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A Conductance Study of Zinc Halides and Perchlorate and of Magnesium Perchlorate in Propylene Carbonate-Tetrahydrofuran Mixtures at 25 °C

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Synopsis. The electrical conductances of zinc halides and perchlorate and of magnesium perchlorate in propylene carbonate (PC)-tetrahydrofuran (THF) (1:1 in volume) have been measured at 25 °C. The conductance data were analysed by a minimization technique using the Lee/Wheaton (L/W) and Murphy/Cohen (M/C) equations. The results indicate that all of these salts behave as "weak electrolytes". Zinc and magnesium perchlorates were found to be anomalous in showing unusually high molar conductance, and in exhibiting a pronounced maximum conductances at low concentrations. Also, it was found that the mode of ionization is specific for the anion involved.

The behavior of an electrolyte solution is determined by ion-ion, ion-solvent and solvent-solvent interaction. Also, it is well-established that the extent of association of a series of electrolytes in different solvents is specific for any ion-solvent combination, rather than being dielectric constant dependent. The association behavior of alkali metal and quaternary ammonium perchlorates in aprotic solvents such as acetonitrile and protic solvents such as methanol1) or in their mixture2) is just one example.

Most studies for electrolyte solutions in nonaqueous media, by using different techniques, indicate that the cationic solvation is strong while the anionic solvation is weak. Beside that, there is a reasonable degree of dissociation for these electrolytes. However, the ability of forming ion pairs and complex ions is higher than that in aqueous solutions, so, we expect that this process is stronger by increasing the charge of the cation.

However, the conductance of 2:1 electrolytes, particullarly in nonaqueous and mixed solvents, has received relatively little attention. This is due in large part to the difficulty encountered in analyzing such data since the usual methods require an arbitrary choice for some of the parameters needed in the analysis. In the present paper, we report conductance measurements of zinc halides and perchlorate and of magnesium perchlorate in a mixture of PC-THF (1:1 in volume). This mixture was chosen because of two reasons. Firstly, it has been reported in attempts to use in high energy batteries3,4,5) and secondly is due to the maximum value of the molar conductivity obtained for some electrolytes at the mixture ratio of about 1 to 1.5) Two conductance equations in current use, the L/W and M/C equations, have been used to analyze conductance data for those electrolytes studied here.

Experimental

Propylene carbonate (PC) and tetrahydrofuran (THF) were purified by the methods described elsewhere4,6) and the final water contents were below 200 ppm in PC and 300 ppm in THF. The conductivities of the final products were in the range 2—4$\times10^{-8}$, 1—2$\times10^{-8}$, and 3—5$\times10^{-8}$ for PC. THF, and their mixture (1:1) respectively in units S cm^{-1} at 25 °C. All salts were purified and used as described in Ref. 7,8.

Conductance measurements were made at constant temperature of 25±0.005 °C with Wayne-Kerr B331 auto balance precision bridge. The conductivity cell used was of the cylindrical type described by Abbo7) with the cell constant 0.16993±0.00028 cm^{-1}.

Solutions for the conductivity measurements were prepared by weighing from the stock solutions and the solvents. Solvent mixtures were also made by weight. Preparation of the solutions and all the other manipulations were performed in a dry box.

Results and Discussion

The experimental molar conductances Λ_{exp} of zinc perchlorate, chloride, bromide, and iodide and of magnesium perchlorate have been measured in this work at different molar concentrations C. Figures 1—3 show Λ_{exp} vs. $\sqrt{C}$ for those electrolytes.

In analyzing the conductance data, two equations were used. The first one represents M/C equation.9)

$$\Lambda=\Lambda_0+BK\Lambda_1+(BK)^2\ln(BK)\Lambda_2'+(BK)^2\Lambda_2 \qquad (1)$$

where $B=-e_1e_2/DkT$ and K is the reciprocal of "Debye length." Λ_1, Λ_2', and Λ_2 are the relaxation, electrophoretic and osmetric terms, as defined in the original paper. At present, Eq. 1 is formulated to the first order in concentration, i.e, to order $(BK)^2$. Also, this equation was modified to allow for various forms of ion association which produces a pair of ions:

$$\Lambda=\alpha[\Lambda_0+BK'\Lambda_1+(BK')^2\ln(BK')\Lambda_2'+(BK')^2\Lambda_2] \qquad (2)$$

where α is the fraction of the electrolyte present as free ions. K' is here a function of the ionic concentration C.

The other equation used is L/W equation.10)

$$\Lambda=\Lambda_0[1+C_1(KR)(\varepsilon K)+C_2(KR)(\varepsilon K)^2+C_3(KR)(\varepsilon K)^3]-\frac{(\rho K)}{(1+KR)}[1+C_4(KR)(\varepsilon K)+C_5(KR)(\varepsilon K)^2+(KR/12)] \qquad (3)$$

where all symbols are the same as defined in the original paper.

