.6	69	36.2	31.9	2.7
60	-77.5	-46.6	87	45.5	42.3	4.5
70	-90.6	-60.5	105	56.6	54.8	9.2
80	-101.8	-71.3	126	71.9	67.8	21.1
90	-110.9	-79.7	146	93.3	83.3	49.9
95	-114.5	-84.9	159	108.9	93.0	78.0
99	-116.3	-83.6	168	123.9	99.1	119.8

Table 134

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various n-propanol concentrations in binary n-propanol-water mixtures.

n-propanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NC1)	AgCl //D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaCl)	pH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-39.6)	0(116.9)	0(346.7)	0(-197.4)	0(-18.3)	0(219.8)
10	-15.3	-8.2	4.9	8.4	5.8	1.4
20	-28.9	-16.0	9.4	14.0	11.8	-0.9
30	-44.8	-27.2	13.5	18.6	18.3	-5.1
40	-58.7	-38.8	18.3	22.8	25.5	-6.5
50	-77.5	-52.8	23.0	27.4	33.2	-7.9
60	-95.5	-70.6	32.3	36.4	47.1	-7.6
70	-121.5	-87.0	44.4	49.6	65.5	-6.0
80	-151.5	-106.3	63.5	71.7	95.1	-0.1
90	-186.3	-126.0	93.2	113.0	144.5	17.6
95	-210.7	-137.9	113.5	149.0	182.4	39.4
99	-222.9	-146.5	133.4	199.9	220.5	81.0

Table 135

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various iso-propanol concentrations in binary iso-propanol-water mixtures.

iso-propanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCI)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaCl)	PH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-39.2)	0(90.5)	0(343.5)	0(-190.4)	0(-18.3)	0(219.8)
10	-15.8	-4.8	3.8	7.0	3.3	2.7
20	-32.4	-11.7	7.4	14.4	9.2	0.7
30	-49.5	-20.8	10.9	20.9	15.1	-4.1
40	-66.5	-30.2	14.4	25.8	21.2	-8.1
50	-90.8	-47.7	20.6	32.3	30.9	-11.3
60	-114.7	-65.5	28.2	42.9	43.1	-12.6
70	-142.8	-85.6	38.3	58.3	61.2	-10.8
80	-177.6	-109.7	55.0	82.7	91.5	-5.6
90	-224.5	-138.6	78.6	127.2	141.5	10.5
95	-251.9	-157.8	94.3	168.3	179.7	32.4
99	-278.2	-174.5	110.7	233.6	223.0	76.9

Table 135

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various iso-propanol concentrations in binary iso-propanol-water mixtures.

iso-propanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NC1)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaCl)	PH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-39.2)	0(90.5)	0(343.5)	0(-190.4)	0(-18.3)	0(219.8)
10	-15.8	-4.8	3.8	7.0	3.3	2.7
20	-32.4	-11.7	7.4	14.4	9.2	0.7
30	-49.5	-20.8	10.9	20.9	15.1	-4.1
40	-66.5	-30.2	14.4	25.8	21.2	-8.1
50	-90.8	-47.7	20.6	32.3	30.9	-11.3
60	-114.7	-65.5	28.2	42.9	43.1	-12.6
70	-142.8	-85.6	38.3	58.3	61.2	-10.8
80	-177.6	-109.7	55.0	82.7	91.5	-5.6
90	-224.5	-138.6	78.6	127.2	141.5	10.5
95	-251.9	-157.8	94.3	168.3	179.7	32.4
99	-278.2	-174.5	110.7	233.6	223.0	76.9

Table 136

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various acetone concentrations in binary acetone-water mixtures.

acetone % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> /LiCl F <sup>-</sup> (KF)	AgCl/Hg, Hg <sub>2</sub> SO <sub>4</sub> Cl <sup>-</sup> (Et <sub>4</sub> NCI)	AgCl/Hg, Hg <sub>2</sub> SO <sub>4</sub> Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS/LiCl Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass/LiCl Na <sup>+</sup> (NaNO <sub>3</sub> )	pH-glass/LiCl H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-7.4)	0(-216.4)	0(6.5)	0(-162.9)	0(-13.0)	0(20.2)
10	-10.2	3.2	12.8	14.3	11.9	9.4
20	-19.7	0.5	26.8	28.7	24.9	17.3
30	-32.7	-3.9	40.9	43.3	37.3	23.8
40	-45.7	-11.7	56.4	60.9	56.1	31.5
50	-59.4	-22.5	78.1	88.1	88.4	47.7
60	-82.8	-42.5	96.7	112.9	115.7	62.8
70	-105.0	-66.0	119.0	143.4	145.8	84.2
80	-138.9	-100.6	141.4	186.2	185.9	118.4
90	-207.7	-162.6	(144.3)*	255.8	244.6	183.5
95	-257.0	-213.4	(145.9)*	324.0	292.8	262.7
99	-330.4	-250.0	-	427.5	302.6	422.1

( )\* Unstable

Table 137

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various 1,4-dioxan concentrations in binary 1,4-dioxan-water mixtures.

1,4-dioxan % m/m	$\Delta E/mV$		
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )
0	0(-42.0)	0(112.5)	0(-200.0)
10	8.1	-2.1	8.9
20	5.1	-9.6	15.7
30	-1.8	-20.0	23.9
40	-11.8	-31.5	32.1
50	-28.5	-46.1	41.8
60	-55.0	-69.0	55.2
70	-80.2	-93.2	72.7
80	-114.1	-123.9	98.3
90	-154.0	-165.1	133.2
95	-152.0	-200.5	169.8
99	+	-282.5	(266)*

(1).\* Considerable potential fluctuation observed for value in bracket, and value indicated represents the mean average over 30 min!

(2) + Potential reading highly unstable.

Table 137

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various 1,4-dioxan concentrations in binary 1,4-dioxan-water mixtures.

1,4-dioxan % m/m	$\Delta E/mV$		
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )
0	0(-42.0)	0(112.5)	0(-200.0)
10	8.1	-2.1	8.9
20	5.1	-9.6	15.7
30	-1.8	-20.0	23.9
40	-11.8	-31.5	32.1
50	-28.5	-46.1	41.8
60	-55.0	-69.0	55.2
70	-80.2	-93.2	72.7
80	-114.1	-123.9	98.3
90	-154.0	-165.1	133.2
95	-152.0	-200.5	169.8
99	* <sup>*</sup>	-282.5	(266)*

(1). \* Considerable potential fluctuation observed for value in bracket, and value indicated represents the mean average over 30 min!

(2) \*<sup>\*</sup> Potential reading highly unstable.

Table 138  
Comparison of changes in potential,  $\Delta E$ , measured for different cell systems,  
in solutions of  $10^{-3}$  M electrolyte and of various ethanol concentrations  
in binary ethanol-methanol mixtures.

ethanol % m/m	$\Delta E/mV$			
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(OAc) <sub>2</sub> )
0	0	0	0	0(-178.1)
10	-5	-2	-1	0.3
20	-11	-7	-2	0.7
30	-16	-12	-3	-1.2
40	-23	-18	-5	1.5
50	-30	-24	-5	2.1
60	-39	-29	-1	2.2
70	-47	-35	-3	2.2
80	-57	-41	-6	2.2
90	-69	-48	-8	1.7
95	-74	-48	-10	2.2
99	-80	-51	-11	-2.0



Table 139

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various n-propanol concentrations in binary n-propanol-methanol mixtures.

n-propanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCl)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaNO <sub>3</sub> )	pH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-154.9)	0(17.3)	0(474.3)	0(-62.7)	0(74.9)	0(371.3)
10	-6.1	-5.4	1.1	6.4	8.0	0.6
20	-12.5	-11.0	2.2	13.9	16.7	0.5
30	-19.0	-16.7	3.1	21.7	26.4	-0.4
40	-26.7	-23.3	3.8	29.7	34.4	-1.6
50	-35.2	-30.2	5.6	38.6	44.0	-3.5
60	-44.3	-35.5	7.4	48.3	54.7	-5.5
70	-55.8	-43.9	8.7	59.3	66.3	-9.3
80	-69.2	-54.1	9.3	76.1	79.0	-14.4
90	-86.4	-66.2	9.9	91.1	93.0	-21.1
95	-95.8	-74.5	11.5	99.1	100.6	-
99	-103.3	-78.6	12.4	106.6	106.6	-29.2

Table 140

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various iso-propanol concentrations in binary iso-propanol-methanol mixtures.

iso-propanol % m/m	$\Delta E/mV$					
	LaF <sub>3</sub> //D/j F <sup>-</sup> (KF)	AgCl//D/j Cl <sup>-</sup> (Et <sub>4</sub> NCI)	AgCl//D/j Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	Sodium-sel. glass//D/j Na <sup>+</sup> (NaNO <sub>3</sub> )	pH-glass//D/j H <sup>+</sup> (HClO <sub>4</sub> )
0	0 (-153.6)	0 (25.6)	0 (481.8)	0 (-67.4)	0 (76.3)	0 (371.3)
10	-9.7	-6.6	-1.2	11.6	4.7	2.4
20	-18.3	-13.3	-2.8	23.6	12.7	3.5
30	-27.7	-20.1	-3.1	40.9	31.3	4.5
40	-38.0	-28.0	-4.0	53.3	26.7	5.6
50	-51.4	-38.4	-4.8	65.8	39.2	7.4
60	-67.4	-49.8	-5.7	82.4	53.5	6.9
70	-85.8	-62.6	-6.2	99.3	67.9	5.9
80	-108.5	-77.3	-6.8	117.7	85.0	4.4
90	-135.4	-95.8	-8.2	142.4	100.9	1.5
95	-151.4	-107.5	-9.6	156.8	134.4	1.0
99	-166.1	-117.0	-10.4	170.6	142.2	-2.8

Table 141

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various acetone concentrations in binary acetone-methanol mixture

acetone % m/m	$\Delta E/mV$					
				Sodium-sel.		
	LaF <sub>3</sub> /LiCl F <sup>-</sup> (KF)	AgCl/Hg, Hg <sub>2</sub> SO <sub>4</sub> Cl <sup>-</sup> (Et <sub>4</sub> NCl)	AgCl/Hg, Hg <sub>2</sub> SO <sub>4</sub> Ag <sup>+</sup> (AgNO <sub>3</sub> )	PbS/LiCl Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )	glass/LiCl Na <sup>+</sup> (NaNO <sub>3</sub> )	pH-glass/LiCl H <sup>+</sup> (HClO <sub>4</sub> )
0	0(-55.4)	0(-272.6)	0(167.2)	0(14.8)	0(186.3)	0(466.1)
10	-12.1	-5.6	8.9	16.3	4.0	-16.6
20	-20.2	-12.4	16.1	30.1	10.1	-12.1
30	-30.5	-19.7	26.1	43.9	18.3	-2.2
40	-42.3	-27.2	34.8	61.4	28.8	10.9
50	-56.2	-37.9	43.0	79.4	43.2	31.9
60	-74.2	-55.1	53.5	99.4	57.9	53.9
70	-99.3	-72.6	61.6	123.5	75.9	82.0
80	-129.6	-98.1	69.0	152.1	100.8	124.9
90	-192.4	-143.0	74.5	192.3	133.3	194.0
95	-240.8	-174.0	73.3	231.5	160.9	270.0
99	-254.1	-217.6	67.4	288.3	194.4	388.0

Table 142

Comparison of changes in potential,  $\Delta E$ , measured for different cell systems, in solutions of  $10^{-3}$  M electrolyte and of various 1,4-dioxan concentrations in binary 1,4-dioxan-methanol mixtures.

1,4-dioxan % m/m	$\Delta E/mV$	
	LaF //D/j F <sup>-</sup> (KF)	PbS//D/j Pb <sup>2+</sup> (Pb(ClO <sub>4</sub> ) <sub>2</sub> )
0	0(-157.7)	0(-72.4)
10	11.4	22.6
20	12.1	36.7
30	8.0	49.0
40	0.2	61.3
50	-11.8	74.1
60	-27.6	86.4
70	-39.6	99.0
80	-54.6	125.2
90	-74.8	158.8
95	(-80.3)	174.8
99	+	+

+ electrode potential unstable.

### 3.3.6 $\Delta\Delta E$ IN BINARY SOLVENT-WATER/SOLVENT-METHANOL MIXTURES

Table 143 shows the  $\Delta\Delta E/mV$  for different systems.

$\Delta\Delta E$  is defined as follow:  $\Delta\Delta E = \Delta E_{H_2O} - \Delta E_{MeOH}$

where  $\Delta E_{H_2O}$  and  $\Delta E_{MeOH}$  are the potential changes associated with solvent-water and solvent-methanol respectively.

In general, three trends of  $\Delta\Delta E$ s are shown:

(i) an increasing trend of  $\Delta\Delta E$  (ii) a decreasing trend of  $\Delta\Delta E$  and (iii) a mixed trend of  $\Delta\Delta E$ .

The first type is characterised by  $Ag^+$ , except in acetic acid, where it shows a mixed trend. The second type are characterised by  $F^-$  and  $Cl^-$ . Whereas  $Pb^{2+}/1-PrOH$ ,  $Na^+/n-PrOH$  and  $Na^+/1-PrOH$  are examples of the third type.

For a given ion, X, one would expect a comparable value of  $\Delta\Delta E$  for the different solvents, which is also expected to compare favourably with  $\Delta E$  for the X-methanol ( $H_2O$ ) system. For instance, different trends for anions and cations, decreasing for the former and increasing for the latter are expected. This is generally true for the fluoride and the chloride ions, but not for all ions. For a given ion, X, some systems show close similarity, in  $\Delta\Delta E$  values, whereas others show dissimilarity. Example of the former include:  $Ag^+$  in  $n-PrOH$  &  $1-PrOH$ ;  $Cl^-$  in  $HOAc$  &  $n-PrOH$  and  $F^-$  in  $EtOH$  &  $n-PrOH$ . Some of the examples of the latter are:  $Pb^{2+}$  in

Acetone & 1,4-dioxan;  $\text{Na}^+$  in 1-PrOH & acetone and  $\text{Ag}^+$  in acetic acid & 1-PrOH).

A careful chemical consideration of what might probably be happening at molecular level may partially account for the seeming anomalies. For instance, ion-ion interaction occur though perhaps to a small extent but varying degree since dilute solutions of ion, X are involved. The effect might be noticeable in high solvent concentration of low dielectric constant, e.g. 1,4-dioxan, acetone and acetic acid. This point may be pertinent to the observed anomalies for  $\text{Na}^+$ /acetone (99% m/m) and  $\text{Ag}^+$ /acetone (90-99% m/m). Solute-solvent and solvent-solvent interactions can also occur. The latter would be expected to be least noticeable at high and low solvent concentrations, and most noticeable around middle % age. This factor may be pertinent to the  $\text{Pb}^{2+}$ /1,4-dioxan, which shows minimal value of  $\Delta\Delta E$  at around middle % age.

However, the resultant effect of all these interactions may not follow a simple algebraic sum or difference, when three solvents are permuted in combination of twos. In other words, it will be an oversimplification to assume that the chemical processes involved in X-solvent ( $\text{H}_2\text{O}$ ) should be equal to the algebraic sum of X-solvent (MeOH) and X-methanol ( $\text{H}_2\text{O}$ ).

