

PRESSURE AND TEMPERATURE EFFECTS ON THE ELECTRICAL CONDUCTIVITIES AND  
WALDEN PRODUCTS OF TETRAETHYLAMMONIUM IODIDE IN SOME PRIMARY AND  
SECONDARY ALCOHOLS

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ABSTRACT

This work is concerned with pressure and temperature effects on the limiting conductances and Walden products of tetraethylammonium salts in different primary and secondary alcohols.

The results were discussed in terms of both the hydrodynamic model and the transition state theory. Complementary conclusions were reached by the two sets of parameters resulting from those theories.

INTRODUCTION

The specific electrical conductivity of most non-aqueous solvents is much lower than of water and so conductance measurements of electrolytes in those solvents can be made at lower concentrations without serious loss of accuracy. On the other hand, these solvents have to be very purified and they require careful protection from atmospheric moisture. This last requirement is of utmost importance for alcoholic solutions where very small amounts of dissolved water can minimize the experimental values of conductances<sup>(1)</sup>.

Investigations on alcoholic solutions are less frequent than in

other non-aqueous solvent systems perhaps because of the electrolytes dissolved in hydrogen bonding solvents exhibit ionic association patterns and structural effects not observed in other solvents. Such behaviour can be attributed to a combination of acidic and basic sites which can solvate both cations and anions and to a multiple association process in which solvent-ion interactions have pronounced effects<sup>(2-4)</sup>.

The majority of works on these systems have been performed near room temperature and at atmospheric pressure, and relatively little information is available for other temperatures and pressures, except for water<sup>(5)</sup>. This is certainly due to the fact these systems do not obey to the Debye-Hückell-Onsager theories as a consequence of micellar and of different types of ionic associations<sup>(6)</sup>. One of us (C.A.N.V.) has recently observed that conductivity - concentration variations of lithium salts in anhydrous alcohols present a minimum and a maximum certainly due to large degree of ionic association<sup>(7)</sup>. Such type of behaviour was not observed for sodium and potassium salts<sup>(7)</sup>.

The object of this paper is to determine whether the conductivities and the Walden's products of tetraethylammonium iodide are differently affected by temperature and pressure in two types of solvents, primary and secondary alcohols on account of the different ways in which the -OH group is attached to the alkyl group. Simultaneously association constants of these salts at the same experimental conditions are also inspected. Such a study is particularly interesting taking into consideration the hydrophobic character and the capacity of being structure makers at solvent surface of these compounds.

The electrical conductivity of an electrolytic solution is of course a very complicated function of pressure (and also of temperature), because every variable and parameter (except temperature in relation to pressure and valence) in the conductivity function is an implicit function of pressure. Viscosity usually increases with pressure: The limiting mobility and the electrophoretic term therefore decrease. The dielectric constant also increases with pressure. Even concentration is pressure dependent; due to compression, the volume concentration of a solution of fixed weight concentration increases with pressure. Such effect is often eliminated by extrapolation to infinite dilution. Different pressure (and temperature) effects have to be explained at the molecular scale. This is certainly the case of different association constants of tetraalkylammonium perchlorates which vary differently with the inverse of cation radius for two solvents of about equal dielectric constants<sup>(8)</sup>.

#### EXPERIMENTAL

There are several difficulties connected with the measurements of the conductances of tetraalkylammonium halides in alcohols, being one of them the limited solubility of these compounds in those solvents mainly in secondary alcohols.

A second difficulty is the possibility of a chemical reaction between the solvent and the acid (HX) eventually resulting from the hydrolysis of the salt and forming alkyl halide<sup>(9,10)</sup>. Fortunately this fact decreases the number of charged species in solution and so it will not be favoured by pressure. Nevertheless to avoid such catalytic reactions conductivity cells with bright platinum rod

and ring electrodes were used and found adequate for the high resistance solutions which have been measured under pressure<sup>(10-12)</sup>. This system has shown to have cell constants which are virtually independent of compression strains up to 3000 bar<sup>(13)</sup>.

Twelve conductivity cells were used and the cell constants were ranged from 0.2310 to 0.6342 cm<sup>-1</sup>. The preparation of solutions was done by weight in a glove box where a dry and oxygen free atmosphere was attained through a stream of dry and oxygen free nitrogen.

