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CARBONATE SOLUTION

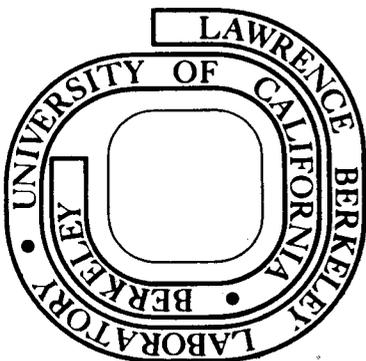
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Conductance Studies of the Alkali Metal Chlorides in Aluminum Chloride-Propylene Carbonate Solution

Jacob Jorné*¹ and Charles W. Tobias

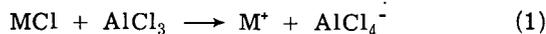
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Conductance of the alkali metal chlorides, LiCl, NaCl, KCl, RbCl, CsCl, in unit molality solution of AlCl₃ in propylene carbonate was measured at 25 and 35°. The measurements were performed in order to characterize the new process for the electrodeposition of the alkali metals at ambient temperature. The results have been interpreted in terms of solvation, ionic equilibrium, and the structure making-breaking ability of the alkali metals in AlCl₃ propylene carbonate solution.

Propylene carbonate (PC) is a polar aprotic solvent which exhibits many useful properties for electrochemical applications. Since the early research on PC was oriented toward the development of high-energy batteries, most of the work was concerned with emf measurements, electrodeposition, stability tests, and conductance at high concentration range. Recently, conductance measurements were performed in the dilute range in order to gain better understanding about the solvent-solute interactions.²⁻⁵

The feasibility of the electrodeposition of all the alkali metals from their chlorides in AlCl₃-propylene carbonate solution has been demonstrated.⁶ Lithium, sodium, potassium, rubidium, and cesium were electrodeposited at ambient temperature showing stable and reversible behavior.^{7,8} The alkali metal chlorides are practically insoluble in PC, however, in the presence of AlCl₃ a complex is formed between the chloride and AlCl₃



where M represents the alkali metal.

The electrodeposition of the alkali metals from their chlorides in AlCl₃-PC solution is proposed as a new process for the electrodeposition and refining of the alkali metals at ambient temperature.⁶ In order to characterize such a process, thermodynamic⁷ and kinetic⁸ measurements were performed. This paper presents the results of conductance studies of the alkali metal chlorides in unit molality AlCl₃ solution in PC, at 25 and 35°, over a wide concentration range of up to 1 *m* alkali metal chloride. The role of AlCl₃ is discussed in the light of earlier work⁶⁻⁸ and a general evaluation of the results is given.

Previous Work

Most of the data on solubilities and conductivities in PC are summarized in Jasinski's review,⁹ and the reader is referred to Table XIII and XIX in that review.

Conductance measurements in dilute solutions were performed in order to obtain the equivalent conductance at infinite dilution. The equivalent conductances at infinite dilution, Λ_0 , were obtained in most cases by extrapolation of a plot of Λ vs. $c^{1/2}$ to infinite dilution.

Harris¹⁰ obtained Kohlrausch plots for NaI and KI in PC, and the equivalent conductances were 28.3 and 31.0 ohm⁻¹ cm² equiv⁻¹, respectively. The slopes of the straight lines were in good agreement with the Onsager limiting law equation. Fuoss and Hirsch^{2a} studied the conductance of tetra-*n*-butylammonium tetrphenylboride in PC and concluded that ion association was negligible. Wu and Friedman^{2b} investigated the conductances and heats of solution of several alkali metal iodides, perchlorates, trifluoroacetates, and tetrphenylborates in PC. The perchlorates were found to be strong electrolytes, whereas the trifluoroacetates showed considerable ion association. Keller, *et al.*³ measured the equivalent conductance of LiClO₄, LiCl, LiBr, TBABR, and TMAPF₆ in PC, and obtained the equivalent conductance at infinite dilution. Mukherjee and Boden⁴ made conductance and viscosity measurements of LiCl, LiBr, LiClO₄, Et₄NCl, Et₄NClO₄, *n*-Bu₄NBr, and *n*-Bu₄NClO₄ in PC. The method of Fuoss and Accascina¹¹ was used to obtain Λ_0 and the individual ion conductances Λ_+^0 and Λ_-^0 . LiCl and LiBr were found to be associated, whereas no association could be detected for the other salts.