Comparative change in potential,  $\Delta\Delta E$ , for a given ion and a given solvent in binary solvent-water/solvent-methanol mixtures

Table 11-3  $\Delta\Delta E/mV$   
Na<sup>+</sup>

% m/m solvent	0	20	40	60	80	90	95	99
n-PrOH	0	-4.9	-8.9	-7.6	16.1	51.5	81.8	113.9
i-PrOH	0	-3.5	-5.5	-10.4	6.6	40.6	45.3	80.8
Acetone *	0	14.8	27.3	57.8	85.1	111.3	131.9	108.3
				<u>Pb<sup>2+</sup></u>				
n-PrOH	0	0.1	-6.9	-11.9	-4.4	21.9	49.9	93.3
i-PrOH	0	-9.2	-27.5	-39.5	-35.0	-15.2	11.5	62.4
Acetone *	0	-1.4	-0.5	13.5	34.1	63.5	92.5	139.2
1,4-dioxan	0	-21.0	-29.2	-31.2	-26.9	-25.6	-5.0	-
				<u>Ag<sup>+</sup></u>				
Acetic acid	0	-6	-8	-3	-13	-1	23	46
n-PrOH	0	7.2	14.5	24.9	54.2	83.3	102.0	121.0
i-PrOH	0	10.2	18.4	33.9	61.8	86.8	103.9	121.1
Acetone *	0	10.7	21.6	43.2	72.4	(69.8)	(72.6)	-
				<u>Cl<sup>-</sup></u>				
Ethanol	0	-20	-33	-57	-67	-82	-98	-109
Acetic acid	0	-13	-21	-36	-48	-55	-63	-55
n-PrOH	0	-5.0	-15.5	-35.1	-52.2	-59.8	-63.4	-67.9
i-PrOH	0	1.6	-2.2	-15.7	-32.4	-42.8	-50.3	-57.5
Acetone *	0	12.9	15.5	12.6	-2.5	-19.6	-39.4	-32.4
				<u>F<sup>-</sup></u>				
Ethanol	0	-19	-41	-67	-94	-106	-114	-1115
Acetic acid	0	-111.6	-136.6	-151.2	-143.7	-139.6	-144.3	-151.6
n-PrOH	0	-16.4	-32.0	-51.2	-82.3	-99.9	-114.9	-119.6
i-PrOH	0	-14.1	-28.5	-47.3	-69.1	-89.1	-100.5	-112.1
Acetone *	0	0.5	-3.4	-8.6	-9.3	-15.3	-16.2	-76.3
1,4-dioxan	0	-7.0	-12.0	-27.4	-59.5	-79.2	-	-

\* For reference electrode other than double-junction.

### 3.4 CONCLUSION

1. In the binary solvent- water system, ISE/X, 0-99% m/m solvent/RE, (ISE is the ion-selective electrode = AgCl, LaF, PbS, sodium-selective glass or PH glass electrode;  $X = F^-$ ,  $Cl^-$ ,  $Ag^+$ ,  $Pb^{2+}$ ,  $Na^+$  or  $H^+$ ; solvent = MeOH, EtOH, n-PrOH, i-PrOH, HOAc, acetone or 1,4-dioxan; RE = reference electrode ) for a given concentration of indicator ion, X and a given reference electrode, the cell potential decreases systematically with an increase in solvent concentration when X is an anion and the reverse is observed when X is a cation.
2. Replacement of water by methanol in the above mentioned systems, viz, direct potentiometry in binary solvent-methanol solutions, constant in indicator ion concentration (iso-concentration condition) and of various solvent concentrations, revealed trends similar to those observed in binary solvent-water mixtures. In general, changes in potential,  $\Delta E$ , for a given solvent and a given ion, X, were greater in the aqueous than in methanolic mixtures.
3. The claim that the sodium-selective glass electrode is 'solvent-insensitive' and is therefore suitable for use as a reference electrode in cells without liquid junction is shown to be incorrect. A method is proposed which allows a correction to be made for the solvent effect on the sodium-

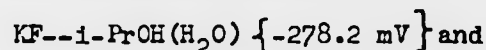
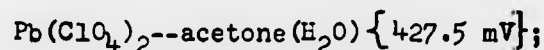


### 3.4 CONCLUSION

1. In the binary solvent- water system, ISE/X, 0-99% m/m solvent/RE, (ISE is the ion-selective electrode = AgCl, LaF, PbS, sodium-selective glass or PE glass electrode;  $X = F^-$ ,  $Cl^-$ ,  $Ag^+$ ,  $Pb^{2+}$ ,  $Na^+$  or  $H^+$ ; solvent = MeOH, EtOH, n-PrOH, i-PrOH, HOAc, acetone or 1,4-dioxan; RE = reference electrode ) for a given concentration of indicator ion, X and a given reference electrode, the cell potential decreases systematically with an increase in solvent concentration when X is an anion and the reverse is observed when X is a cation.
2. Replacement of water by methanol in the above mentioned systems, viz, direct potentiometry in binary solvent-methanol solutions, constant in indicator ion concentration (iso-concentration condition) and of various solvent concentrations, revealed trends similar to those observed in binary solvent-water mixtures. In general, changes in potential,  $\Delta E$ , for a given solvent and a given ion, X, were greater in the aqueous than in methanolic mixtures.
3. The claim that the sodium-selective glass electrode is 'solvent-insensitive' and is therefore suitable for use as a reference electrode in cells without liquid junction is shown to be incorrect. A method is proposed which allows a correction to be made for the solvent effect on the sodium-

selective glass electrode.

4. For a given concentration of ion, X, the observed systematic change of cell potential with variation in solvent concentration provides a graphical method for the rapid determination of organic solvents in binary solvent-water/methanol mixtures. This method is particularly useful for systems characterised by large changes in potential,  $\Delta E$ , three of which, showing  $\Delta E$  values in brackets, are listed below:



5. The results of the effect of solvent on cell potential (under iso-concentration conditions), obtained by direct potentiometry, have been verified by 'indirect' measurements derived from electrode calibration graphs. From a series of 10-12 Nernstian-type graphs, potentials for the same concentration of X are abstracted and these plotted against the percentage by mass of solvent. From a series of such graphs the one with the largest  $\Delta E_{\text{max}}$  and the best linearity provides the optimum value for the concentration of X in the direct method.
6. The reversibilities of the systems are checked by constructing Nernstian-type graphs for solutions of the same concentration of solvent and different concentrations

of X (in the approximate range of  $10^{-6}$ - $10^{-3}$  M X).

The graphically obtained electrode slopes allow a 'chemical' insight into the variation in cell potential. Sub-Nernstian slopes can be attributed to variations in liquid-junction potential, activity coefficients of X and to non-attainment of equilibrium at high solvent concentration.

7. For some systems, electrode calibration graphs reveal hitherto unreported 'points of inversion' in the lower concentration range ( $10^{-4}$ - $10^{-6}$  M X). This behaviour is characteristic of silver and lead ions, especially in ethanol/water, n-propanol/water, n-propanol/methanol, and iso-propanol/water binary solvent systems. Studies of stability of potentials over larger periods of time show that this anomaly is, at least in part, due to a lack of equilibration.
8. Throughout the study, emphasis is placed on a comparative approach to experimental results, e.g., comparison of changes in potential,  $\Delta E$ , for a given X and of various solvent concentrations in different solvent mixtures; comparison of different cell systems in different solvent systems; comparative change in potential,  $\Delta \Delta E$ , for a given ion and a given solvent in binary solvent-water and solvent-methanol mixtures.

of X (in the approximate range of  $10^{-6}$ - $10^{-3}$  M X).

The graphically obtained electrode slopes allow a 'chemical' insight into the variation in cell potential. Sub-Nernstian slopes can be attributed to variations in liquid-junction potential, activity coefficients of X and to non-attainment of equilibrium at high solvent concentration.

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8. Throughout the study, emphasis is placed on a comparative approach to experimental results, e.g., comparison of changes in potential,  $\Delta E$ , for a given X and of various solvent concentrations in different solvent mixtures; comparison of different cell systems in different solvent systems; comparative change in potential,  $\Delta \Delta E$ , for a given ion and a given solvent in binary solvent-water and solvent-methanol mixtures.

## EXPERIMENTAL

## 4. EXPERIMENTAL

### 4.1 PREPARATIONS

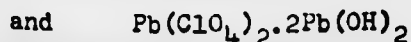
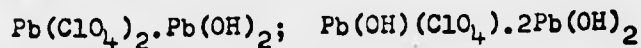
#### 4.1.1 VARIOUS SOLUTION MIXTURES

For all aqueous preparations, the density of de-ionised water was assumed unity at room temperature, and various aqueous-organic and methanol-organic solvent mixtures of known compositions (expressed as % m/m organic solvent component) were prepared by measuring to the nearest 0.1 ml of the calculated volume corresponding to a given composition (see appendix I).

#### 4.1.2 0.1 M LEAD PERCHLORATE IN METHANOL

Lead perchlorates, like other perchlorates, is very soluble<sup>168</sup> in water and also reasonably soluble in methanol. The solubility is 81 gm/ 100 gm of water at 25°C.

However, because the anhydrous solution in methanol is explosive, no attempt was made to prepare the methanolic lead perchlorate via the anhydrous route. The method used involved the dissolution of lead monoxide in a small excess of aqueous perchloric acid, to prevent the formation of basic salts<sup>169</sup>, several of which include:



The resultant solution was cautiously adjusted to a pH of about 3 with standard solution of 2M sodium hydroxide, followed by a subsequent dilution to give 1M aqueous lead perchlorate solution.

10 ml of the 1M aqueous lead perchlorate was diluted ten fold with methanol to give 0.1M 90% methanol solution of lead perchlorate, from which subsequent serial dilutions were made with methanol to obtain  $10^{-2}$ M and  $10^{-3}$  M lead perchlorate containing 1% and 0.1% water which inevitably resulted.

#### 4.2 MEASUREMENT TECHNIQUES

Except for 'indirect' measurements of sodium ion with the sodium-selective glass electrode, where the initial low level of sodium ion concentration necessitated the addition of 1 ml of aqueous or methanolic 0.1M  $\text{NH}_4\text{OH}$ , in order to minimize interference from hydrogen ions, the techniques of measurement were the same for all electrodes.

Two methods were used, referred to as 'direct' and 'indirect' techniques.

##### 4.2.1 DIRECT METHOD

In the direct method, a series of solutions having constant concentration of ion, X, and varying solvent concentrations (0-99% m/m organic solvent component) were

prepared, and potential measurements were made in an enclosed system to minimize loss of solvent through evaporation. The mixtures were placed, each at a time, in a 100 ml three-necked round-bottom flask, fitted with indicator and reference electrodes, and stirred magnetically to facilitate quick equilibration. Measurements were recorded over several minutes to allow for reasonable equilibration.

#### INDIRECT METHOD

The 'indirect' method served as an electrochemical scan of the X - solvent (base) systems. Electrode graphs were constructed for solutions of constant solvent concentration and varying concentration of X ( $2 \times 10^{-6}$ - $10^{-3}M$ ). In essence, the technique involves the addition of known increments of stock solutions of X to the solvent-base mixture. After each addition, potentials were recorded over a period of 3-10 minutes.

#### 4.3. REAGENTS

Standard solutions were prepared from the purest grade of chemical available. In almost all cases, analar grade reagents were used.



#### 4.4 APPARATUS

##### 4.4.1 METERS

Two types of Corning millivolt meters were used.

A model 10 expanded-scale pH meter, with a range of  $\pm 300$  mV and accurate to  $\pm 1$  mV. The other Corning instrument was Model 130 digital pH-meter with the following specifications:

Resolution: 0.1 mV

Relative accuracy:  $\pm 0.2$  mV or  $\pm 0.1$  mV

Repeatability:  $\pm 0.1$  mV

Recorder output:  $\pm 180$  mV

Modes: STANDBY, pH, REL. MV, MV.

##### 4.4.2 INDICATOR ELECTRODES

Corning: pH glass electrode cat No 476022

Beckman: Sodium ion-selective glass electrode  
cat No 39278

Lead model 94-82 Orion research inc.

Chloride model 94-17A Orion research inc.

Fluoride model 94-09 Orion research inc.

#### 4.4.3 REFERENCE ELECTRODES

Orion inc. model 90-02 (double-junction) reference electrode (0.1M sodium nitrate/Methanol as outer filling were generally used except where sodium-selective glass electrode was used, in which case 0.01M potassium nitrate/MeOH outer filling was used instead). Orion inc. model 90-01 silver-silver chloride (single-junction). Mercury-mercurous sulphate (1M  $\text{Na}_2\text{SO}_4$ ), Radiometer SCE(LiCl), Type K901.

#### 4.4.4 MISCELLANEOUS APPARATUS

Electrode stability was recorded on chart paper using a SERVOSCRIBE POTENTIOMETER SCHREIBER TYPE RE 511.

Solutions were stirred with a TEFLON coated bar magnet driven by a GALLENKAMP stirrer-hotplate. Hewlett - Packard 9862A calculator/plotter was used for plotting the potential-time graph for the electrode stability study. The g.l.c used was of the Pye-Unican type, with F.I.D. detector and a porapak column.

#### 4.4.5 GLASSWARE

All glassware used for measurement were of grade 'A' type.

APPENDICES

APPENDIX IICALCULATION OF VOLUME EQUIVALENT OF A GIVEN m/m PER CENT OF A  
SOLVENT IN A BINARY SOLVENT MIXTURETable 144<sup>175</sup>

SOLVENT	DENSITY (AT 20°C) gm/ml
MeOH	0.791
EtOH	0.790
HOAc	1.049
Acetone	0.790
n-PrOH	0.804
1-PrOH	0.785
1,4-dioxan	1.033

## 1.1

WATER-ORGANIC SOLVENT MIXTURES

Consider a 100 ml solution of a binary water-organic solvent mixture:

Let  $V_1, V_2$  be the Vol. (in ml) of organic solvent (say, acetone) and water, respectively, in the mixture.

