

## EMF MEASUREMENTS IN NON-AQUEOUS MEDIA.

(a) STANDARD ELECTRODE POTENTIAL DETERMINATION OF THE SILVER-SILVER CHLORIDE ELECTRODE IN NON-AQUEOUS ALCOHOLIC SOLUTIONS AT 15, 20 AND 30 °C.

(b) ION PRODUCT OF ALIPHATIC ALCOHOLS AT 15, 20 AND 30 °C.

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### Summary

The standard emf of the silver-silver chloride electrode in EtOH, PrOH, i-PrOH, BuOH and i-BuOH solutions at 15, 20 and 30 °C, has been determined and its thermal coefficient computed.

The ion product of EtOH, PrOH, i-PrOH, BuOH and i-BuOH at 15, 20 and 30 °C has been evaluated. The experiments were carried out by an electrometric method, where a cell without transference, consisted of a platinum and a silver-silver chloride electrode, has been used.

**Key words** : Standard emf, silver-silver chloride electrode, hydrogen electrode, non-aqueous solvents, ion product, thermal coefficient.

### Abbreviations

R	: C <sub>2</sub> H <sub>5</sub> -, C <sub>3</sub> H <sub>7</sub> -, i-C <sub>3</sub> H <sub>7</sub> -, C <sub>4</sub> H <sub>9</sub> -, i-C <sub>4</sub> H <sub>9</sub> -	$\alpha$	: mean distance of closest approach
M	: Li, Na,	k	: $\frac{2.3RT}{F}$
I	: ionic strength	EtOH	: C <sub>2</sub> H <sub>5</sub> OH
D	: dielectric constant	PrOH	: C <sub>3</sub> H <sub>7</sub> OH
d <sub>0</sub>	: density of the pure solvent	i-PrOH	: i-C <sub>3</sub> H <sub>7</sub> OH
A'	: A.d <sub>0</sub> <sup>1/2</sup>	BuOH	: C <sub>4</sub> H <sub>9</sub> OH
B'	: B.d <sub>0</sub> <sup>1/2</sup>	i-BuOH	: i-C <sub>4</sub> H <sub>9</sub> OH

## Introduction

Whereas the ionization constant (K) of water has been determined with great accuracy and at a large extent of temperatures, small number of measurements concerning the determination of the ionization constants of solvents other than water, has been reported. This could be attributed to the big experimental difficulties which arise at the handling of non-aqueous solvents. Considering the first aliphatic alcohols, only the K of MeOH has been determined at a series of temperatures (0-45°).<sup>1</sup> The K of EtOH has been estimated at 20°,<sup>3</sup> and at 25°. <sup>2,3</sup> and of PrOH and i-PrOH at 20 and 25°. <sup>3</sup>

The method used in all cases was an electrometric one. It can be seen that the above mentioned measurements do not cover the subject of the acidic character of these solvents. In this work is presented a more systematic study of the ionization constant of aliphatic alcohols. The K of MeOH has not been redetermined, as the temperature range covered, is large. The measurements in EtOH, PrOH i-PrOH at 20° have been repeated. That way a comparison is possible which leads to conclusions about the experimental difficulties and the precautions taken. The ionization constant determined concerned the EtOH, PrOH, i-PrOH, BuOH, i-BuOH at 15,20 and 30°C.

The first part of this work is consisted of the determination of the standard electrode potential (E\*) of the silver-silver chloride electrode in each solvent and temperature.

The results obtained by different investigators appear in Table I. It is

TABLE I : Standard electrode potential of the silver-silver chloride electrode in non-aqueous aliphatic alcohols

$E_m^*$ (volt)	$t^\circ\text{C}$	solvent	ref.
-0.0098	25	MeOH	1
-0.0099	25	MeOH	5
-0.04462	25	EtOH	6
-0.0365	25	EtOH	7
-0.0883	25	EtOH	8
+0.02190	25	EtOH	9
-0.08138	25	EtOH	10
-0.079	25	EtOH	4
-0.0723	25	EtOH	3
-0.065	20	EtOH	3
-0.102	25	PrOH	3
-0.092	20	PrOH	3
-0.122	25	i-PrOH	3
-0.0995	20	i-PrOH	3

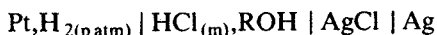
apparent that a serious discrepancy exists as to the value of  $E^*$  in EtOH.