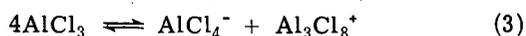
TABLE I: Equivalent Conductance and Ionic Conductance in PC ($\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$)

Salt	Λ	λ_+	λ_-	Ref
LiCl	25.6			3
	26.2			3
	27.5	7.30	20.20	4
LiBr	26.2			3
	27.35	7.30	20.05	4
LiClO ₄	25.6			3
	26.2			12, 13
	26.08	7.30	18.78	3
	26.3			14
NaI	28.2			10
NaClO ₄	28.3			2b
KI	30.75	11.97	18.78	5
	31.0			10
KClO ₄	30.75	11.97	18.78	5
Et ₄ NClO ₄	32.06	13.28	18.78	5
<i>n</i> -Bu ₄ NClO ₄	28.17	9.39	18.78	5
<i>n</i> -Bu ₄ NBr	28.65	9.39	19.26	5
(<i>i</i> -Am) ₄ N(<i>i</i> -Am) ₄ B	16.37	8.185	8.185	5
(<i>i</i> -Am) ₄ NI	26.95	8.185	18.675	5

Table I presents the equivalent conductances and ionic conductances at infinite dilution for several electrolytes in PC. The ionic conductance of Li⁺ is the lowest, which means that the ion has a large effective size. The ionic conductance of ClO₄⁻, I⁻, Br⁻, and Cl⁻ are approximately the same. Anions are poorly solvated in PC, and their ionic conductance is higher than the conductance of the cations.

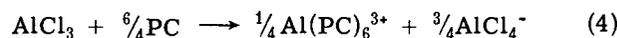
Conductance Measurements of AlCl₃ in PC

AlCl₃, a strong Lewis acid which is very soluble in PC (3.2 M), increases the solubility of salts that are insoluble in pure PC by forming complex ions with the anions of these salts. AlCl₃ in combination with LiCl was investigated as an electrolyte for high-energy batteries (ref 3 and 14–19). Conductance measurements and nmr studies were performed in order to understand the transport properties and the species present in AlCl₃ solutions in PC. Boden¹⁴ measured the specific conductance of AlCl₃ in PC over a wide concentration range. The maximum specific conductance of approximately $10^{-2} \text{ohm}^{-1} \text{cm}^{-1}$ occurs at an AlCl₃ concentration of 1.2 M. The specific conductance falls off at higher concentrations because of the increasing viscosity of the solution and due to ion association at high concentrations. Breivogel and Eisenberg¹⁵ measured the equivalent conductance of dilute solutions of AlCl₃ and LiCl–AlCl₃ in PC, using a dc conductivity method. The results were interpreted through the Onsager equation, after being corrected for viscosity effect using the Walden rule. The limiting equivalent conductance of LiAlCl₄ was estimated to be $34.5 \text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$, although the extrapolation was somewhat uncertain.¹⁵ The experimental slope in the case of LiAlCl₄ did not agree with the calculated Onsager slope. Breivogel and Eisenberg¹⁵ attempted to explain the anomalous minimum in the equivalent conductance of AlCl₃ by the presence of different ionic species in different concentration regions. The rapid increase in the equivalent conductance was explained as being caused by an increase in the number of ions per mole of solute as the concentration increases. The following equilibrium reactions were proposed as being able to explain such an increase in the equivalent conductance



Although either of the equations can explain qualitatively the anomalous behavior, further work is required to confirm this hypothesis. A different approach was proposed by Keller, *et al.*,³ who found the same anomalous behavior of AlCl₃ at low concentrations. The minimum in the plot of Λ_0 vs. $C^{1/2}$ was explained by the hydrolysis of AlCl₃ with traces of water to give aluminum hydroxide and HCl.