Then,

$$V_1 + V_2 = 100 : \quad V_2 = (100 - V_1)$$

Let  $X = m/m\%$  acetone in the mixture, and hence:

$$X = \frac{V_1 \times 0.790}{V_2 \times 1 + V_1 \times 0.790} \times 100$$

$$= \frac{79 V_1}{(100 - V_1) + 0.790 V_1}$$

rearranging

$$79 V_1 = X (100 - 0.21 V_1)$$

i.e.

$$V_1 (79 + 0.21 X) = 100 X$$

and thus,

$$V_1 = \frac{100 X}{79 + 0.21 X}$$

the equation reduces to the form which can be solved for  $V_1$   
at any given value of  $X$

Conversion of weight percent solvent to volume percent  
in water-solvent mixtures

Table 145

% m/m Organic Solvent	Vol of Organic Solvent / ml						
	MeOH	EtOH	HOAc	n-PrOH	i-PrOH	Acetone	1,4- Dioxan
0	0	0	0	0	0	0	0
10	12.3	12.3	9.6	12.1	12.4	12.3	9.7
20	24.0	24.0	19.2	23.7	24.2	24.0	19.5
30	35.2	35.2	29.0	34.8	35.3	35.2	29.3
40	45.8	45.8	38.9	45.3	45.9	45.8	39.2
50	55.9	55.9	48.8	55.4	56.0	55.9	49.2
60	65.5	65.5	58.8	65.1	65.6	65.5	59.2
70	74.7	74.7	69.0	74.4	74.8	74.7	69.3
80	83.5	83.5	79.2	83.3	83.6	83.5	79.5
90	91.9	91.9	89.6	91.8	92.0	91.9	89.7
95	96.0	96.0	94.8	95.9	96.0	96.0	94.8
99	99.2	99.2	99.0	99.2	99.2	99.2	99.0

$$= \frac{79 V_1}{(100 - V_1) + 0.790 V_1}$$

rearranging

$$79 V_1 = X (100 - 0.21 V_1)$$

i.e.

$$V_1 (79 + 0.21 X) = 100 X$$

and thus,

$$V_1 = \frac{100 X}{79 + 0.21 X}$$

the equation reduces to the form which can be solved for  $V_1$   
at any given value of  $X$

Conversion of weight percent solvent to volume percent  
in water-solvent mixtures

Table 145

% m/m Organic Solvent	Vol of Organic Solvent / ml						
	MeOH	EtOH	HOAc	n-PrOH	i-PrOH	Acetone	1,4- Dioxan
0	0	0	0	0	0	0	0
10	12.3	12.3	9.6	12.1	12.4	12.3	9.7
20	24.0	24.0	19.2	23.7	24.2	24.0	19.5
30	35.2	35.2	29.0	34.8	35.3	35.2	29.3
40	45.8	45.8	38.9	45.3	45.9	45.8	39.2
50	55.9	55.9	48.8	55.4	56.0	55.9	49.2
60	65.5	65.5	58.8	65.1	65.6	65.5	59.2
70	74.7	74.7	69.0	74.4	74.8	74.7	69.3
80	83.5	83.5	79.2	83.3	83.6	83.5	79.5
90	91.9	91.9	89.6	91.8	92.0	91.9	89.7
95	96.0	96.0	94.8	95.9	96.0	96.0	94.8
99	99.2	99.2	99.0	99.2	99.2	99.2	99.0

1.2. METHANOL-ORGANIC SOLVENT MIXTURES

For a 100 ml of solution made up of, say,  $V_1$  of MeOH and  $V_2$  of n-propanol. Let  $D_{\text{MeOH}}$  and  $D_{\text{n-p}}$  represent the densities of methanol and n-propanol, respectively

$$V_1 + V_2 = 100$$

$$\frac{V_2 D_{\text{n-p}}}{V_1 D_{\text{MeOH}} + V_2 D_{\text{n-p}}} \times 100 = X \quad (\text{where } X = \% \text{ m/m n-propanol})$$

By caculation similar to that of appendix (1.1) different volumes of  $V_2$  can be obtained for given values of  $X$

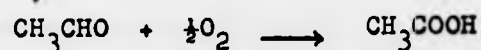
Table 146  
Conversion of Weight percent solvent to volume percent  
in methanol-organic solvent mixtures

% m/m Organic Solvent	Vol. of Organic Solvent / ml					
	EtOH	HAc	i-PrOH	n-PrOH	Acetone	1,4-dioxan
0	0	0	0	0	0	0
10	10.0	7.7	10.1	9.9	10.0	7.8
20	20.0	15.9	20.1	19.7	20.0	16.1
30	30.0	24.4	30.2	29.7	30.0	24.7
40	40.0	33.5	40.2	39.6	40.0	33.8
50	50.0	43.0	50.2	49.6	50.0	43.4
60	60.0	53.1	60.2	59.6	60.0	53.5
70	70.0	63.8	70.2	69.7	70.0	64.1
80	80.0	75.1	80.1	79.7	80.0	75.4
90	90.0	87.2	90.1	89.9	90.0	87.3
95	95.0	93.5	95.0	94.9	95.0	93.6
99	99.0	98.7	99.0	99.0	99.0	98.7

APPENDIX 2APPLICATIONUSE OF ION SELECTIVE ELECTRODES (ISE) IN MONITORING THE  
CONVERSION OF ETHANOL TO VINEGARVINEGAR

Vinegar has been defined in several ways<sup>171-173</sup>. However, all definitions have in common, the fact that it is essentially a dilute solution of acetic acid in water (about 4-10% acetic acid).

Historically, the production of vinegar started about 5000 years ago<sup>174</sup>. It was the only acid reagent distinctly recognized by the ancients and it was obtained by fermentation of alcohol, a process which employs the aerobic bacterial oxidation of alcohol to acetic acid. This process is considered to occur in two stages:



Modern commercial processes employ the Orleans process, or the quick vinegar process<sup>174</sup> in which blackstrap molasses are used as aqueous solution containing about 10% ethanol and 1% acetic acid.



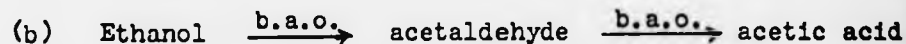
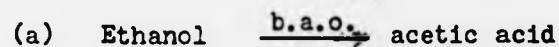
## MODEL STUDY

### Preliminary Survey

Since the conversion of ethanol to vinegar (acetic acid) can proceed via acetaldehyde, the aqueous mixture (0-10% m/m solvent) of the individual solvent, and also their dual combinations in water were studied. Different indicator ions ( $F^-$ ,  $Cl^-$ ,  $Ag^+$ ,  $H^+$ ) and the corresponding ion-selective electrodes were employed, using various reference electrodes for each indicator ion.

From the results (figs. 128-132), the less promising reference electrodes and ISE were eliminated.

Two possible reaction path ways were envisaged for the biochemical aerial oxidation (b.a.o.) process:



Process "a" involves a simple and direct oxidation, and hence a more complex model.

From our preliminary study, we had ground to suppose that acetaldehyde is only a very short-lived intermediate.

This is supported by the low pH of its aqueous solution, suggesting a partial conversion to acetic acid under atmospheric condition at room temperature. This was confirmed by g.l.c. analysis for acetic acid and acetaldehyde, showing the appearance of two peaks in a solution of acetaldehyde (one corresponding to acetic acid, the other a broadish peak, was thought to be paraldehyde) on standing for about 20 min.

Thus the subsequent investigation was centred on a model based on pathway "a".

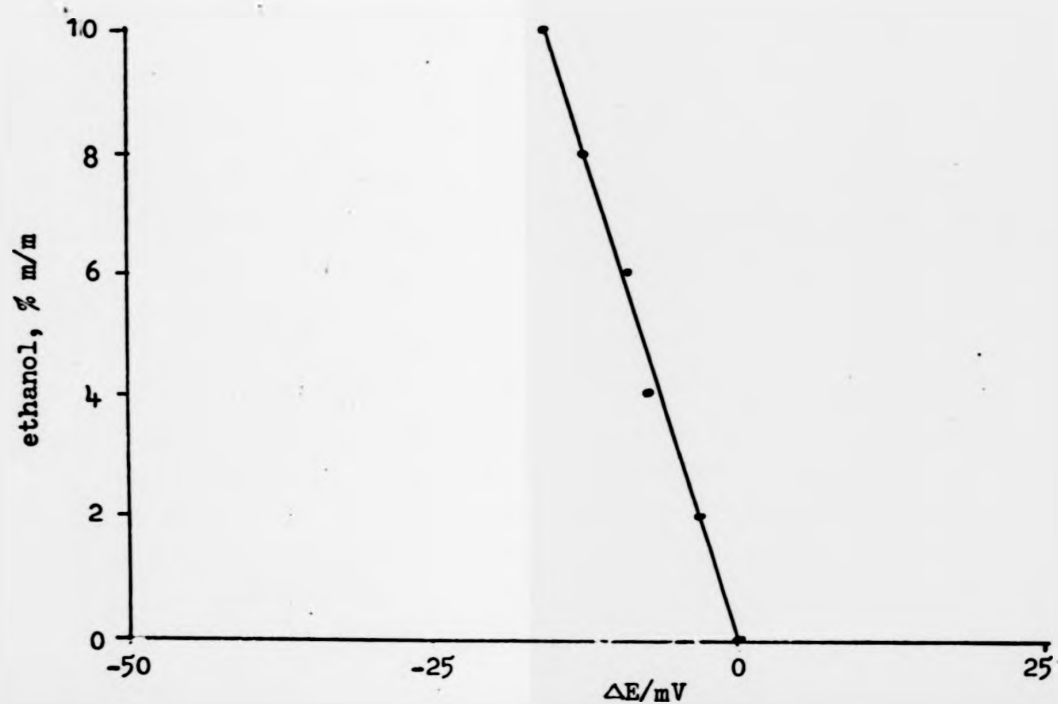


Fig. 128 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

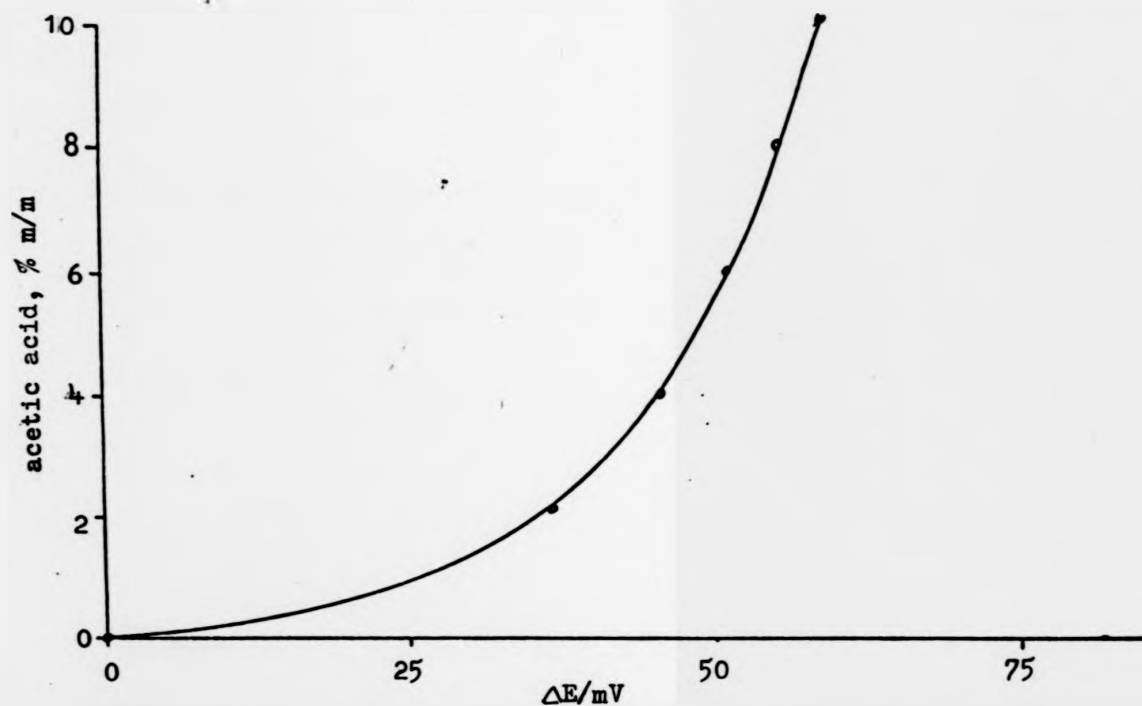


Fig.129 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

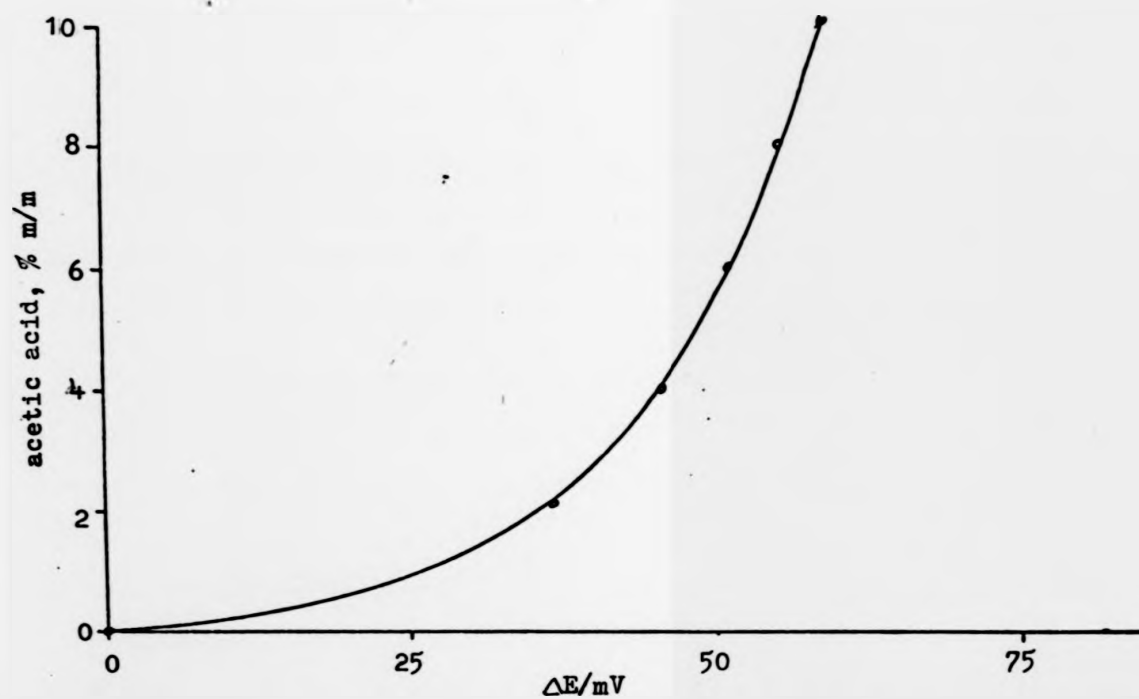


Fig.129 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

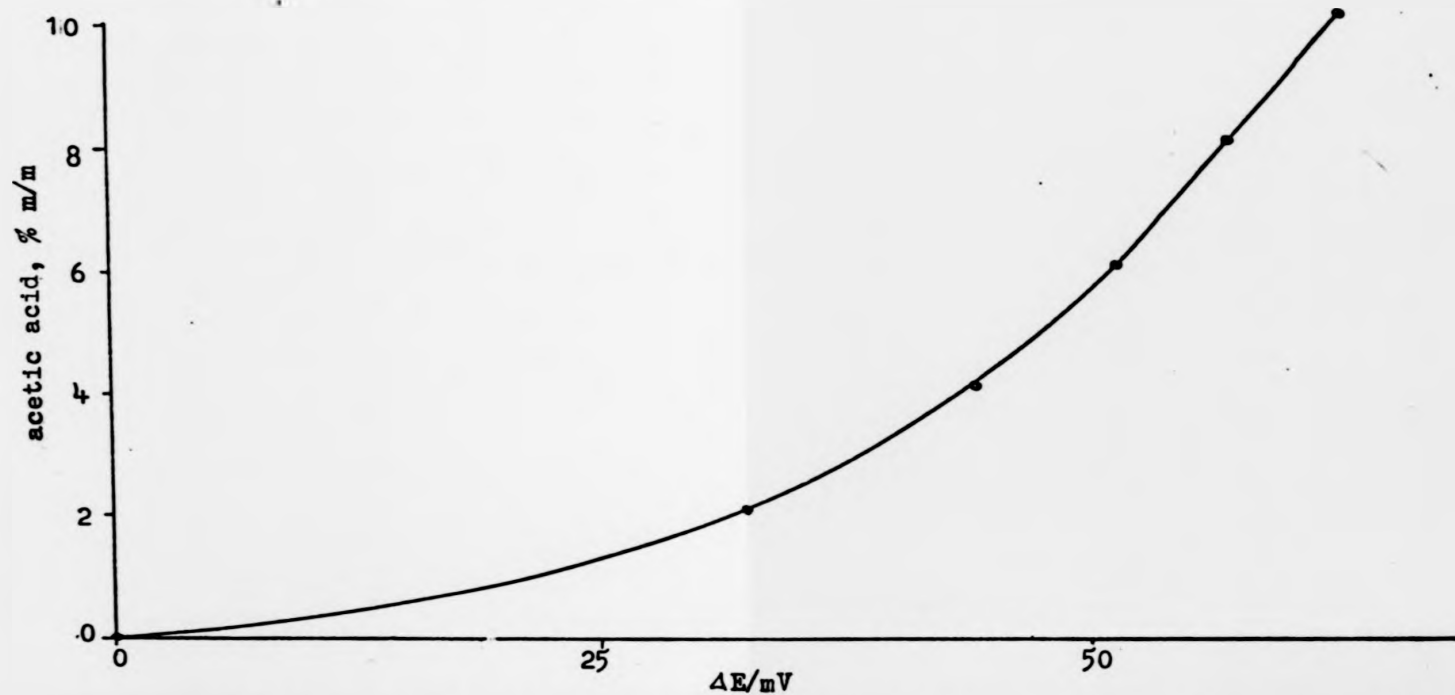


Fig.130 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and SCE electrodes.