Various systematic errors arise in the emf measurements of non-aqueous solutions. Concerning the EtOH, the most important of them, seems to be the influence of traces of water, and for that reason appears a large number of measurements in this solvent. It is reported that to attain an accuracy of 0.1 mV in  $E^*$ , the molality of water should be less than  $2 \cdot 10^{-6}$  m, practically unachievable<sup>4</sup>. Other systematic errors can be, the oxidation of solvent by the air (which has an opposite effect on the emf than the influence of traces of water) and, the reaction of EtOH with HCl. The emf of other non-aqueous cells does not depend so seriously on the traces of water. The oxidation of the solvent by the air, and the poisoning of the electrode(s) by the solvent, are other effects which may affect the accuracy of the results. Thus it seems that the difference between precision and accuracy in non-aqueous emf measurements, often is large.

From the above mentioned it is obvious that a redetermination of  $E^*$  was necessary, as the results depend highly on the way of execution of the experiment, on the kind of solvent and on the precautions taken to avoid the possible errors. So it was determined the  $E^*$  for the already mentioned alcohols at 15, 20 and 30°C. From these values can be calculated the temperature coefficient of the standard emf of the silver-silver chloride electrode in these solvents; the only available estimate appears to be in EtOH<sup>11</sup>.

## Theoretical part

(a) *Determination of the standard emf (molar), of the silver-silver chloride electrode, in HCl-abs.ROH solutions.* The cell used was :



The measured emf was corrected to one atmosphere partial pressure of the hydrogen gas. This value was called the «observed emf», and was related to the molality of the solution, with the equation

$$E = E^* - \frac{RT}{F} \ln m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} \quad (1)$$

$$E = E^* - \frac{2RT}{F} \ln m_{\pm} - \frac{2RT}{F} \ln \gamma_{\pm} \quad (1a)$$

The mean ion activity coefficient is given by the Debye-Hückel extended type equation

$$-\log \gamma_{\pm} = \frac{A (I d_0)^{1/2}}{1 + \alpha B (I d_0)^{1/2}} - \beta I \quad (2)$$

which for a single electrolyte and dilute solution reduces to

$$-\log \gamma_{\pm} = \frac{A (m d_0)^{1/2}}{1 + \alpha B (I d_0)^{1/2}} - \beta m \quad (2a)$$

A and B were calculated from the equations<sup>20</sup>

$$A = 1.82455 \cdot 10^6 (DT)^{-3/2}, \quad B = 50.2904 \cdot 10^8 (DT)^{-1/2}$$

The dielectric constants and the densities of the pure solvents at various temperatures were taken from reported values<sup>12</sup>. The value of  $\alpha$  was 3.99 Å. It was used the same value for all solvents and temperatures of this work. The parameter  $\beta$  is the «interaction coefficient». Combining equations (1a) and (2a) is obtained

$$E = E^* - 2k \log m + 2k \frac{A (m d_0)^{1/2}}{1 + \alpha B (m d_0)^{1/2}} - 2k \beta m \quad (3)$$

A quantity  $E^{*'}$  is defined by :

$$E^{*'} \equiv E + 2k \log m - 2k \frac{A' m^{1/2}}{1 + \alpha B' m^{1/2}} \quad (3a)$$

and equation (3) becomes,

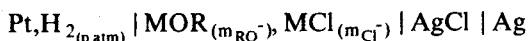
$$E^{*'} = E^* - 2k \beta m \quad (4)$$

A plot of  $E^{*'}$  against molality ( $m$ ), yields a straight line of intercept  $E^*$  on the  $m = 0$  axis, and of slope  $2k\beta$ , from which  $\beta$  can be calculated. Once  $E^*$  is known,  $\gamma_{\pm}$  can also be calculated from the equation (1a).

(b) *Determination of the ion product of aliphatic alcohols.* The ion product of an aliphatic alcohol is given by the equation

$$K = \alpha_{RO^-} \times \alpha_{ROH_2^+}$$

The galvanic cell used was of the type



where  $(m_{RO^-})$  and  $(m_{Cl^-})$ , are the molalities of the alcoxide and the chloride salt of Na or Li, respectively.

The «observed emf» is given by the equation

$$E = E^* - \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{\alpha_{Cl^-}}{\alpha_{RO^-}} \quad (5)$$

which can be also written, as,

$$E = E^* - \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{m_{Cl^-}}{m_{RO^-}} - \frac{RT}{F} \ln \frac{\gamma_{Cl^-}}{\gamma_{RO^-}} \quad (6)$$

A quantity  $E^{*''}$  is defined as

$$E^{*''} \equiv \frac{E - E^*}{k} + \log \frac{m_{Cl^-}}{m_{RO^-}} \quad (6a)$$

thus equation (6) becomes

$$E^{*''} = -\log K - \log \frac{\gamma_{Cl^-}}{\gamma_{RO^-}} \quad (7)$$

The term  $\log \frac{\gamma_{Cl^-}}{\gamma_{RO^-}}$  is directly proportional to the ionic strength<sup>13</sup>, in dilute solutions, and a plot of the  $E^{*''}$  against (I) should yield  $(-\log K)$  by linear extrapolation to infinite dilution.