High purity solvents were always used and tested through the Karl Fisher reagent. Water content was never greater than 0.1%. The specific conductivities of solvents were comparable with the best values appearing in the literature<sup>(14)</sup>. Aristar potassium chloride (BDH - 45215, m.w. 74.55; maximum of impurities 12 ppm) was kept in an excicator with phosphorous pentoxide and silica gel and under reduced pressure. Tetraethylammonium iodide (Merck 8109 for polarography tests and m.w. 257.16) was used and the argentimetric test has shown a purity higher than 99%. Complementary this salt was reduced to powder and kept in an excicator with phosphorous pentoxide and silica gel, under low pressure. Conductivity water freshly prepared by tetra-distillation was used on the preparation of potassium chloride solutions.

Hot solvent vapour was passed through all the glassware, including conductivity cells, before using it.

Different concentration ranges were used for primary and secondary alcohols according to tetraethylammonium iodide solubilities in the different solvents. So  $5.0 \times 10^{-4}$  -  $7.5 \times 10^{-3}$  mol dm<sup>-3</sup> and  $1.0 \times 10^{-4}$  -  $1.5 \times 10^{-3}$  mol dm<sup>-3</sup> concentration intervals were chosen respectively.

## RESULTS

The molar conductivity was determined as a function of temperature, pressure and solvent as it was referred above.

The calculation of limiting molar conductivity  $\Lambda^0$  was based on both the Fuoss-Onsager equation<sup>(15)</sup>

$$\Lambda = \Lambda^0 - S(c\gamma)^{1/2} + Ec \gamma \log(c\gamma) + (J - F \Lambda^0) c\gamma - K_A c\gamma \Lambda f_{\pm}^2$$

where S, E and J depend on the same solvent properties; F corrects  $\Lambda$  for the effect of the electrolyte on the solvent viscosity;  $f_{\pm}$  is the mean ionic activity coefficient;  $\gamma$  is the fraction of the free ions;

and on the following quadratic equation

$$\Lambda = \Lambda^0 + a_1 c^{1/2} + a_2 c$$

after the use of convenient programming adjustment between  $a_1$  and  $a_2$ . The two sets of results are very similar and those obtained from the last equation are comparable to some of the best ones which are available in the literature as it is illustrated in table 1.

Tables 2 and 3 show limiting molar conductivities,  $\Lambda^0$ , as a function of temperature and pressure which were obtained in this work.

The determination of association constants led to the values appearing in table 4 and 5.

TABLE 1 -  $\Lambda^0$  for ethanolic and propanolic solutions of  $\text{Et}_4\text{NI}$  at 1 atm and 298.15 K

SOLVENT	$\Lambda^0 / \text{S cm}^2 \text{mol}^{-1}$	
MeOH	124.2 (a)	128 $\pm$ 1 (c)
EtOH	56.34 (b)	57.7 $\pm$ 0.5 (c)
1-PrOH	29.01 (b)	30.2 $\pm$ 0.3 (c)

(a) Ref. (16) (b) Ref. (17) (c) This work

TABLE 2 - Limiting molar conductivities of  $\text{Et}_4\text{NI}$  in different alcohols at 1 atmosphere and different temperatures (one atmosphere cells).

$[\Lambda^0 \pm \sigma(\Lambda^0)] / \text{Scm}^2 \text{mol}^{-1}$

Solv \ T/K	298,15	303,15	308,15	313,15	318,15	323,15	328,15
MeOH	128 $\pm$ 1	136 $\pm$ 1	144 $\pm$ 2	153 $\pm$ 4	162 $\pm$ 3	176 $\pm$ 3	195 $\pm$ 1
EtOH	57,7 $\pm$ 0,5	61,0 $\pm$ 0,7	66 $\pm$ 2	71 $\pm$ 1	78 $\pm$ 1	86,8 $\pm$ 0,9	95 $\pm$ 2
1-PrOH	30,2 $\pm$ 0,3	32,5 $\pm$ 0,2	36,8 $\pm$ 0,3	39,3 $\pm$ 0,1	44,7 $\pm$ 0,2	51,6 $\pm$ 0,7	57 $\pm$ 1
1-BuOH	—	20,8 $\pm$ 0,6	23,5 $\pm$ 0,6	26,0 $\pm$ 0,7	28,6 $\pm$ 0,8	31,4 $\pm$ 0,8	34 $\pm$ 1
2-BuOH	—	17,1 $\pm$ 0,4	19,8 $\pm$ 0,4	22,5 $\pm$ 0,4	25,3 $\pm$ 0,4	28,2 $\pm$ 0,4	31,1 $\pm$ 0,3

TABLE 3 - Limiting molar conductivities of  $\text{Et}_4\text{NI}$  in different alcohols at 313.15 K and different pressures (Pressure cells)