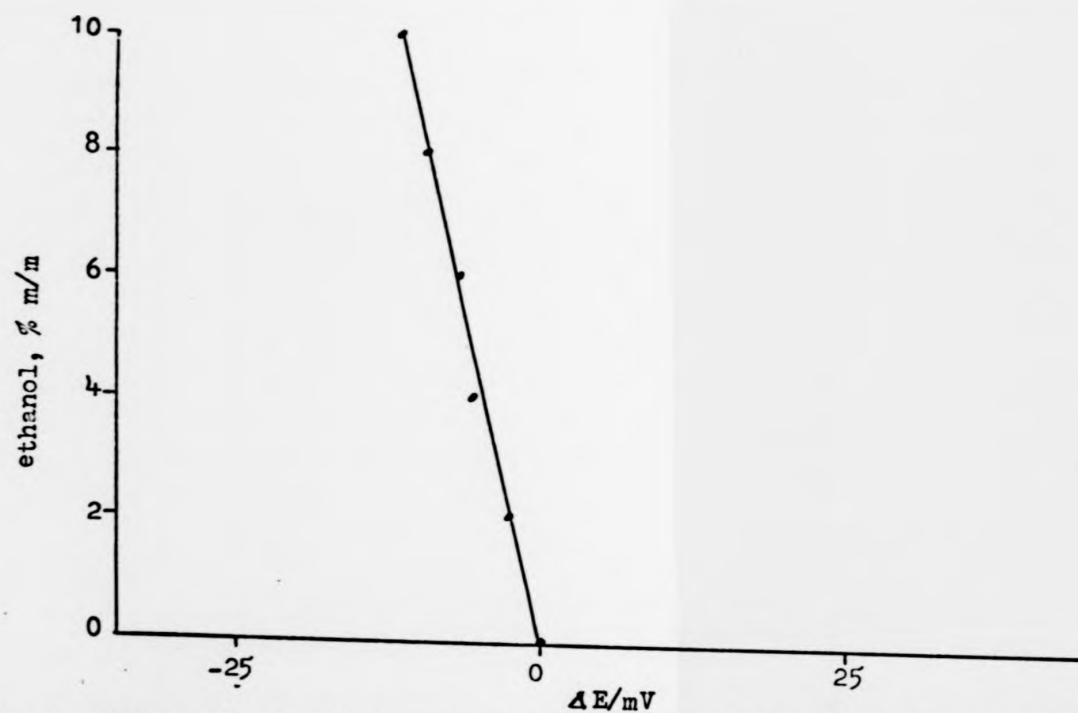


Fig. 131 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and SCE electrodes.

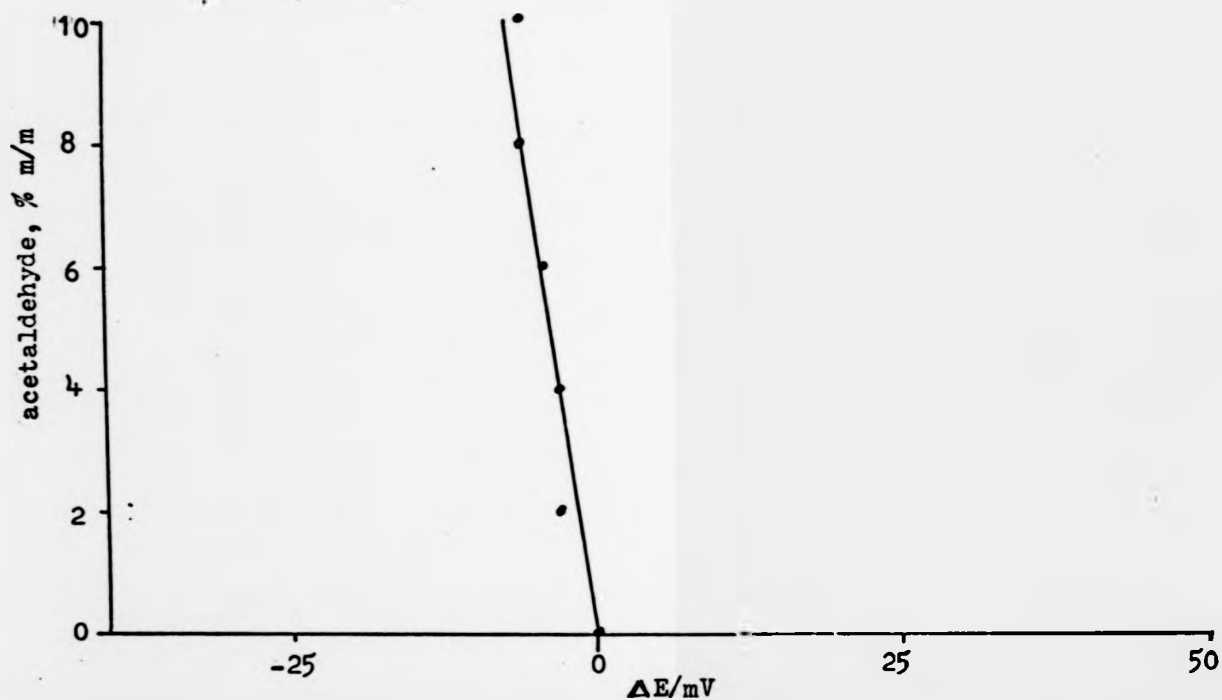


Fig. 132 Change in potential,  $\Delta E$ , for the system, NaF-acetaldehyde( $H_2O$ ), in solutions of  $10^{-3}$  M sodium fluoride and various acetaldehyde concentrations, measured by using lanthanum fluoride and SCE electrodes.



Figures 133-136 show the dual systems for some of the determinations.

The best cell systems for  $F^-$ ,  $Cl^-$  and  $Ag^+$  were further explored. Indirect measurements were made, from which calibration graphs were obtained for different solvent concentrations (0-99% m/m HOAc and EtOH). See figures 15, 16, 38 and 39 for chloride and fluoride ions.

From the calibration graphs,  $\Delta E$  values along cross sections of constant concentration of indicator ions were abstracted for different solvent concentrations, and plotted as functions of % m/m solvent. From this, it was evident that the fluoride system was the best. The resultant graphs corresponding to  $10^{-3}M$ ,  $10^{-4}M$  and  $10^{-5}M F^-$  are shown in figure 137-142.

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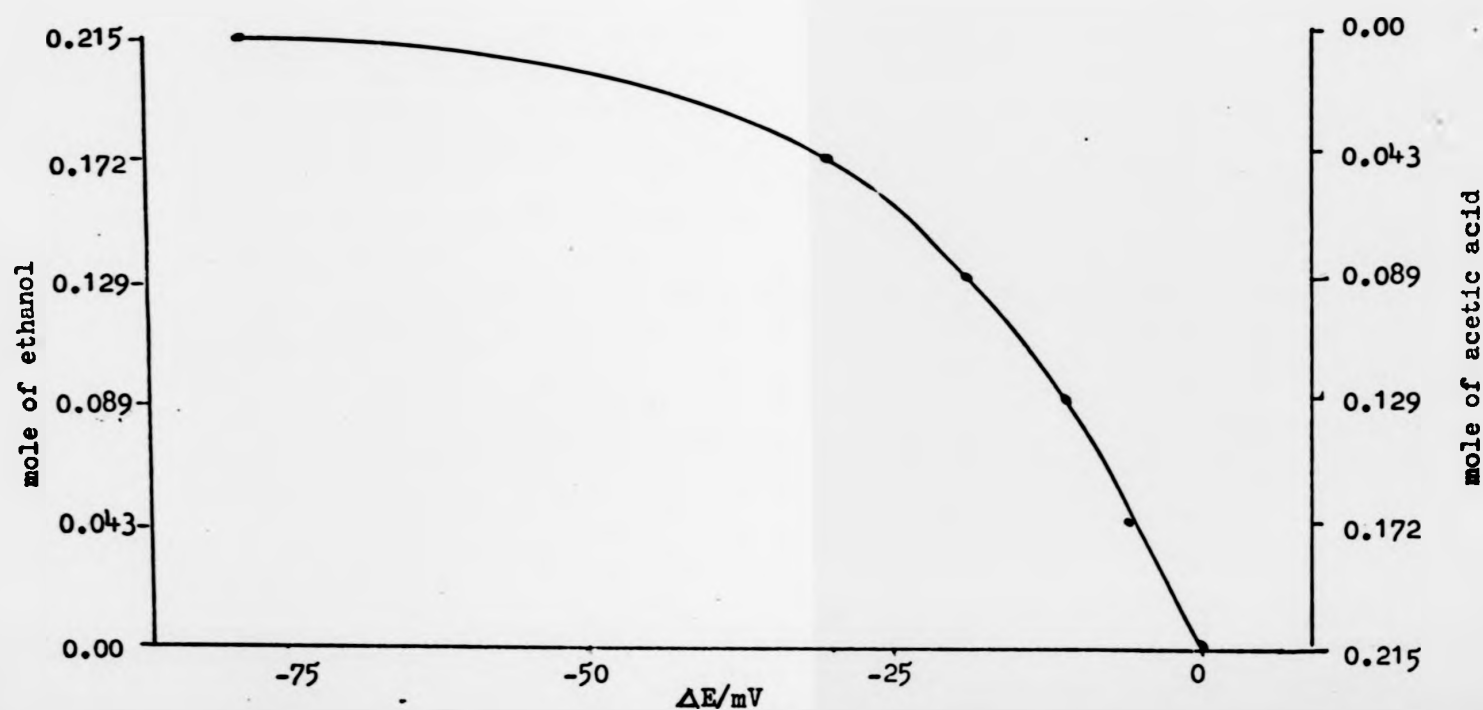


Fig.133 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol, acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

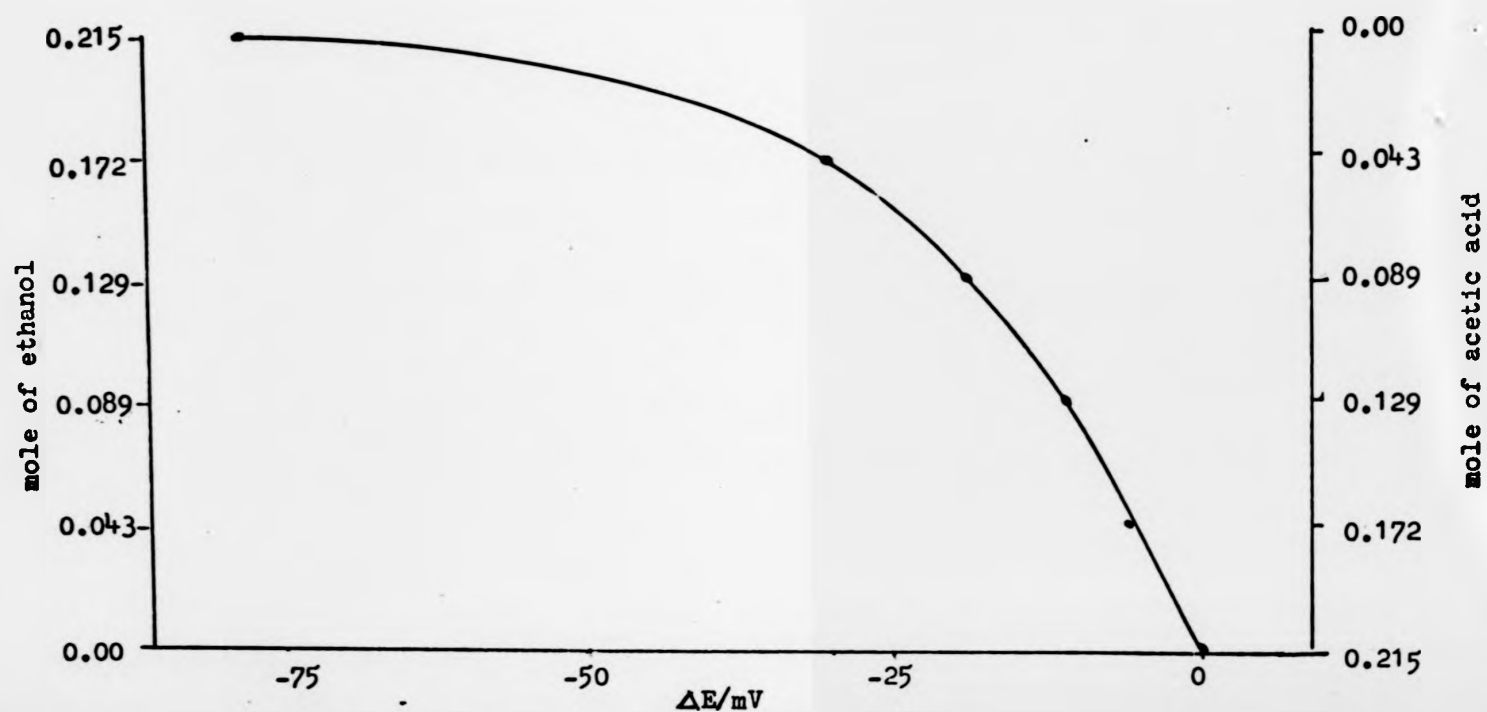


Fig.133 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol, acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