## Experimental

*Cell design and apparatus.* The cell was made of Pyrex glass and was designed in a special way, so that a possible diffusion of the hydrogen gas from the hydrogen electrode to the silver-silver chloride electrode compartment, be prevented.

The electrodes were connected to the cell through ground joints, so that no contact with the air be possible. The glass cell, as well as, a presaturator bubbler for the incoming hydrogen, were immersed in a thermostat maintained at  $t \pm 0.05^\circ\text{C}$ . The cell contained about  $55 \text{ cm}^3$  of the solution and the pressaturator  $150 \text{ cm}^3$ .

The emf measurements were carried out using a Cambridge Vernier type potentiometer, equipped with a Cambridge Standard cell and a mirror type galvanometer. The precision of the system was 0.001 mV.

All density measurements of the solutions were made by a thermostated digital densitometer of Anton Paar K.G. DMA 02C Type.

*Electrodes.* The hydrogen electrodes were prepared from a platinum foil, of total area  $2 \text{ cm}^2$  and thickness  $0.015 \text{ cm}$ , which was platinized according to the Hills and Ives method<sup>14</sup>. They were washed in de-ionized water and stored in dilute hydrochloric acid solution. Before their use they were pre-soaked in an alcoholic-hydrochloric acid solution, of the same concentration to the one used. The hydrogen gas (of purity 99.999%), during a measurement, was presaturated by bubbling through a solution of the same concentration and of double volume, before passing into the electrode compartment.

An hydrogen flowing rate of one bubble per second, was maintained throughout each experiment.

The test of equilibrium was a constant emf value for one hour. It was observed that the time required for obtaining a stable emf value, was increasing with the number of measurements; that could be attributed to the electrode becoming inert. Thus a cleaning and replatinizing of the electrode surface became necessary before any new experiment.

The silver-silver chloride electrodes were of the «silver mirror» type<sup>15,16</sup>. They were prepared from a platinum foil of a total area  $2 \text{ cm}^2$  and thickness  $0.015 \text{ cm}$ , on which silver was deposited by the Rochelle salt mirror process<sup>17</sup>. The silver coating was anodized in dilute hydrochloric acid solution for 2-3 min, at a current density of  $1.0 \text{ mA.cm}^{-2}$ . A conversion of 15-25% of Ag to AgCl was achieved. This type of electrode has been used to an excellent effect<sup>18</sup>, as it is free from aging effects, very well reproduced (better than  $0.05 \text{ mV}$ )<sup>15,16</sup>. It is recommended for use in media of low dielectric constants.

The present work consists the first use of the mirror-type electrode in non-aqueous media.

In these experiments two electrodes were used, chosen from a group which showed the lowest bias potentials against an aged one. Storage was achieved by transfer to an alcoholic-hydrochloric acid solution.

Concerning the reproducibility and the long life of the electrode, the following precautions were taken :

(i) The electrodes were stored in a dark place and the experiments were carried out in a dark room, as the light could influence the percentage of the silver on the surface.

(ii) The solutions were deoxygenated before their use, by bubbling  $\text{N}_2$  gas through them, because the air dissolved could cause a slow oxidation of the silver, in the acidic solutions.

(iii) A diffusion of the hydrogen gas from the hydrogen electrode to the silver-silver chloride compartment, was hindered by a special design of the measuring cell, as the hydrogen could cause reduction of the silver in the AgCl.

The two electrodes used were frequently checked and were proved to be of an extremely good reliability, up to the end of the present work.

Thus, provided that the precautions mentioned are taken, the use of this type of electrode in low-dielectric media, is confirmed. The bias potential was very low ( $\pm 0.02 \text{ mV}$ ), and the reproducibility extremely good, as it didn't need a reparation throughout all series of experiments in this work.

## Chemicals

The starting alcohols were of pA grade. They were subject to purification by fractional distillation in an all-glass system. A Na-Hg amalgam was introduced into the distillate, so that the last traces of water be moved.