Several computer programms have been developed to compute the three parameters Λ_0, a, and K_{A} independently which all were based on a minimization technique.11) This technique will give, through a succesive approximation for the number of experimental points N, the standard deviation σ:

$$S^2=\sum_{1}^{N}[\Lambda_{\mathrm{calc}}-\Lambda_{\mathrm{expt}}]^2;\ \sigma=(S^2/N)^{1/2} \qquad (4)$$

This method is capable of giving the type or mode of ionization at certain concentrations.

According to the nature of the electrolytes studied here, four possible modes of ionization were suggested:

$$MA_2 \rightleftarrows MA^+ + A^- \quad (5)$$

$$MA_2 \rightleftarrows M^{2+} + 2A^- \quad (6)$$

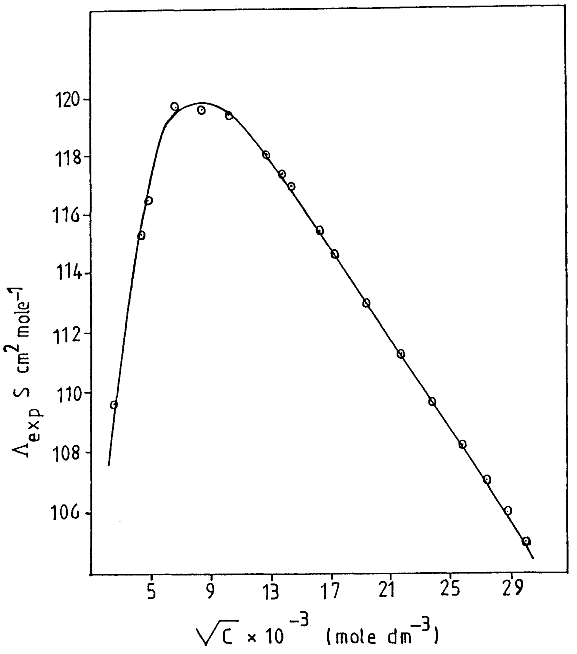

Fig. 1. Variation of Λ_{expt} (S cm^2 mol^{-1}) with $\sqrt{C}$ (mol dm^{-3}) for $Mg(ClO_4)_2 \cdot 6H_2O$ in a mixture of PC-THF (1 : 1 in volume) at 298 K.

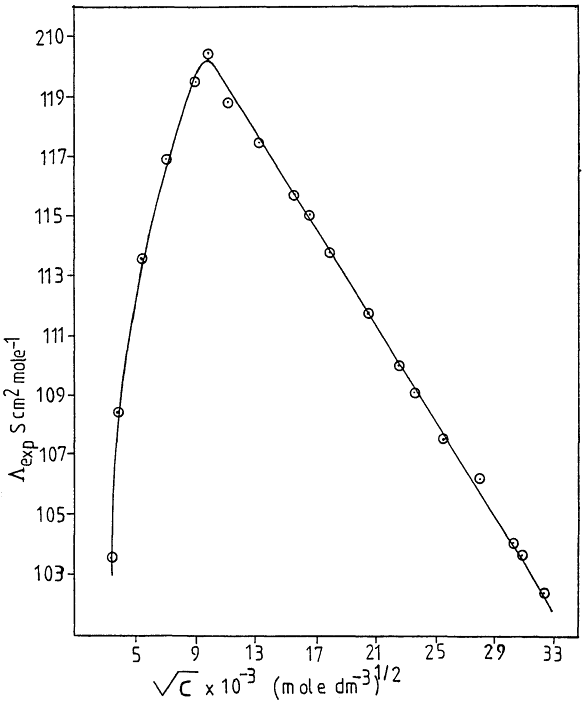

Fig. 2. Variation of Λ_{expt} (S cm^2 mol^{-1}) with $\sqrt{C}$ (mol dm^{-3}) for $Zn(ClO_4)_2 \cdot 6H_2O$ in a mixture of PC-THF (1 : 1 in volume) at 298 K.

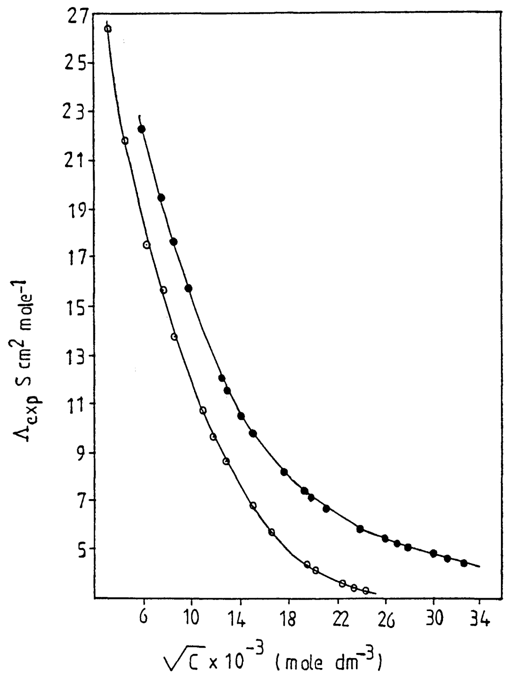

Fig. 3. Variation of Λ_{expt} (S cm^2 mol^{-1}) with $\sqrt{C}$ (mol dm^{-3}) for both $ZnBr_2$ (○) and $ZnCl_2$ (●) in a mixture of PC-THF (1 : 1 in volume) at 298 K.