$[\Lambda^0 \pm \sigma(\Lambda^0)] / \text{Scm}^2 \text{mol}^{-1}$

Solv \ P/bar	1	100	250	500	1000	1500	2000
MeOH	160 $\pm$ 4 153 $\pm$ 4 (a)	149 $\pm$ 2	136 $\pm$ 2	124 $\pm$ 1	102 $\pm$ 4	93 $\pm$ 7	84 $\pm$ 9
EtOH	81 $\pm$ 2 71 $\pm$ 1(a)	77 $\pm$ 1	72 $\pm$ 1	65 $\pm$ 1	54 $\pm$ 1	47 $\pm$ 1	41 $\pm$ 1
1-PrOH	41,7 $\pm$ 0,8 39,3 $\pm$ 0,1(a)	39,2 $\pm$ 0,8	36,0 $\pm$ 0,8	31,8 $\pm$ 0,8	25,5 $\pm$ 0,7	20,9 $\pm$ 0,6	17,4 $\pm$ 0,6
1-BuOH	30 $\pm$ 2 26,0 $\pm$ 0,7(a)	29 $\pm$ 2	27 $\pm$ 1	24 $\pm$ 1	19,0 $\pm$ 0,9	15,4 $\pm$ 0,7	12,7 $\pm$ 0,6
2-PrOH	36 $\pm$ 1	32 $\pm$ 2	28 $\pm$ 1	24 $\pm$ 1	20 $\pm$ 1	13 $\pm$ 1	10,5 $\pm$ 0,9
2-BuOH	27,7 $\pm$ 0,3 22,5 $\pm$ 0,4(a)	25,5 $\pm$ 0,2	23,0 $\pm$ 0,2	19,6 $\pm$ 0,1	14,5 $\pm$ 0,1	10,9 $\pm$ 0,2	8,4 $\pm$ 0,2

(a) Results obtained with one atmosphere cells.

TABLE 4 - Association constants  $K_A$ , as a function of temperature and solvent at 1 atm

		$K_A$		
		T/K		
Solv.	T/K	298.15	313.15	328.15
MeOH		49	51	64
EtOH		139	126	153
1-PrOH		379	342	477
1-BuOH		857	841	927

TABLE 5 - Association constants  $K_A$ , as a function of pressure and solvent at 313.15 K.

		$K_A$		
		P/bar		
Solv.	P/bar	1	1000	2000
MeOH		51	20	18
EtOH		126	110	86
1-PrOH		342	182	139
1-BuOH		841	628	487
2-PrOH		583	259	71
2-BuOH		4212	1924	1198

### DISCUSSION

Results presented in tables 2 and 3 show that the limiting molar conductivities always increase with temperature and decrease with pressure respectively. Such behaviour is of course compatible with a very small ionic solvation which is not surprising taking into account the large ionic radii of both cation and anion. On the other hand, the association constants are always large and they increase with the length of the solvent carbon chain. This behaviour is observed for both primary and secondary alcohols and the high values of  $K_A$  are certainly related to the formation of triple ions or even to a large ionic association degree as it seems to be revealed through the  $\Lambda c^{1/2}$ ,  $c$  variations, particularly for those solvents of low dielectric constants (figure 1).

Different types of analysis of conductance data of the electrolytic solutions have been performed along the years. Among them the one based on the phenomenological Stokes' law is the most commonly used though a more formal thermodynamic type treatment of the results based on the transition state theory have been several times used. We have followed both methods and therefore some complementary aspects of the same phenomena have been observed.

From the results it is possible to see that all the salts are weakly dissociated 1:1 electrolytes although the association constants are significantly dependent upon the solvent. A comparison of the limiting molar conductivities in different solvents (table 2 and 3) allows us to obtain some information with regard to the solvation of the several ions<sup>(18)</sup>. As we referred such analysis is often based on the Stokes' law