The hydrochloric acid solutions were prepared by bubbling HCl gas, directly into the alcohol in the glass vessel. Anhydrous hydrogen chloride was prepared in an all glass apparatus, by introducing concentrated sulphuric acid on sodium chloride, and dehydrated by passing through a series of glass containers with  $\text{CaCl}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{P}_2\text{O}_5$ , in order to be fully dehydrated. An amount of about  $50 \text{ cm}^3$  absolute alcohol was introduced from the distillation apparatus in the glass vessel, which was connected to the last part of the hydrogen chloride production apparatus. The gas produced was permitted to bubble in the alcohol for some minutes. Afterwards the vessel was closed and put in the thermostat. This way any contact of the solution with the air was avoided. The hydrochloric acid solutions were prepared just before their use.

The alcoxide solutions were prepared by direct addition of the metal in the absolute alcohol (Na in ethanol and Li in the other alcohols). The process took place in a glove box, in a nitrogen atmosphere. The stoke solutions were diluted in conceivable molalities and the title was determined titrimetrically. The alcoxide solutions were prepared at the same time of the experiment.

Salt, alcoholic solutions (NaCl in ethanol and LiCl in the other alcohols).

Stoke solutions were prepared by dilution of p.a. grade salt in the alcohol. The title was determined gravimetrically. The solutions were rejected every second day and new ones were prepared.

## Procedure

(a) The hydrochloric acid-abs. alcohol solution was prepared directly in the glass vessel as previously described, put in the thermostat and connected to the hydrogen gas bubblers. After some minutes of the hydrogen flow, the electrodes were introduced into the measuring cell and, emf measurements were taken every 2-3 min. Equilibrium was reached when the emf values were stable within 0.00003 volt for 60 min.

Afterwards the title of the solution was estimated by titration with a NaOH standard solution; no difference was found with the titration done before the measurement. The solutions were of random concentrations so that systematic errors to be avoided.

(b) A mixture of alcoxide and salt solution, of total ionic strength not exceeding 0.13 m, consisted the solution to be measured, for the second part of the experiments, which were carried out as previously described. Equilibrium was reached within 60 min, when the emf was stable at 0.00003 volt.

The measurement lasted 120 min. All experiments were carried out in a dark room.

## Results and Discussion

(a) The results of the emf measurements of the cell  $\text{Pt, H}_2 | \text{HCl}_{(m)}, \text{ROH} | \text{AgCl} | \text{Ag}$  are given in Table II. A typical graphical representation of the function  $E^*$ , as identified by eq.(3a), against the molality ( $m$ ) of HCl, ROH solutions, is shown in Fig. 1.

This plot should result in a straight line of zero slope, provided correct value of the parameter  $\alpha$  is chosen. As it is observed in Fig. 1 the plot gave a straight line of a very small slope, for an  $\alpha$  equal to  $3.99 \text{ \AA}$ , over the whole concentration range.

The value  $3.99 \text{ \AA}$  of  $\alpha$ , is proved to be correct for HCl-ROH solutions<sup>10</sup>, but no measurable differences in the standard potentials were obtained by using, in the present calculations, a different  $\alpha$  value which made the curve horizontal, thus confirming that the small magnitude of the slope did not decrease the accuracy of the extrapolation. The curves are drawn according to the least squares' method and, the obtained standard (molal) emfs are summarized in Table III.

The standard emfs, plotted against the absolute temperature ( $T$ ), are shown in Fig. 2. In the curve of EtOH in this Fig., a value at  $10^\circ\text{C}$  is placed ( $-0.0313 \text{ v}$ ) taken from an unpublished work of the author, which fits very well in the graph. From this representation the thermal coefficient  $\frac{(\partial E^*)}{(\partial T)}$  of the standard emf is obtained, which appears to exceed a stable value for all alcohols within  $\pm 0.0004 \text{ volt K}^{-1}$ .

To compare the  $E^*$  values in EtOH appearing in this work with those in references, an interpolated value at  $25^\circ$  is obtained from Fig. 2, which is  $-0.067 \text{ volt}$ .

This is more negative than the ones of Harned and Fleysher<sup>6</sup>, and Lucasse<sup>7</sup>, and less negative than those of Taniguchi and Janz<sup>10</sup>, Woolcock and Hartley<sup>8</sup>, Schaal and Teze<sup>3</sup>, LeBas and Day<sup>4</sup>. The  $E^*$  in PrOH and *i*-PrOH at  $20^\circ$  deviate from those of Schaal and Teze<sup>3</sup>, being more negative about  $0.005 \text{ volt}$ .

(b) The results of the emf measurements of the cell  $\text{Pt, H}_2 | m_{\text{RO}^-}, m_{\text{Cl}^-}, \text{ROH} | \text{AgCl} | \text{Ag}$  are given in Table IV, together with the ionic strength ( $I = m_{\text{RO}^-} + m_{\text{Cl}^-}$ ) of the solution.