$$2MA_2 \rightleftarrows MA^+ + MA_3^- \quad (7)$$

$$2MA_2 \rightleftarrows M^{2+} + MA_4^{2-} \quad (8)$$

Because the behavior of some electrolytes in (PC-THF) mixture is different from that in each single solvent by having a higher molar conductivity, specially in about 1 : 1 ratio,[5] so the conductance measurements of zinc and magnesium perchlorates and of zinc chloride and bromide (but not zinc iodide due to the change of its properties during the measurements) have been done and the results are given in Fig. 1—3. The comparison of the present results with those obtained in PC alone[8] has shown the same maximum Λ_{expt} with respect to the two perchlorate salts at low concentrations. The shape of both Figs. 1 and 2 and the maxima observed, could be attributed to the fact that different ionic species predominate in different concentration ranges. However, it is difficult to suggest what the complex ions might be in the present case. Alternatively, the effect of changes in the nature of the solvent environment with concentration of the multivalent cation might provide an explanation. Also, the common characteristic point of analyzing data for all electrolytes (apart from zinc bromide) is that their molar conductivities are higher than that in each single solvent. The same behavior has been observed with some electrolytes in a mixture of 1,2-dimethoxyethane -PC (1 : 1).[12] The very significant factors affecting the conductance of ionic solutions would be the dielectric constant and the viscosity in connection with the solvation of the ions and the solvent-solvent interaction.

It would be assumed that the increase in molar conductivity of the solution with the addition of THF to PC is caused by the effect of the low viscosity of THF on Walden's product[5] ($\Lambda_{expt} \cdot \eta$=constant, where

Table 1. The Mode of Ionization and the Best Fit Values of Λ_0, a, and K_A

$Mg(ClO_4)_2$	$Mg(ClO_4)_2 \rightleftarrows Mg^{2+} + 2ClO_4^-$	
	L/W	M/C
K_A/mol dm^{-3}	9240	8080
Λ_0/S cm^2 mol^{-1}	142.76±0.02	142.28±0.02
a/Å	3.4	7.5
δ	0.062	0.123
$Zn(ClO_4)_2$	$Zn(ClO_4)_2 \rightleftarrows Zn^{2+} + 2ClO_4^-$	
	L/W	M/C
K_A/mol dm^{-3}	13680	12640
Λ_0/S cm^2 mol^{-1}	136.50±0.02	136.10±0.02
a/Å	3.2	6.4
δ	0.063	0.104
$ZnCl_2$	$ZnCl_2 \rightleftarrows Zn^{2+} + 2Cl^-$	
	L/W	M/C
K_A/mol dm^{-3}	3.214×10^7	2.852×10^7
Λ_0/S cm^2 mol^{-1}	109.12±0.02	108.64±0.02
a/Å	6.1	8.4
δ	0.049	0.089
$ZnBr_2$	$ZnBr_2 \xrightarrow{K_1} ZnBr^+ + Br^-$ $ZnBr^+ \xrightarrow{K_2} Zn^{2+} + Br^-$	
	L/W	M/C
K_1/mol dm^{-3}	8.5×10^3	8.2×10^3
K_2/mol dm^{-3}	6.2×10^9	5.1×10^9
$\lambda^0 Zn^{2+}$/S cm^2	14.48	13.06
$\lambda^0 ZnBr^+$/S cm^2	22.82	13.06
$\lambda^0 Br^-$/S cm^2	33.34	32.5
Λ_0/S cm^2 mol^{-1}	47.82	45.76
δ	0.143	0.293

η is viscosity). Also, this phenomenon might be caused by some variation of solvation of the cation and the anion, and the Stokes' law radii, and these would be concerned with the specific solvation.[13–15]

The result analysis of these experimental measurements for the conductances of zinc perchlorate and chloride and of magnesium perchlorate, by using both L/W and M/C equations, does not give any indication for the presence of different ionic species. The experimental results, for all these three electrolytes, are best fitted by equilibrium (6), as shown in Table 1. The best fit values of the three parameters K_A, Λ_0 and a are listed at the same Table together with the corresponding values of σ (Eq. 4).

Analysis of the experimental conductance data of zinc bromide did not give any satisfactory fit for all four modes of ionization. So, it is suggested that this electrolyte undergoes two modes of ionization at the same time. Table 1 includes the results of such suggestions; the single ion conductances shown were also obtained by the minimization method.

Concerning the results of both equations, it is clear that the L/W equation is preferable to M/C equation for our present system. The reason for this, as has been discussed previously,[16] may be due to the inclusion of third order terms in the plasma parameter (εK) of their equation.

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