$$r = |Z| F^2 / 6\pi N\eta\lambda^0$$

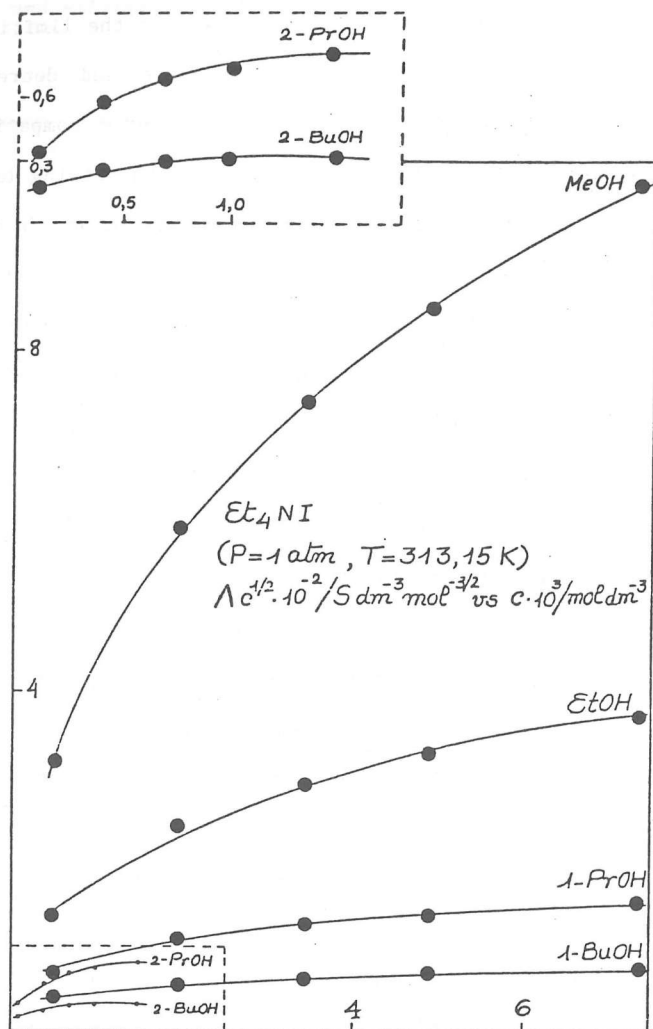


FIGURE 1

where  $r, \eta, \lambda^0, F, N$  are the radius of a spherical particle, the viscosity of the medium, the limiting equivalent ionic conductivity, a frictional force and the Avogadro's constant respectively. From that analysis it was previously shown that several large ions of similar mobility have almost the same behaviour in water when comparison is made through the variation of the Walden's products with temperature which is similar anyway. The conclusions of such type of study are of course dependent on ionic radii constancy. However this situation is very closely the one of our systems, taking into account that solvation is never large and therefore the cationic and anionic radii are almost constant.

In figure 2 it is shown that  $\Lambda^0 \cdot \eta, T$  variation (viscosity of pure solvent) is almost constant for all alcohols with a possible exception for the one - butanol solution. These results are of course compatible with similar ionic mobilities in most of solvents.

The analysis of the results based upon the hydrodynamic model was amplified through the variations of the Walden's product with pressure and chain length. This is shown in figure 3 and 4 respectively.

A slight increasing of  $\Lambda^0 \eta$  with pressure is observed for both primary and secondary propanol. In principle such variation should be constant. However, both electroforetic and relaxation effects are pressure dependent and the latter depends on the dielectric constant which increases with increasing pressure. As a conclusion the limiting molar conductivity does not decrease as fast as the macroscopic fluidity ( $1/\eta$ ) decreases.

An interesting result is the one shown in figure 4 where negative and positive slopes related to  $\Lambda^0 \eta, n$  variations were