A typical graphical representation of the function  $E^*$  as identified by eq.(6a), against  $I$ , is given in Fig. 3. The extrapolated values ( $pK$ ), as well as the  $K$  values calculated from them, are summarized in Table V. Comparing the  $K$  of EtOH at  $20^\circ$  with the one of Schaal and Teze<sup>3</sup>, a discrepancy is noticed ( $pK = 18.95$ ) whereas a fairly good agreement is observed for  $K$  of PrOH and *i*-PrOH at the same temperature ( $pK = 19.33$  and  $20.73$  respectively).



TABLE II : EMF readings of the cell:  $\text{Pt, H}_{2(\text{p atm})} | \text{HCl}_{(\text{m})}, \text{ROH} | \text{AgCl} | \text{Ag}$ , at various molalities, at 15, 20, 30 °C.

t (°C)	EtOH			i-PrOH			BuOH			i-BuOH		
	m (mol kg <sup>-1</sup> )	E (volt)	m (mol kg <sup>-1</sup> )	E (volt)	m (mol kg <sup>-1</sup> )	E (volt)	m (mol kg <sup>-1</sup> )	E (volt)	m (mol kg <sup>-1</sup> )	E (volt)	m (mol kg <sup>-1</sup> )	E (volt)
15	0.0013	0.28970	0.0006	0.29010	0.0039	0.20502	0.0043	0.18063	0.0143	0.13630	0.0266	0.12102
	0.0025	0.26690	0.0012	0.25680	0.0214	0.14700	0.0330	0.11650	0.0290	0.11487	0.0452	0.10200
	0.0104	0.20311	0.0062	0.19349	0.0223	0.14698	0.0375	0.11200	0.0509	0.09700	0.0733	0.08801
	0.0152	0.18990	0.0271	0.13802	0.0450	0.12608	0.0590	0.10003	0.0811	0.08780	0.10383	
	0.0248	0.17193	0.0476	0.12153	0.0765	0.11282	0.0811	0.08780				
	0.0259	0.17030	0.0886	0.10002	0.1030	0.10383						
20	0.0012	0.29248	0.0062	0.18400	0.0065	0.17828	0.0075	0.15950	0.0143	0.13301	0.0200	0.11781
	0.0068	0.22350	0.0130	0.15688	0.0159	0.15150	0.0186	0.13220	0.0247	0.11520	0.0290	0.10200
	0.0088	0.20852	0.0270	0.13350	0.0196	0.14403	0.0265	0.11813	0.0541	0.09111	0.0733	0.08801
	0.0119	0.19502	0.0471	0.11110	0.0208	0.14227	0.0650	0.09347	0.0290	0.11200		
	0.0213	0.17590	0.0509	0.10772	0.0454	0.11600	0.0920	0.08303				
			0.0610	0.10128	0.0765	0.10400						
30	0.0018	0.26170	0.0031	0.19980	0.0063	0.17277	0.0137	0.13703	0.0010	0.20700	0.0055	0.15279
	0.0029	0.23980	0.0107	0.15302	0.0079	0.16650	0.0156	0.12748	0.0204	0.11331	0.0291	0.10690
	0.0032	0.23420	0.0200	0.12750	0.0082	0.16420	0.0336	0.10600	0.0291	0.10690	0.0542	0.08602
	0.0134	0.17161	0.0295	0.11902	0.0210	0.13349	0.0530	0.09400	0.0291	0.10690		
	0.0212	0.15550	0.0722	0.08500	0.0298	0.12401	0.0598	0.09002				
	0.0232	0.15321			0.0764	0.09790						

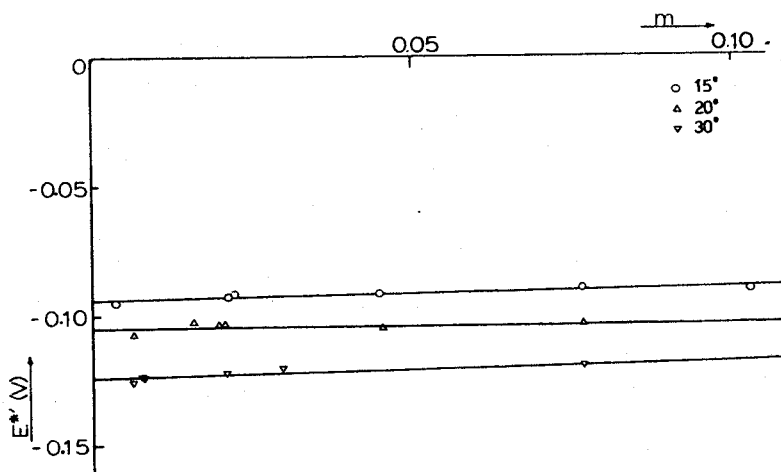


FIG. 1 : Graphical representation of the  $E^*$  against molality, for HCl-abs.i-PrOH solutions, and evaluation of the standard emf  $E_{(m)}$  of the silver-silver chloride electrode in i-PrOH solutions, at 15,20,30 °C.