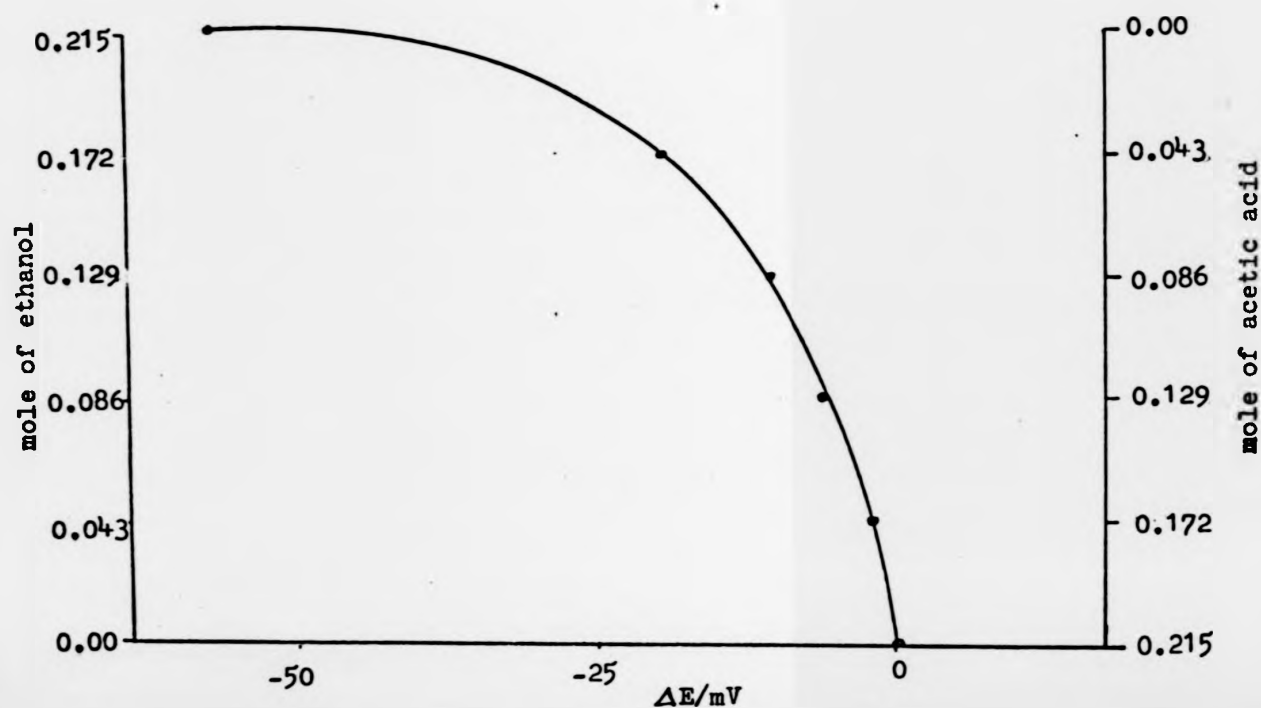


Fig.134 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol, acetic acid concentrations, measured by using lanthanum fluoride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes

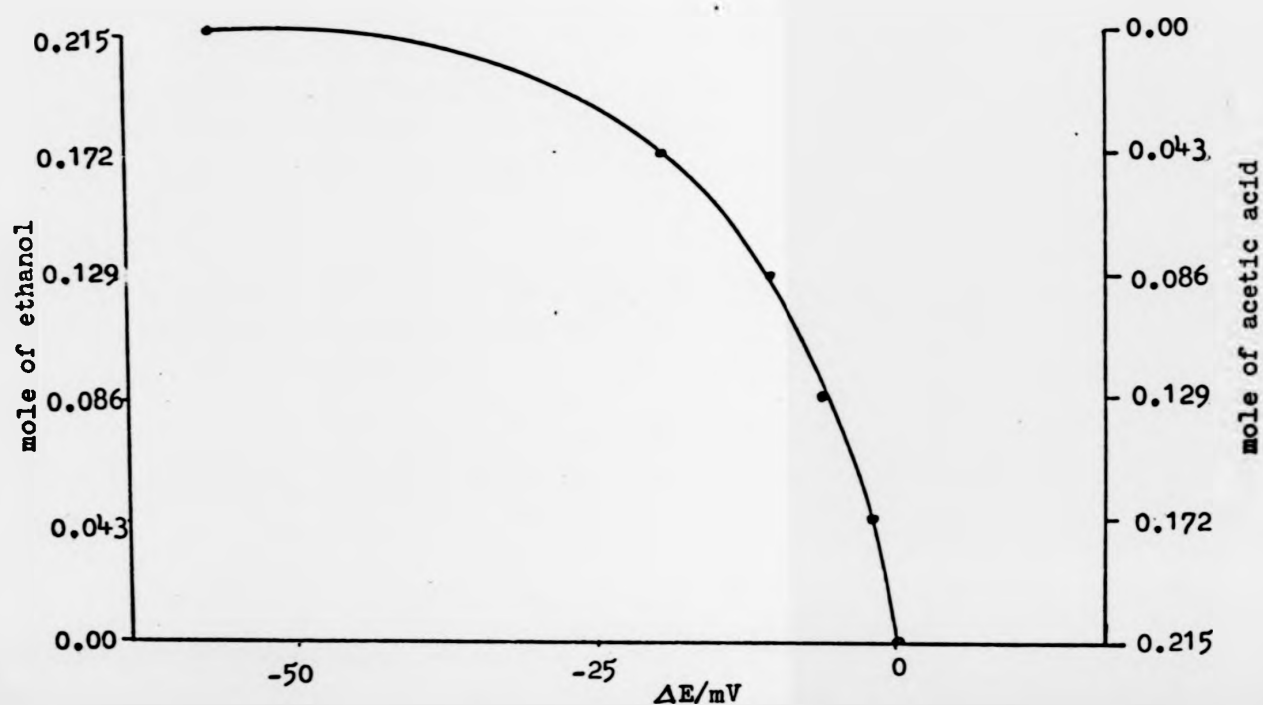


Fig.134 Change in potential,  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol, acetic acid concentrations, measured by using lanthanum fluoride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes

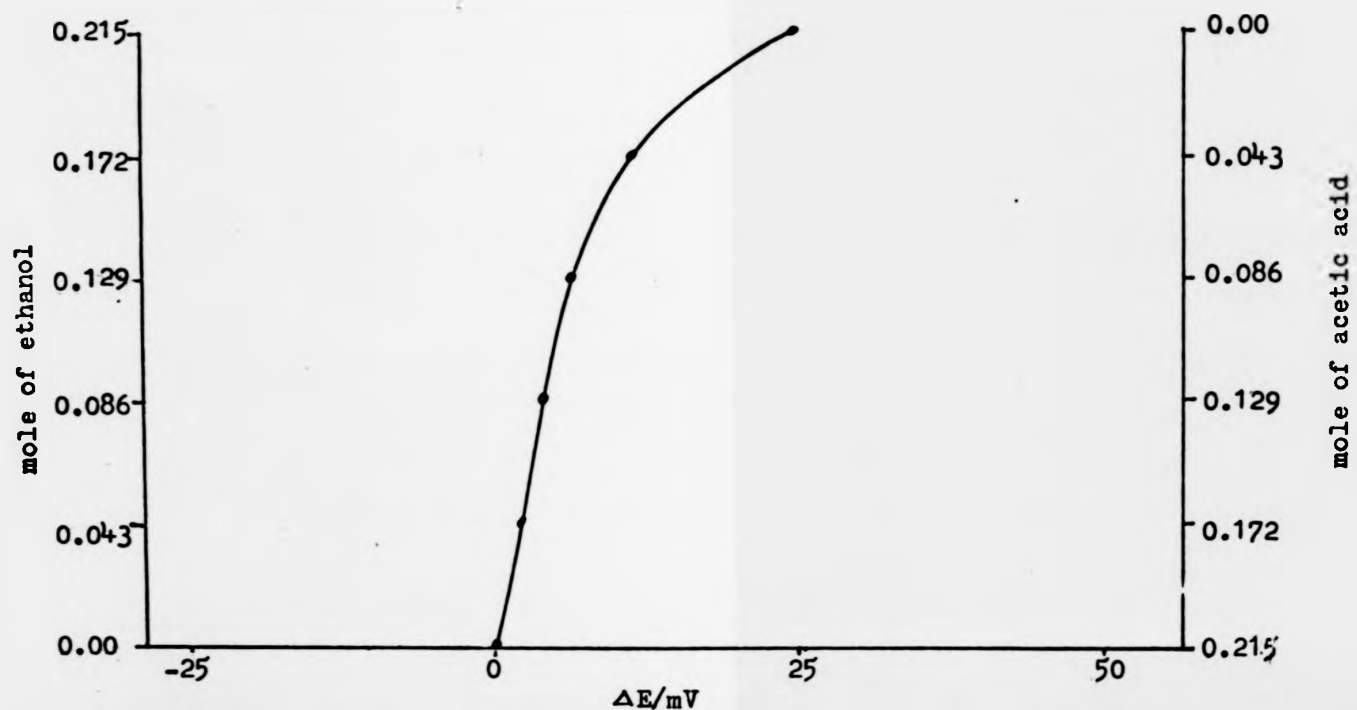


Fig.135 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various ethanol, acetic acid concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

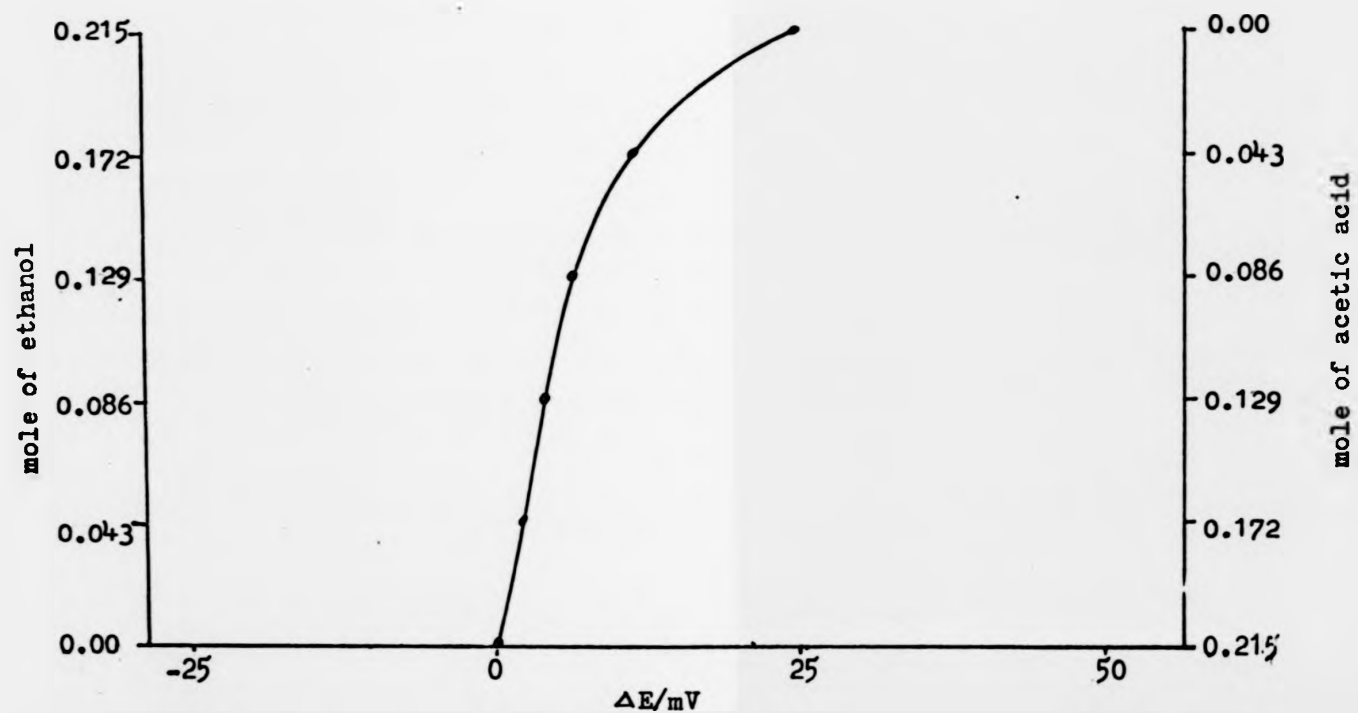


Fig.135 Change in potential,  $\Delta E$ , for the system,  $\text{NaCl}-\text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium chloride and various ethanol, acetic acid concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.



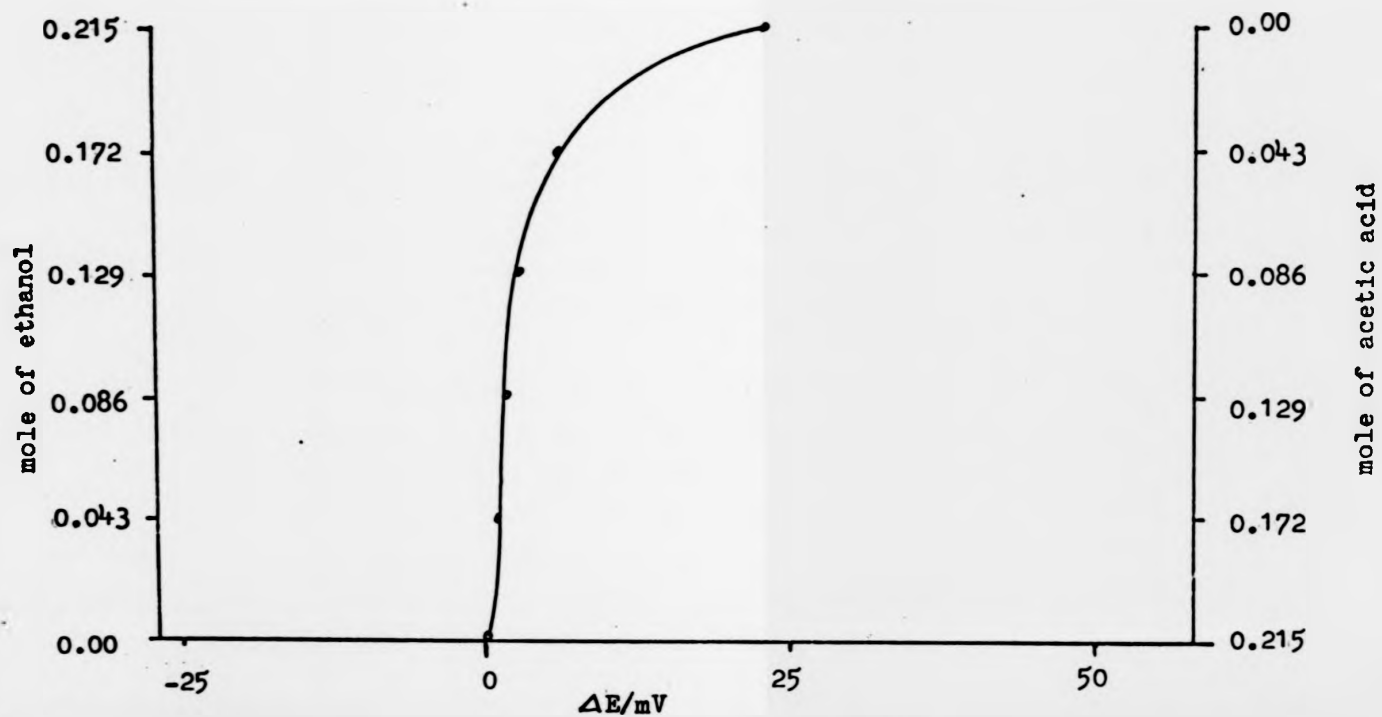


Fig. 136 Change in potential,  $\Delta E$ , for the system,  $\text{AgNO}_3 - \text{EtOH}/\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M silver nitrate and various ethanol, acetic acid concentrations, measured by using silver chloride and mercury-mercurous sulphate ( $1\text{M Na}_2\text{SO}_4$ ) electrodes.