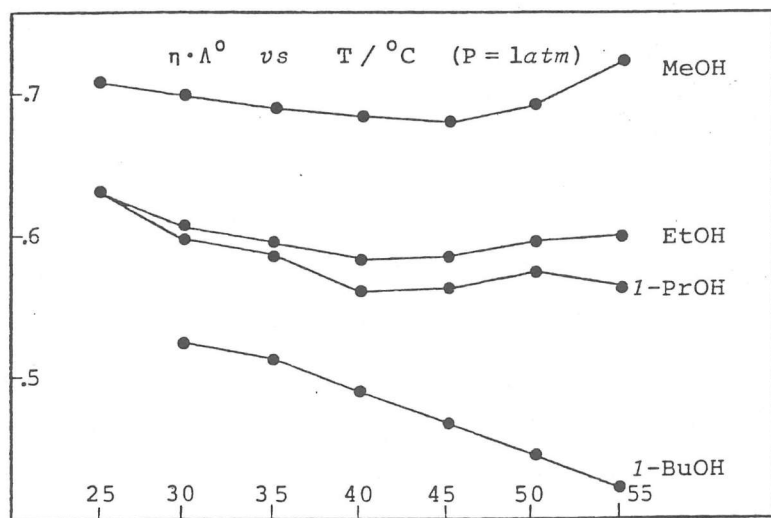


FIGURE 2

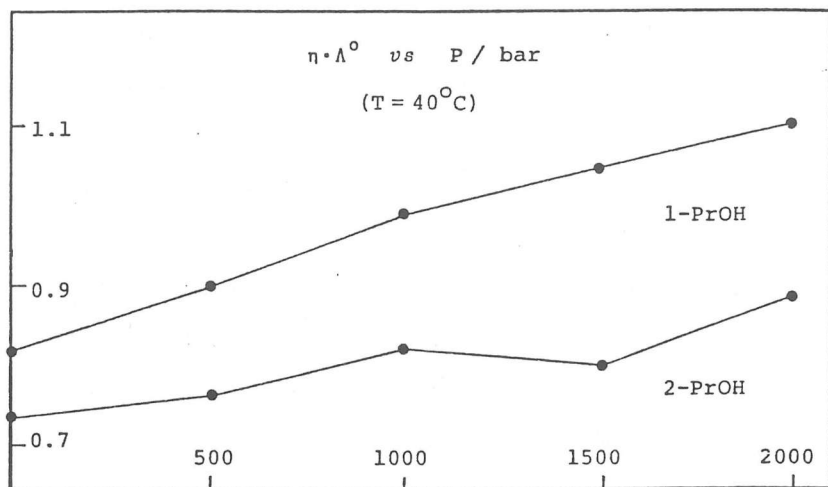


FIGURE 3

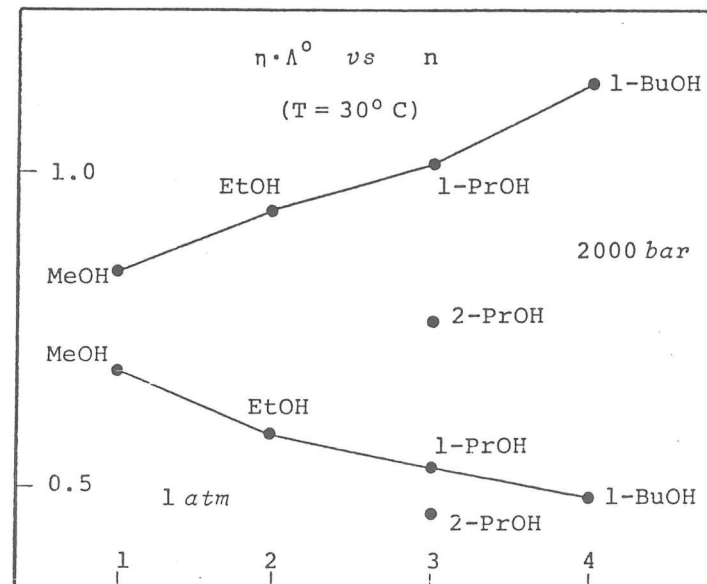


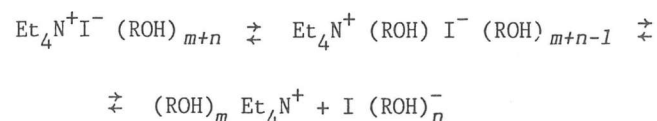
FIGURE 4

obtained at one and 2000 bar respectively. It seems that the "normal" behaviour should be situated between 1 and 2000 bar respectively. In this respect a deeper theoretical analysis will be developed elsewhere.

As referred above complementary conclusions were reached applying transition state theory to our results. The following equations were use and from them different thermodynamic functions of activation were obtained (table 6).

The numerical values of these functions expressed in free energies, enthalpies, entropies and volumes of activation are shown in table 7.

From these results, as we will show ahead the solvation mechanism can be interpreted as follows



As already mentioned,  $Et_4N^+$  and  $I^-$  are large ions, so their charge densities are small and for this reason they should be little solvated ( $n$  and  $m$  must be small); the values of the activation thermodynamic parameters certainly reflect such facts.