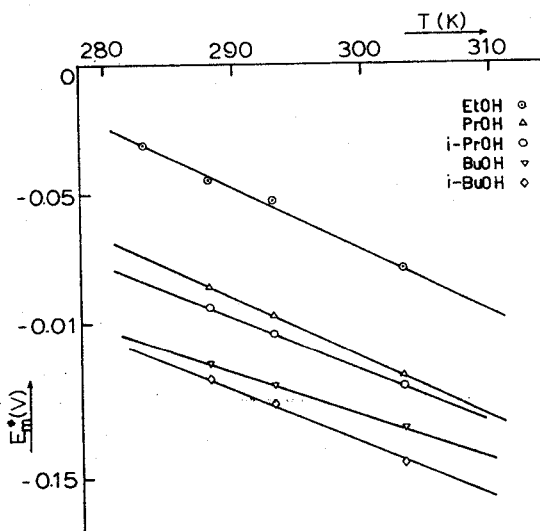


FIG. 2 : Standard electrode potentials of the silver-silver chloride electrode, in various alcoholic solutions, plotted as a function of temperature.

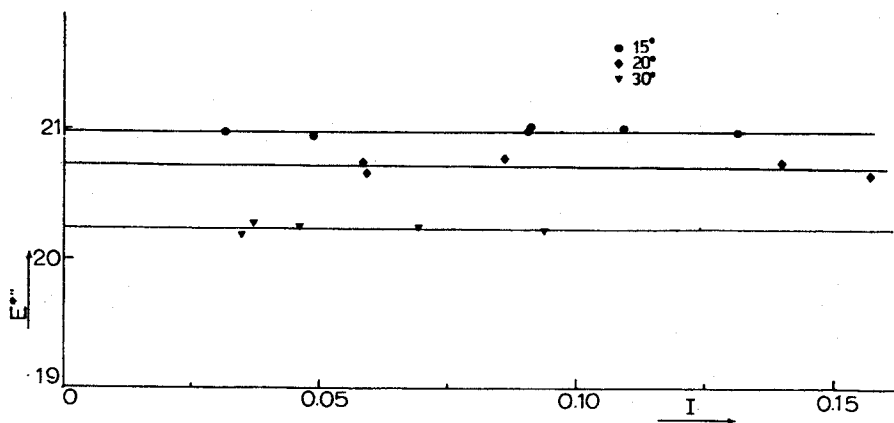


FIG. 3 : Graphical representation of the  $E_m^*$  against the ionic strength of a LiCl, *i*-PrOLi, abs. *i*-PrOH solution, and evaluation at the  $I=0$  axis of the  $pK$  of *i*-PrOH at 15, 20, 30 °C.

TABLE III : Standard EMF ( $E_m^*$ ) in molality scale of the silver-silver chloride electrode in HCl-alcoholic solutions, and its thermal coefficient

$t^\circ$	EtOH	PrOH	<i>i</i> -PrOH	BuOH	<i>i</i> -BuOH
15	-0.04496	-0.08630	-0.09432	-0.11590	-0.12172
20	-0.05250	-0.09715	-0.10484	-0.12498	-0.13159
30	-0.07938	-0.12117	-0.12459	-0.14153	-0.15526
$\frac{(\partial E_m^*)}{(\partial T)}$ (voltK <sup>-1</sup> )	-0.00244	-0.00239	-0.00210	-0.00173	-0.00210

In Fig. 4, the  $pK$  values are plotted against the absolute temperature, and it is observed that, as was expected, the  $pK$  decreases with the temperature.

At constant temperature, a gradual drop of the  $K$  values (an increase in  $pK$ ), is observed, as the chain of the molecule gets longer, with the exception of *i*-PrOH, which deviates towards the smallest value.

The order they follow is,  $K_{EtOH} > K_{PrOH} > K_{BuOH} > K_{i-BuOH} > K_{i-PrOH}$ . This could be explained considering two factors which mainly affect the acidity of the alcohols, making them less acidic than water:

The inductive effect, which alkyl groups, replacing an H atom of the molecule, display, and the magnitude of the dielectric constant of the molecule.