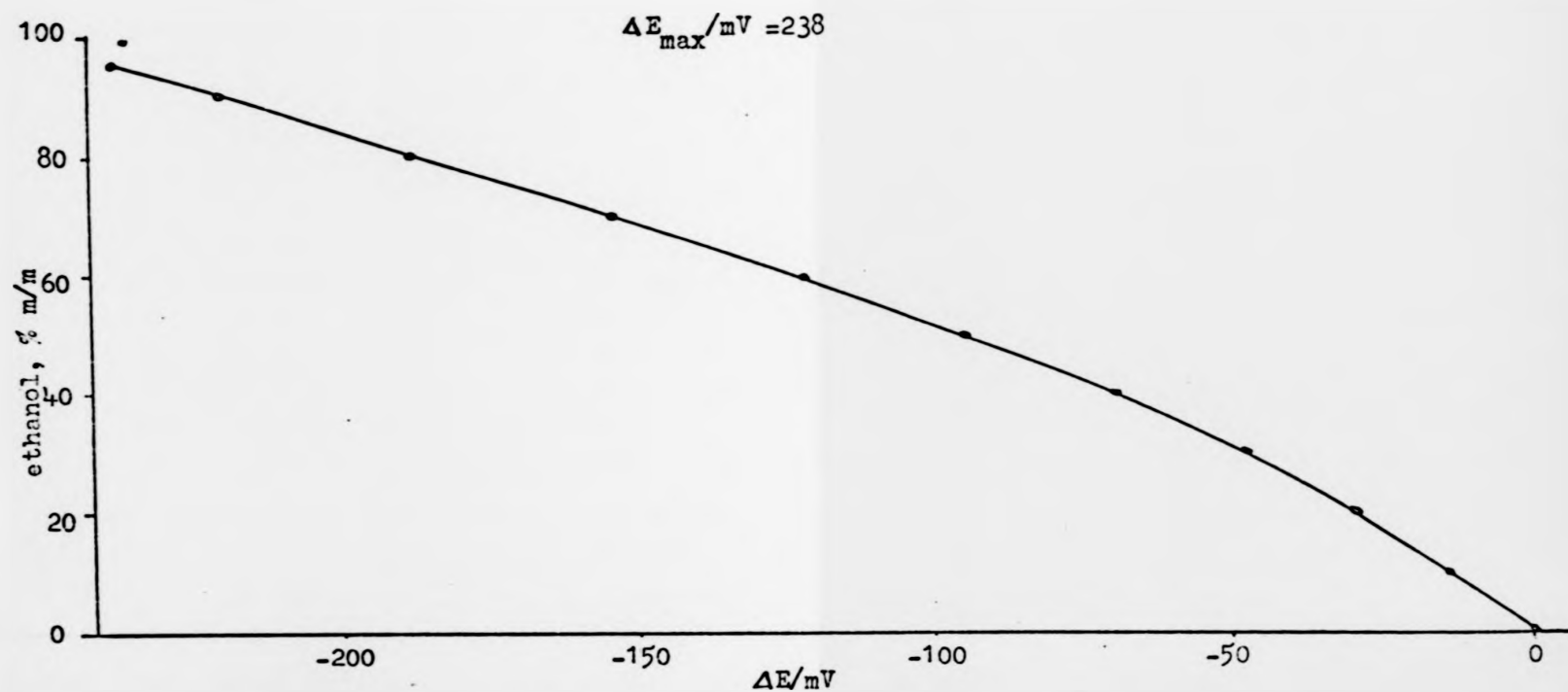


Fig.137 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system, NaF-EtOH(H<sub>2</sub>O), in solutions of 10<sup>-5</sup> M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

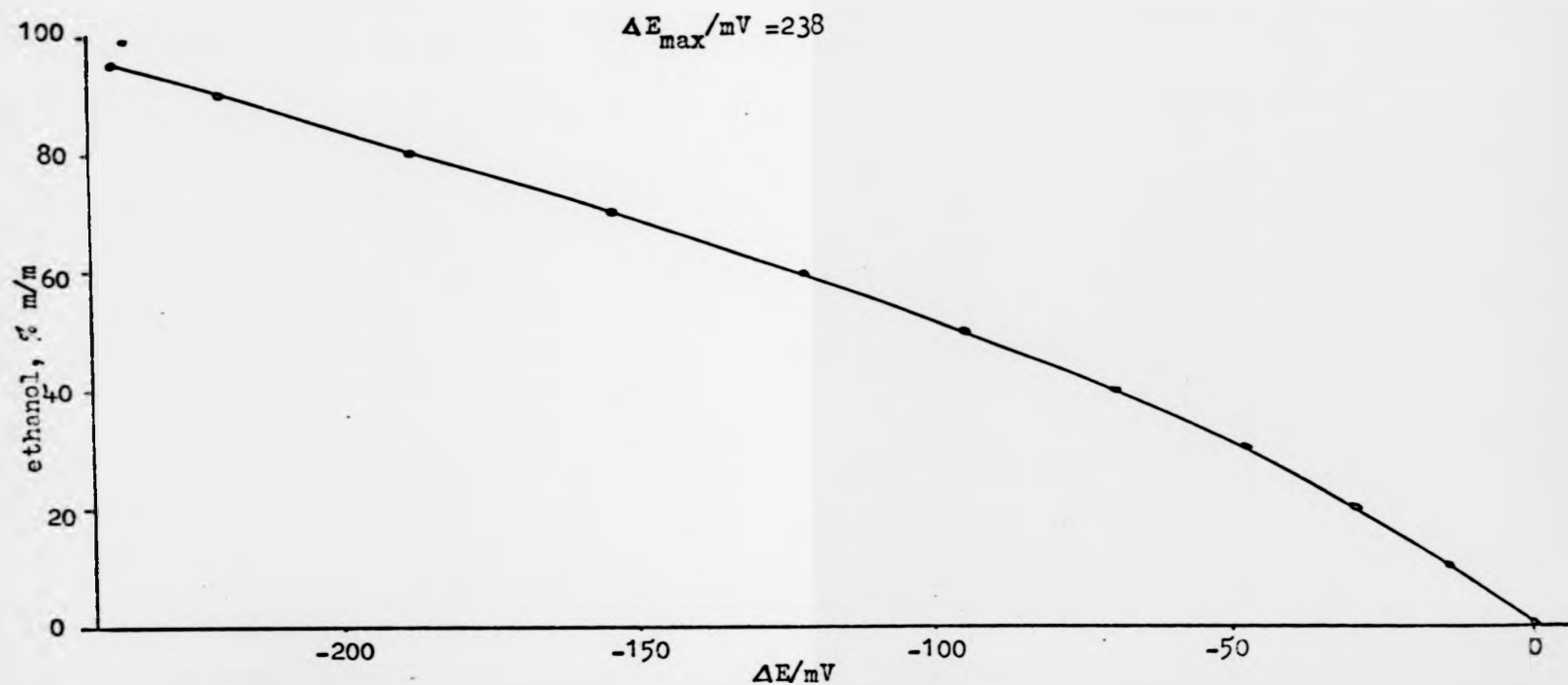


Fig.137 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-5}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