Keller, *et al.*,³ also studied directly the ionic equilibria of AlCl₃ in PC using nmr techniques. From the ²⁷Al spectra, Keller concluded that the main species are Al(PC)_{*n*}³⁺ and AlCl₄⁻, similar to the species present in an AlCl₃ solution in acetonitrile. High-resolution ¹H spectra of 1 M AlCl₃–PC indicate peaks due to coordinated PC as well as bulk PC. From the ¹H and the ²⁷Al spectra, Keller showed that the Al coordination number (*n*) is six. Therefore, the dissolution of AlCl₃ in PC proceeds according to



Furthermore, it was observed that the addition of LiCl to an AlCl₃–PC solution reduces the concentration of the coordinated Al species, and at the saturation point, where the LiCl:AlCl₃ ratio is 1:1, the coordinated Al species disappears. Such observations can be explained by the reaction between LiCl and Al(PC)₆³⁺ to give AlCl₄⁻.

Keller³ discusses the complexing strength of Al³⁺ toward several aprotic solvents and chloride ion. The complexing strength of Al³⁺ toward Cl⁻ is stronger than toward PC, AN, and water, but weaker than toward DMF. This ionic equilibria analysis of AlCl₃ in PC, according to Keller, *et al.*, is in contrast to the analysis of Breivogel and Eisenberg.¹⁵ Neither of these workers succeeded in explaining quantitatively the minimum in the equivalent conductance plot of AlCl₃ in PC.

Experimental Section

Conductivities of the alkali metal chloride in AlCl₃–PC solutions were measured at 25 and 35° using an ac bridge. Sinusoidal signals at 20 kHz and amplitude of around 15 V were generated by an ac generator detector, Model 861 A, Electro Scientific Industries, Portland, Oreg. The cell resistance and capacitance were balanced with an impedance bridge, Model 290 A, Electro Scientific Industries, Portland, Oreg., and with variable decade capacitors, Models CDA-2 and CDA-3, Cornell-Dubilier Electronic Division, Federal Pacific Electric Division.

The conductance cell consisted of two parallel bright platinum disk electrodes. Because of the relatively low conductivities of the nonaqueous solutions, the cell was designed to give a relatively low cell constant, 0.439cm^{-1} , which was determined using 0.1 and 0.01 N aqueous KCl solution. All electrical wires were shielded. At the frequency of 20 kHz the results were independent of the frequency.

The solutions were prepared in an argon drybox by dissolving weighed amounts of the alkali metal chlorides in 1 M AlCl₃ solution in PC. The volumetric concentrations in moles per liter were calculated from the measured densities of the solutions. The alkali metal chloride concentration varied from 0 to 1 M, all in the presence of AlCl₃ (1 M). The preparation of the solutions was similar to the procedure described for the potential measurements.^{6,7} The AlCl₃ salt was added very slowly to PC to prevent heating and darkening of the solution.

Propylene carbonate (Jefferson Chemical Co., Houston, Tex.) was distilled at 0.5 mm pressure by means of a commercially available distillation column (Semi-CAL series

TABLE II: Specific Conductance of LiCl in AlCl₃ (1 *m*)-PC Solution at 25 and 35°

<i>m</i> , mol/kg of PC	<i>C, M</i>		10 ³ <i>κ</i> , ohm ⁻¹ cm ⁻¹	
	25°	35°	25°	35°
0.02	0.0251	0.0250	6.708	8.315
0.1	0.1262	0.1253	6.741	8.442
1.0	1.2594	1.2512	6.700	8.434

TABLE III: Specific Conductance of NaCl in AlCl₃ (1 *m*)-PC Solution at 25 and 35°

<i>m</i> , mol/kg of PC	<i>C, M</i>		10 ³ <i>κ</i> , ohm ⁻¹ cm ⁻¹	
	25°	35°	25°	35°
0.01	0.0126	0.0125	6.971	8.702
0.10	0.1264	0.1253	6.955	8.693
0.25	0.3163	0.3138	6.910	8.662
0.50	0.6330	0.6279	7.119	8.941

TABLE IV: Specific Conductance of KCl in AlCl₃ (1 *m*)-PC Solution at 25 and 35°

<i>m</i> , mol/ kg of PC	<i>C, M</i>		10 ³ <i>κ</i> , ohm ⁻¹ cm ⁻¹	
	25°	35°	25°	35°
0.0025	0.0031	0.0031	6.915	8.591
0.01	0.0126	0.0125	6.994	8.763
0.10	0.1261	0.1254	7.278	9.108
0.25	0.3167	0.3143	7.754	9.649
0.50	0.6390	0.6330	8.516	10.630
1.00	1.300	1.2920	10.210	12.725