TABLE IV : EMF readings of the cell:  $\text{Pt, H}_2(\text{p atm}) | \text{MOR}(\text{mRO}), \text{MCl}(\text{mCl}), \text{ROH} | \text{AgCl} | \text{Ag}$ , at various ionic strengths (I = mRO + mCl) at 15, 20 and 30 °C.

t (°C)	EtOH			PrOH			i-PrOH			BuOH			i-BuOH			
	I	E	E	I	E	E	I	E	E	I	E	I	E	E	I	E
	(mol kg <sup>-1</sup> )	(V)	(V)	(mol kg <sup>-1</sup> )	(V)	(V)	(mol kg <sup>-1</sup> )	(V)	(V)	(mol kg <sup>-1</sup> )	(V)	(mol kg <sup>-1</sup> )	(V)	(V)	(mol kg <sup>-1</sup> )	(V)
	0.049	1.02280	1.01352	0.0219	1.01352	1.08002	0.0315	1.08002	1.01188	0.0299	1.01188	0.0189	1.01188	0.99511	0.0189	0.99511
	0.0489	1.02517	1.02000	0.0238	1.02000	1.05590	0.0484	1.05590	1.01600	0.04376	1.01600	0.0320	1.01600	1.00610	0.0320	1.00610
	0.0611	1.03191	1.02501	0.0426	1.02501	1.00510	0.0909	1.00510	1.02311	0.0453	1.02311	0.0322	1.02311	0.99000	0.0322	0.99000
	0.0785	1.04921	1.03000	0.0472	1.03000	1.04403	0.1091	1.04403	1.01802	0.0747	1.01802	0.0402	1.01802	0.96521	0.0402	0.96521
	0.1237	1.03900	0.99200	0.0597	0.99200	0.98600	0.1313	0.98600	0.98900	0.0794	0.98900	0.0435	0.98900	0.98300	0.0435	0.98300
	0.0417	1.04332	1.00301	0.0289	1.00301	1.06517	0.0583	1.06517	1.01608	0.0194	1.01608	0.0279	1.01608	0.96778	0.0279	0.96778
	0.0449	1.03478	1.02100	0.0356	1.02100	1.03500	0.0592	1.03500	1.02812	0.0274	1.02812	0.0318	1.02812	0.98101	0.0318	0.98101
	0.0727	1.04550	1.00298	0.0557	1.00298	1.01602	0.0861	1.01602	1.01930	0.0350	1.01930	0.0404	1.01930	0.96002	0.0404	0.96002
	0.0856	1.05878	0.94701	0.0841	0.94701	1.02928	0.1397	1.02928	1.02180	0.0380	1.02180	0.0435	1.02180	0.98100	0.0435	0.98100
	0.1052	1.06220	0.99900	0.0998	0.99900	1.00200	0.1572	1.00200	0.98100	0.0536	0.98100	0.0547	0.98100	0.98579	0.0547	0.98579
	0.0209	1.04440	1.01701	0.0225	1.01701	1.03511	0.0349	1.03511	1.03108	0.0220	1.03108	0.0166	1.03108	1.02000	0.0166	1.02000
	0.0279	1.01448	1.03400	0.0258	1.03400	1.06008	0.0370	1.06008	1.02780	0.0294	1.02780	0.0223	1.02780	1.02309	0.0223	1.02309
	0.0398	1.05700	0.99401	0.0290	0.99401	1.03300	0.0458	1.03300	1.01000	0.0343	1.01000	0.0320	1.01000	1.00110	0.0320	1.00110
	0.0548	1.03400	1.03308	0.0527	1.03308	1.04101	0.0693	1.04101	1.02212	0.0421	1.02212	0.0419	1.02212	0.99000	0.0419	0.99000
	0.1232	1.07088	0.96903	0.1062	0.96903	0.99019	0.0938	0.99019	0.98210	0.0983	0.98210	0.0698	0.98210	0.98278	0.0698	0.98278

TABLE V : Ion product (K) of EtOH, PrOH, i-PrOH, BuOH, i-BuOH at 15, 20 and 30 °C.