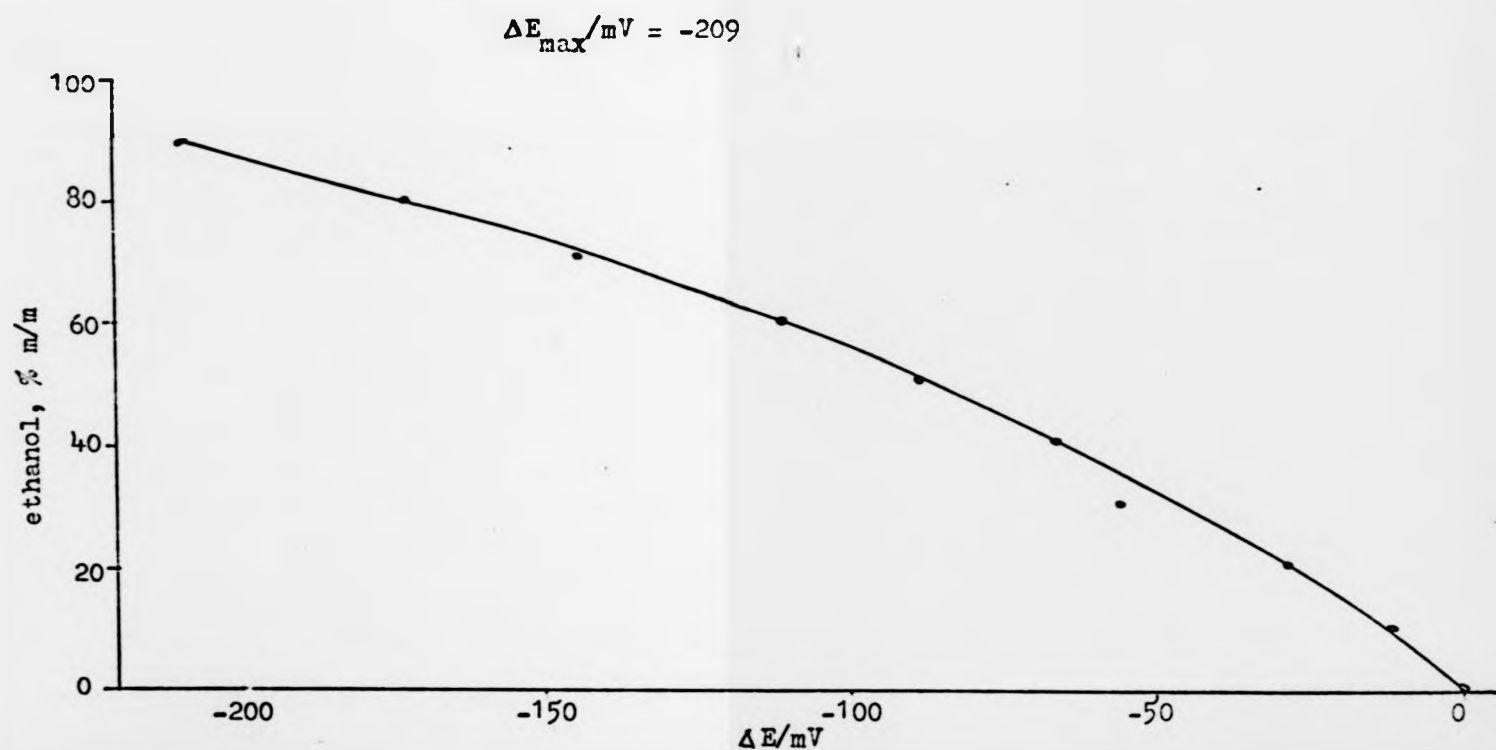


Fig.138 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

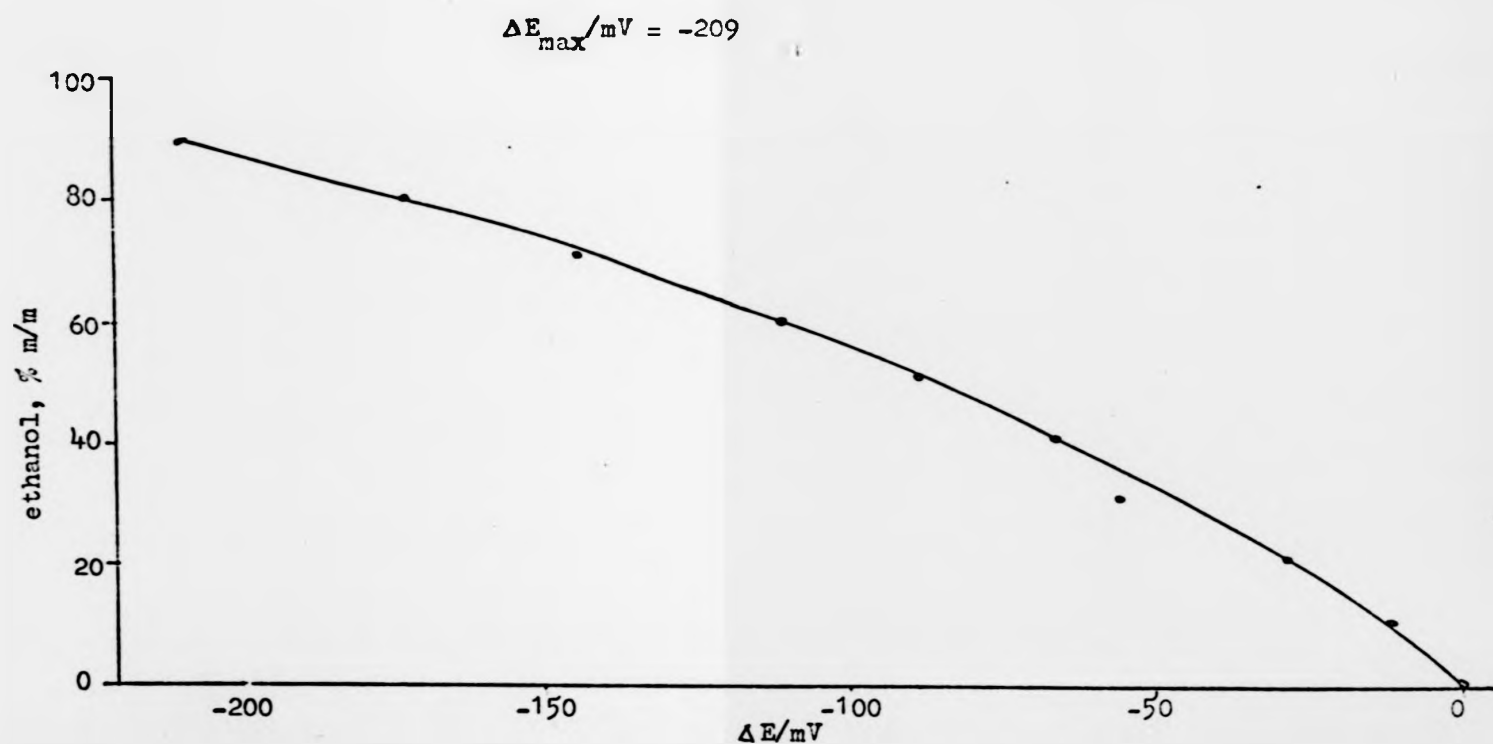


Fig.138 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

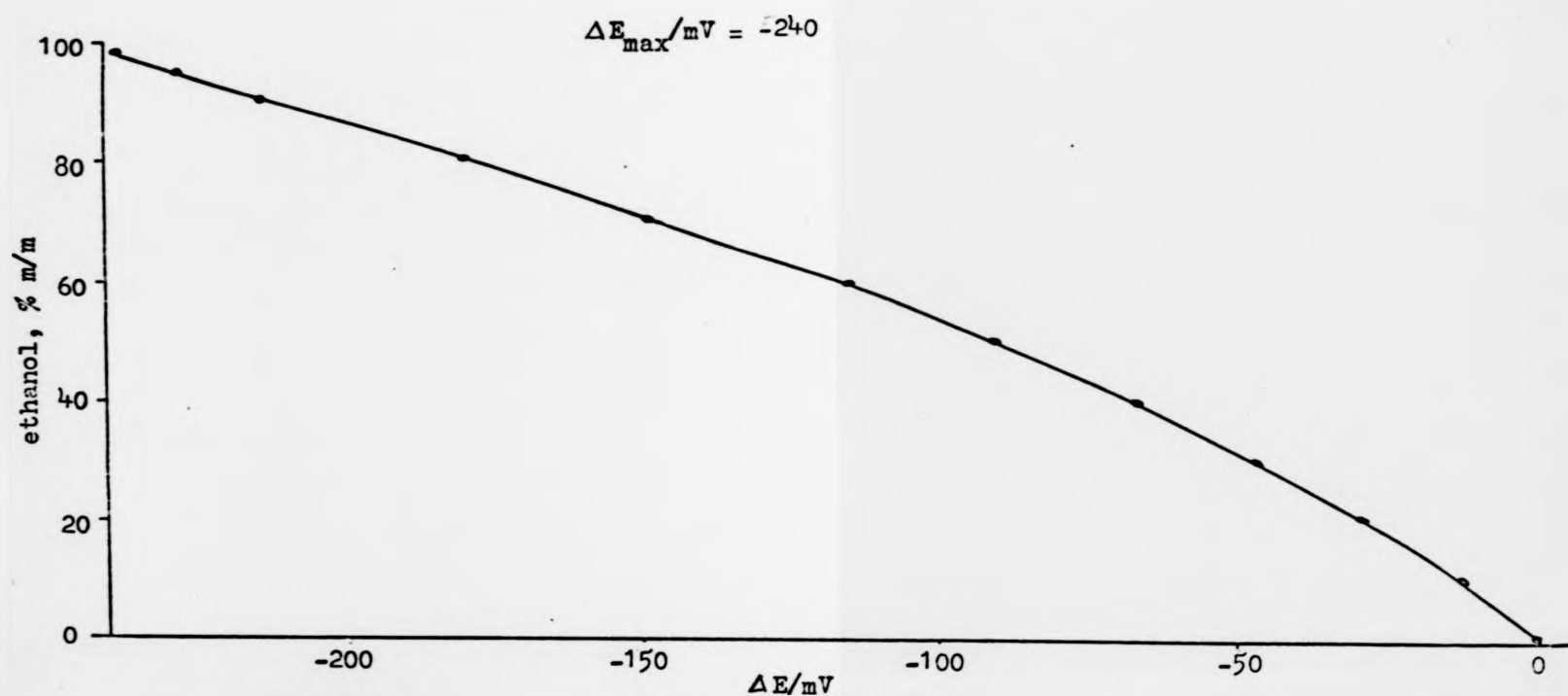


Fig.139 Change in potential (obtained from 'indirect measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-4}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

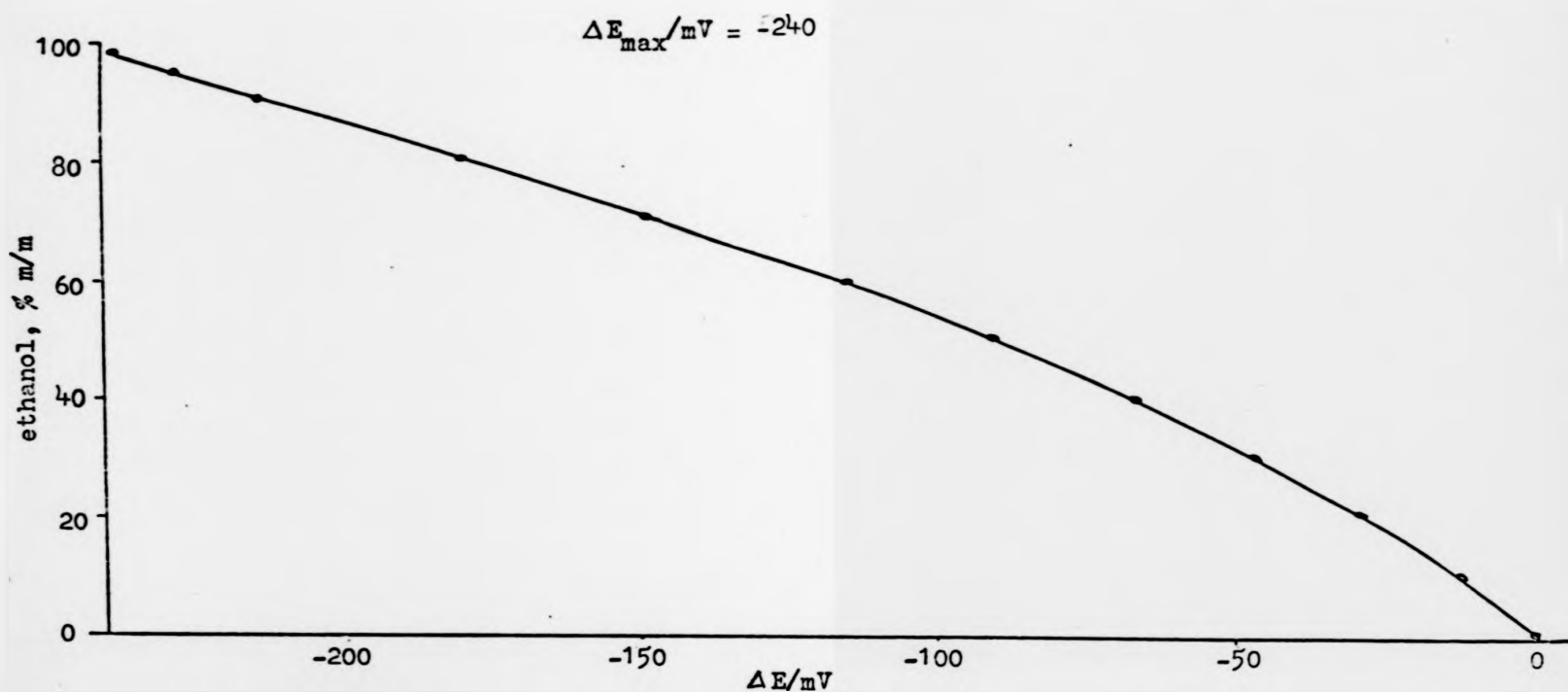


Fig.139 Change in potential (obtained from 'indirect measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{EtOH}(\text{H}_2\text{O})$ , in solutions of  $10^{-4}$  M sodium fluoride and various ethanol concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

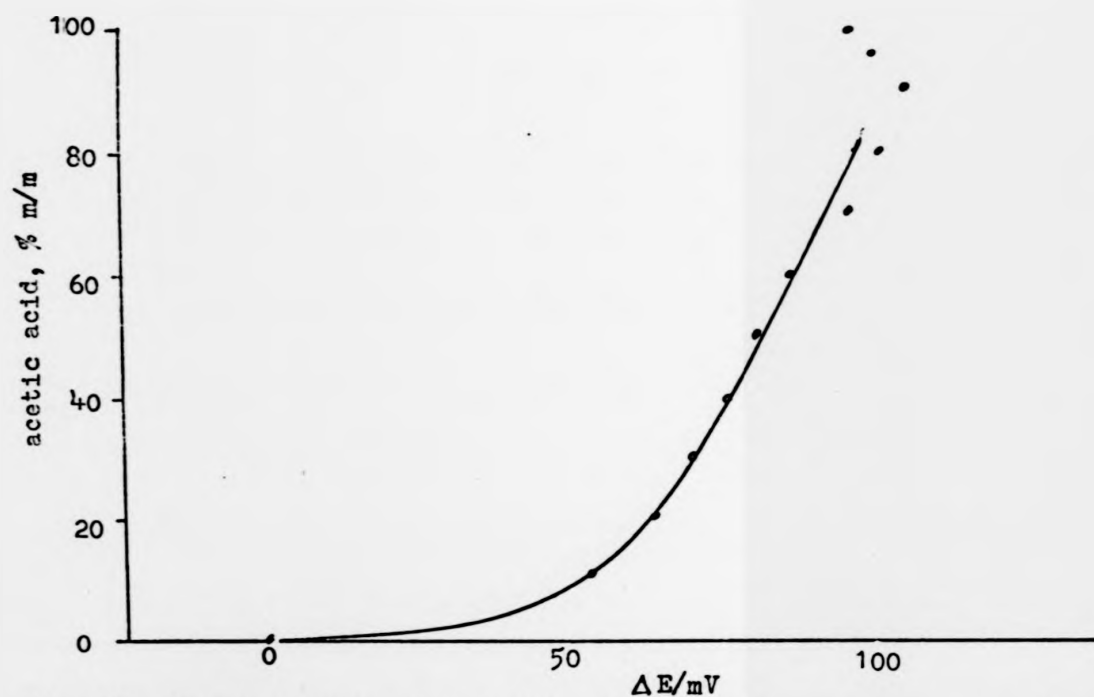


Fig. 140 Change in potential (obtained from 'indirect measurements'),  $\Delta E$ , for the system.  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-3}$  M sodium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.



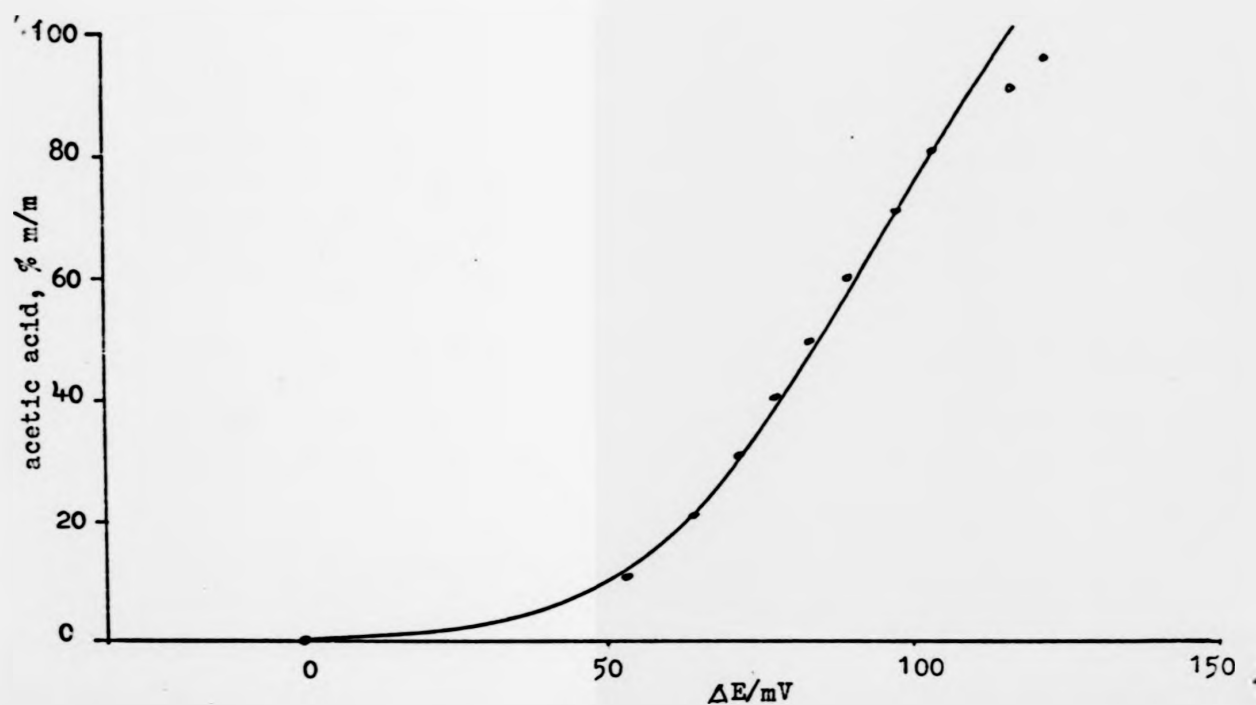


Fig.141 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system,  $\text{NaF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-4}$  M sodium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

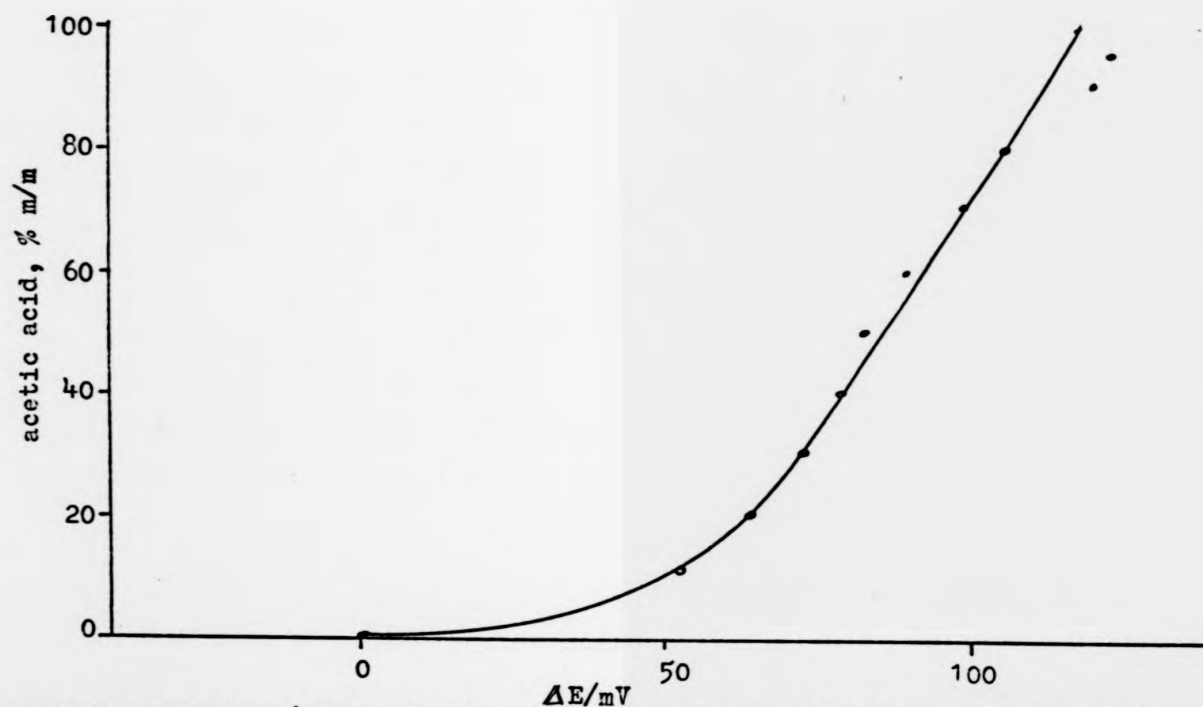


Fig.142 Change in potential (obtained from 'indirect' measurements),  $\Delta E$ , for the system,  $\text{KF}-\text{HOAc}(\text{H}_2\text{O})$ , in solutions of  $10^{-5}$  M potassium fluoride and various acetic acid concentrations, measured by using lanthanum fluoride and silver-silver chloride (single-junction) electrodes.