The ions separation and translation energy are certainly the two major factors contributing to the enthalpy of activation  $\Delta^\ddagger H^0$  which is always small. Therefore, ion separation does not need much energy since interionic attraction is small; on the other hand the ionic migration does not develop large attractive ion-dipole (ion-solvent)

TABLE 6 - Equations used to determine the thermodynamic functions of activation

Equation	Thermodynamic functions of activation
	$\Delta^\ddagger G^0 = -RT[\ln \Lambda^0 - \ln(\frac{ZeFL^2}{6h})]$ $\sigma(\Delta^\ddagger G^0) = -RT[\frac{\sigma(\Lambda^0)}{\Lambda^0} + \frac{2}{3} \frac{\sigma(V_m)}{V_m}]$
$\ln \Lambda^0 = a + bT + cT^2$	$\Delta^\ddagger H^0 = RT^2[(b+2cT) - \frac{2}{3}\alpha]$ $\sigma(\Delta^\ddagger H^0) = RT^2\{[\sigma^2(b) + 4T^2\sigma^2(c) + 4T\sigma^2(b,c)]^{1/2} + \frac{2}{3}\sigma(\alpha)\}$ $\Delta^\ddagger S^0 = R\{\ln \Lambda^0 + T[(b+2cT) - \frac{2}{3}\alpha] - \ln(\frac{ZeFL^2}{6h})\}$ $\sigma(\Delta^\ddagger S^0) = R\{\frac{\sigma(\Lambda^0)}{\Lambda^0} + T[\sigma^2(b) + 4T^2\sigma^2(c) + 4T\sigma^2(b,c)]^{1/2} + \frac{2}{3}\sigma(\alpha)T + \frac{2}{3} \frac{\sigma(V_m)}{V_m}\}$
$\ln \Lambda^0 = a + bP + cP^2$	$\Delta^\ddagger V^0 = -RT[(b+2cP) + \frac{2}{3}\kappa]$ $\sigma(\Delta^\ddagger V^0) = -RT\{[\sigma^2(b) + 4P^2\sigma^2(c) + 4P\sigma^2(b,c)]^{1/2} + \frac{2}{3}\sigma(\kappa)\}$



TABLE 7 - Thermodynamic functions of activation related to  $\Lambda^{\circ}$  of different  $\text{Et}_4\text{NI}$  solutions  
(P=1 atm, T=313,15 K)

Solvent	$[\Delta^{\ddagger}G^{\circ} \pm \sigma(\Delta^{\ddagger}G^{\circ})]$ / $\text{kJmol}^{-1}$	$[\Delta^{\ddagger}H^{\circ} \pm \sigma(\Delta^{\ddagger}H^{\circ})]$ / $\text{kJmol}^{-1}$	$[\Delta^{\ddagger}S^{\circ} \pm \sigma(\Delta^{\ddagger}S^{\circ})]$ / $\text{JK}^{-1}\text{mol}^{-1}$	$[\Delta^{\ddagger}V^{\circ} \pm \sigma(\Delta^{\ddagger}V^{\circ})]$ / $\text{cm}^3\text{mol}^{-1}$
MeOH	9.78±0.07	10.1±0.4	1±1	11.7±0.9
EtOH	12.38±0.04	11.6±0.9	- 2±3	9.4±0.4
1-PrOH	14.32±0.01	17.2±0.9	9±3	12.2±0.4
1-BuOH	15.79±0.07	17.7±0.5	6±2	11.4±0.2
2-PrOH	—	—	—	19.0±1.3
2-BuOH	16.20±0.05	19.4±0.4	10±1	15.9±0.4

interactions on account of charges densities of ions which is also confirmed by near zero entropies of activation. This is in accordance with a near ion pair transition state and again a little ionic solvation of the ion.

Large and positive volumes of activation  $\Delta^{\ddagger}V^{\circ}$ , correspond to large deformations of solvent layers when large ions migrate through them. Under these conditions small ion-solvent attractive interactions are expected and so small electrostrictive forces should be developed which agrees with the results.

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**EFFECT OF THE TEMPERATURE ON THE RESPONSE CHARACTERISTICS OF "ALL SOLID STATE" ISES BASED ON MERCURY SALTS APPLIED TO ELECTRICALLY CONDUCTIVE SUPPORTS\***

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**ABSTRACT**

A study of temperature effects on the response of ISEs made with membranes constituted by  $\text{HgS}/\text{Hg}_2\text{Cl}_2$  applied to electrically conductive epoxy supports of several types is reported. Results for operational temperature ranges, slope and standard potential variations with temperature, isopotential points, stabilization times and hysteresis curves have been obtained. These results confirm that the equilibria reached by membranes with this sensor are thermodynamically metastable, which explains why the operation of these electrodes is more troublesome than for  $\text{AgCl}/\text{Ag}_2\text{S}$  electrodes. It is shown that the decrease in the lower limit of linear response obtained by cooling the electrodes below room temperature is very limited.

**KEYWORDS**

Chloride-selective electrode; mercury salts; conductive epoxy-based ion-selective electrodes; temperature effects; slope coefficient; potential coefficient; isopotential point; hysteresis curves.

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