t (°C)	EtOH		PrOH		i-PrOH		BuOH		i-BuOH	
	pK	K	pK	K	pK	K	pK	K	pK	K
15	18.27	$5.37 \cdot 10^{-19}$	19.54	$2.88 \cdot 10^{-20}$	20.97	$1.07 \cdot 10^{-21}$	19.98	$1.05 \cdot 10^{-20}$	20.48	$3.31 \cdot 10^{-21}$
20	18.15	$7.08 \cdot 10^{-19}$	19.40	$3.98 \cdot 10^{-20}$	20.74	$1.82 \cdot 10^{-21}$	19.87	$1.34 \cdot 10^{-20}$	20.26	$5.50 \cdot 10^{-21}$
30	18.02	$9.54 \cdot 10^{-19}$	19.22	$6.02 \cdot 10^{-20}$	20.26	$5.50 \cdot 10^{-21}$	19.52	$3.02 \cdot 10^{-20}$	19.86	$1.38 \cdot 10^{-21}$

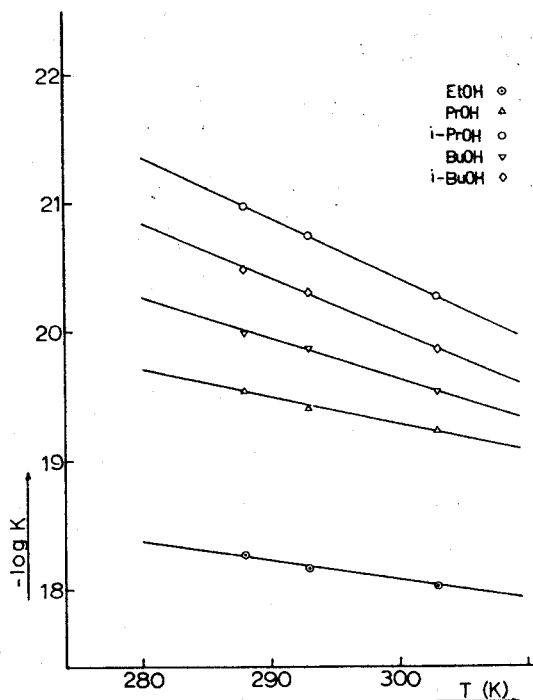


FIG. 4 :  $pK$  values of EtOH, PrOH, *i*-PrOH, BuOH and *i*-BuOH as a function of absolute temperature.

The alkyl groups are poorer electron attractors than the hydrogen atoms, and display an «electron donating», positive, inductive effect. This effect increases the electron availability of the O atom (of the OH<sup>-</sup>), thus decreasing the acidic character of the molecule. The relative magnitude of the inductive effect of alkyl groups is normally found to follow the order,

$\text{Me}_2\text{CH} \rightarrow \text{MeCH} \rightarrow \text{CH}_3$  which is also the order of increase of the electron availability of the O atom; hence this is the order of decrease of the acidic character of the molecule<sup>19</sup>.

The  $K$  of *i*-PrOH being smaller than these of BuOH and *i*-BuOH, although the chain is shorter, is well explained by the fact, that the *i*-PrOH molecule contains two methyl groups substituted on the  $\alpha$ -carbon atom. The inductive effect is in that case stonger (the methyls are closer to the O atom), than the one existing in the longer molecules of BuOH and *i*-BuOH. The dielectric constants of these alcohols are decreasing in the same order with the  $K$ .

A lower dielectric constant means greater energy to separate charges. So this factor together with the inductive effect could explain the order of  $K$  obtained in this work.

## Περίληψη

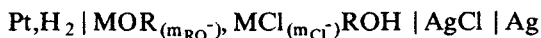
«Μετρήσεις ΗΕΔ σε μη ύδατικά διαλύματα αλειφατικών αλκοολών. Προσδιορισμός ιοντικού γινομένου».

Από μετρήσεις ΗΕΔ του στοιχείου  $Pt, H_2 | HCl_{(m)}, ROH | AgCl | Ag$  υπολογίζεται τό κανονικό δυναμικό ( $E^*$ ) του ηλεκτροδίου αργύρου-χλωριούχου αργύρου, σε μη ύδατικά διαλύματα EtOH, PrOH, i-PrOH, BuOH, i-BuOH στους 15,20 και 30°C.

Χρησιμοποιείται για πρώτη φορά ό τύπος του ηλεκτροδίου «κατόπτρου» αργύρου-χλωριούχου αργύρου, πού αποδεικνύεται εξαιρετικά σταθερό και άναπαραγωγίσιμο σε όλη τήν διάρκεια των πειραμάτων.

Υπολογίζεται επίσης ό θερμικός συντελεστής του κανονικού δυναμικού για κάθε ένα διαλύτη.

Από τίς τιμές αυτές και από μετρήσεις ΗΕΔ του στοιχείου



υπολογίζονται τά ιοντικά γινόμενα των παραπάνω αλειφατικών αλκοολών για τίς ίδιες θερμοκρασίες.

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