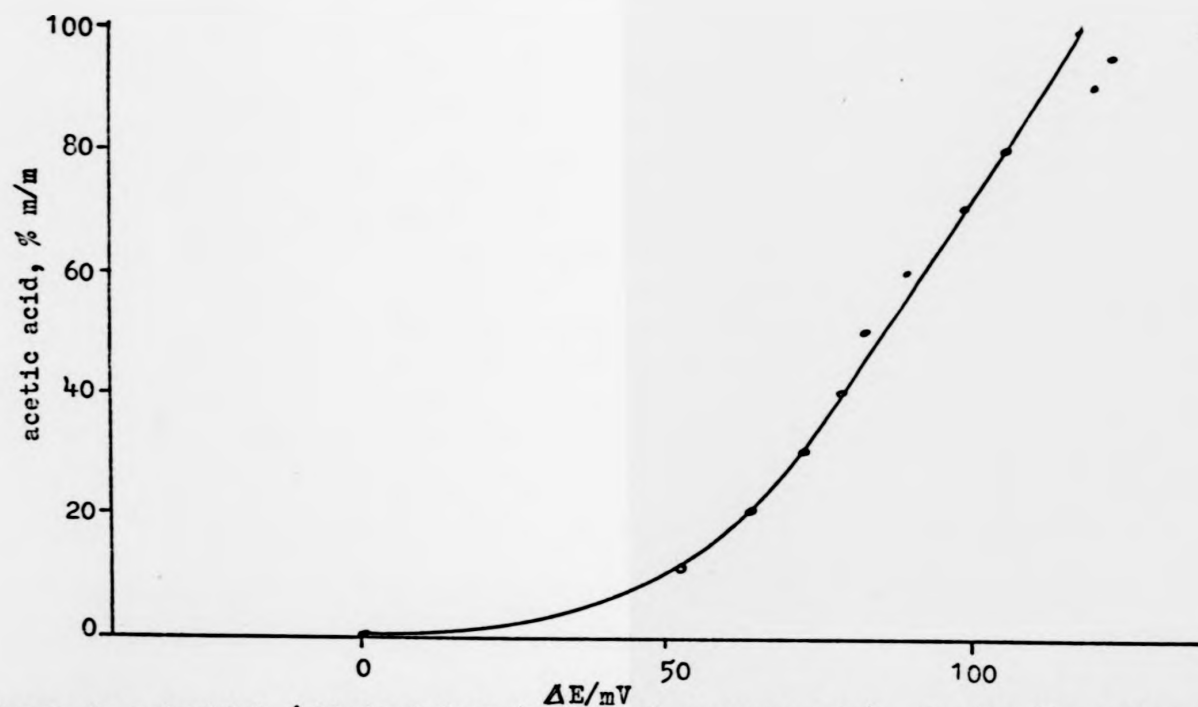


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### Recommended Condition for Measurement

The recommended condition for measurement were considered in the light of three criteria.

(1) Electrode slopes for the various systems:

As regards the slopes, it is evident that the closer the slopes are to the theoretical value, the better the understanding, and perhaps the simpler the system under investigation. Thus  $\text{LaF}_3(\text{F}^-) \text{ Ag/AgCl}_{\text{s.j.}}$  is the preferred system.

(2) Magnitude of  $\Delta E$  (change in electrode potential).

$\Delta E$  of the above cell increases negatively in ethanol-water system, with increasing concentration of ethanol, whereas it increases positively for acetic acid-water system, with increasing acetic acid concentration. This is a tremendous advantage in that a large overall (sum of the two  $|\Delta E|$ )  $\Delta E$  will be expected in a process involving quantitative conversion of ethanol to acetic acid and vice versa.

(3) Concentration of indicator ion: In the cell above, it was observed that  $\Delta E$  increases with decrease in concentration of indicator ion within the optimum range of a given organic solvent concentration in both ethanol and acetic acid. Clearly from figs. 138-142, a concentration of  $10^{-5} \text{ M F}^-$  is recommended.

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In summary, of all the systems investigated the cell  $\text{LaF}_3//\text{Ag}/\text{AgCl}_{\text{s.j.}}$  at  $10^{-5} \text{ M F}^-$  is recommended for use as monitoring system.

The method is reasonably accurate, and shows a good reproducibility.

In addition it has the advantage of simple instrumentation, and above all it is easily amenable to automation, since potential measurements can be chart-recorded.

APPENDIX 3METHANOL - AND WATER-ACETIC ACID SYSTEMS

Figures 143, and 144 show the direct plot of % m/m acetic acid as a function of change in potential,  $\Delta E$  in the acetic acid-methanol system using a pH glass electrode.

Figure 145 shows a similar plot for the acetic acid-water system.

No conscious indicator ion was added, since the inherent protons in acetic acid due to its appreciable ionization are sufficient to keep the glass electrode comfortable in the system.

Figure 143 and 144 were obtained by using SCE(LiCl) and silver-silver chloride (double-junction), respectively as reference electrodes. A close similarity is shown between the two figures with only a slight difference in the overall  $\Delta E_{\text{max}}$ . A striking feature is the remarkable linearity of the plot from about 10-99% m/m acetic acid with  $\Delta E = 200$  mV within this concentration range. Evidently this will be very useful analytically for determining acetic acid-methanol mixture in this interval when dealing with a strictly binary acetic acid mixture.

Figure 145 is the corresponding plot in the water-based system. A comparison of this figure with figure 144 shows that there is a loss of linearity in the former, but both have comparable  $\Delta E$  values.

$$\Delta E_{\max}/\text{mV} = 394.6$$

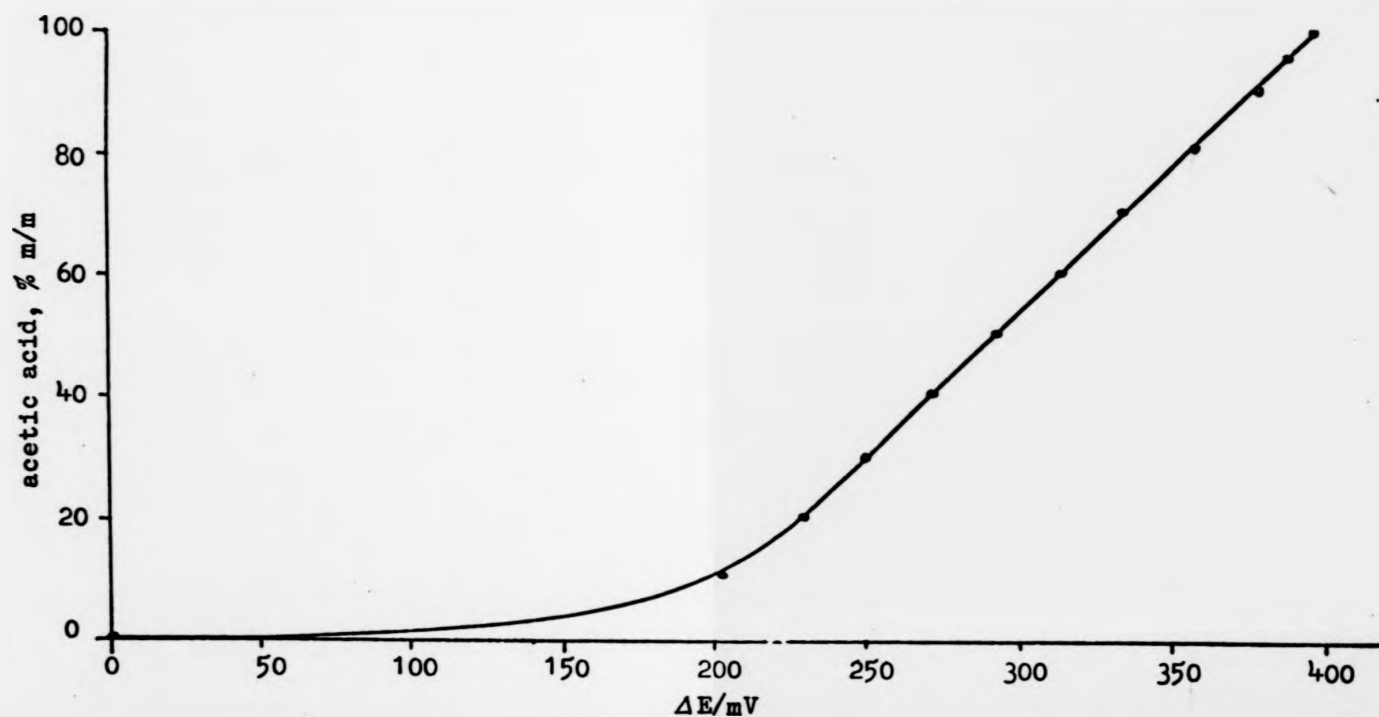


Fig.143 Change in potential,  $\Delta E$ , for the system;  $\text{HOAc}(\text{MeOH})$ , in solutions, of various acetic acid concentrations, measured by using pH glass and  $\text{SCE}(\text{LiCl})$  electrodes.



$$\Delta E_{\max}/\text{mV} = 376.6$$

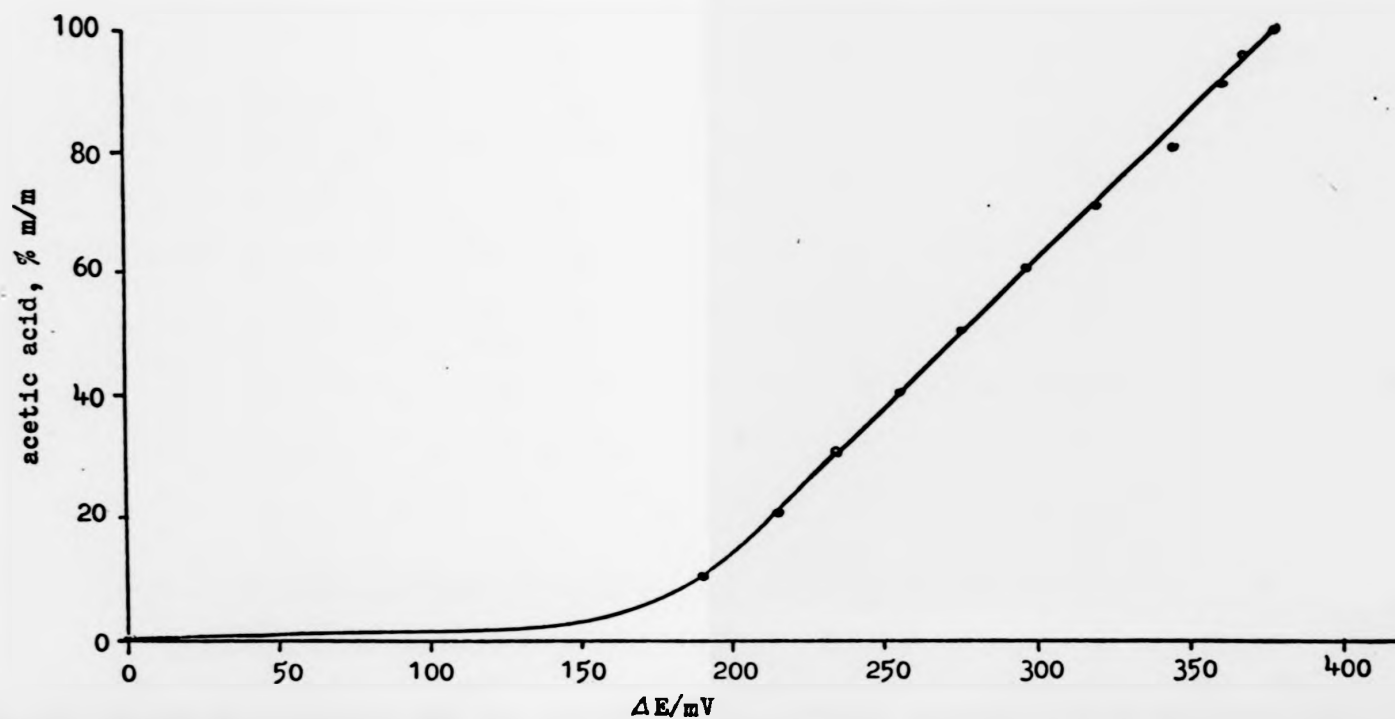


Fig. 144 Change in potential,  $\Delta E$ , for the system,  $\text{HOAc}(\text{MeOH})$ , in solutions of various acetic acid concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

$$\Delta E_{\max}/\text{mV} = 384$$

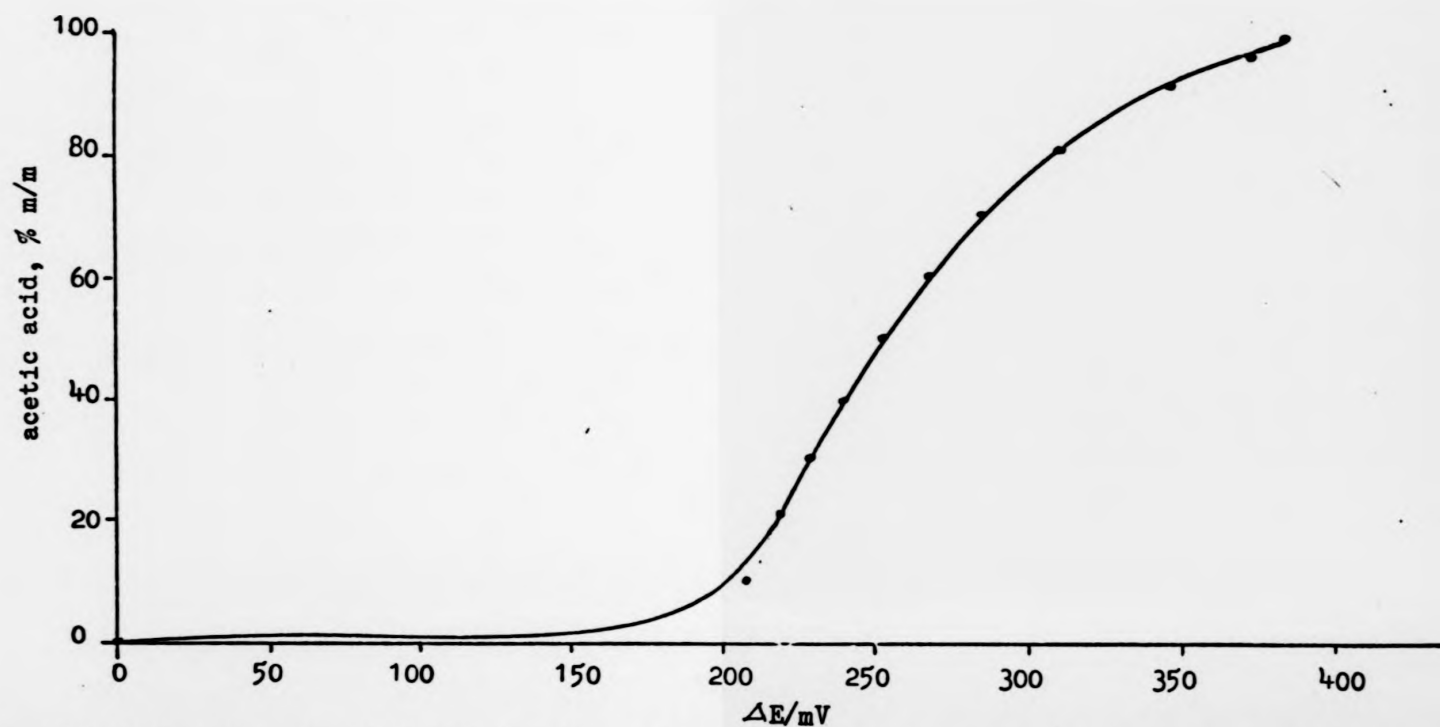


Fig. 145 Change in potential,  $\Delta E$ , for the system,  $\text{HOAc}(\text{H}_2\text{O})$  in solutions of various acetic acid concentrations, measured by using pH glass and silver-silver chloride (double-junction) electrodes.

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