TABLE V: Specific Conductance of RbCl in AlCl₃ (1 *m*)-PC Solution at 25 and 35°

<i>m</i> , mol/ kg of PC	<i>C, M</i>		10 ³ <i>κ</i> ohm ⁻¹ cm ⁻¹	
	25°	35°	25°	35°
0.0025	0.0031	0.0031	7.157	8.914
0.01	0.0126	0.0125	7.041	8.743
0.05	0.0632	0.0626	7.242	9.020
0.10	0.1272	0.1261	7.294	9.101
0.25	0.3194	0.3168	8.022	9.950
1.00	1.3195	1.3091	11.003	13.719

3650, Podbielniak, Franklin Park, Ill.) packed with stainless steel helices. The reflux ratio was 60 to 100 and the head temperature 65°. The first 10% and the last 25% of the solvent were discarded. The "as received" solvent contains a few tenths of a per cent of the following impurities: water, propylene glycol, propion aldehyde, and propylene oxide.⁹ Gas chromatographic analysis of the product performed in this laboratory showed the water content to be always below 50 ppm.⁶

The salts were dried in a vacuum oven (Hotpack, Philadelphia, Pa.) at 200° and approximately 50 μ pressure for at least 24 hr. The final solutions were treated with molecular sieves (Linde 4A) in order to remove traces of water. The molecular sieves were treated before use by heating (300°), high vacuum, and several flashes with argon.

Measurements were made at 25 and 35 \pm 0.01°. Densities of solutions of different alkali metal chloride molalities were measured using a pycnometer at 25 and 35°.

Results

The specific conductance of the alkali metal chlorides in AlCl₃ (1 *m*)-PC solution at 25 and 35° is given in Tables II-VI. The concentration is given on molarity basis (mole/

TABLE VI: Specific Conductance of CsCl in AlCl₃ (1 *m*)-PC Solution at 25 and 35°

<i>m</i> , mol/ kg of PC	<i>C, M</i>		10 ³ <i>κ</i> , ohm ⁻¹ cm ⁻¹	
	25°	35°	25°	35°
0.0025	0.0031	0.0031	6.848	8.508
0.01	0.0126	0.0125	6.732	8.410
0.10	0.1264	0.1259	6.773	8.676
0.25	0.3238	0.3215	7.910	9.756
0.50	0.6597	0.6555	9.070	11.171
1.00	1.3597	1.3481	11.257	13.806

TABLE VII: Densities of the Alkali Metal Chlorides in AlCl₃ (1 *m*)-PC at 25 and 35°

Salt	<i>m</i> , mol/kg of PC	ρ (g/ml)	
		25°	35°
LiCl	0.5	1.262	1.252
	1.0	1.261	1.218
NaCl	0.01	1.259	1.251
	0.10	1.262	1.252
KCl	0.10	1.263	1.253
	0.25	1.265	1.255
	0.50	1.266	1.255
	0.0025	1.261	1.252
	0.01	1.262	1.252
RbCl	0.10	1.261	1.254
	0.25	1.266	1.257
	0.50	1.278	1.267
CsCl	0.01	1.263	1.253
	0.05	1.265	1.253
RbCl	0.10	1.272	1.261
	0.25	1.277	1.267
CsCl	1.00	1.319	1.309
	0.0025	1.263	1.253
	0.01	1.263	1.253
	0.50	1.319	1.310
	1.00	1.359	1.348

liter) and was transferred from the molality basis by multiplying by the density of the solution.

Densities of different molalities of the alkali metal chlorides in AlCl₃ (1 *m*)-PC solution at 25 and 35° are presented in Table VII.

Discussion

The specific conductance of the alkali metal chlorides in AlCl₃ (1 *m*)-PC solution is presented in Figures 1 and 2 at 25 and 35°, respectively. The general trend, with the exception of LiCl, is that the specific conductance increases with an increase in the concentration of the alkali metal chloride, MCl. In the case of NaCl, the specific conductance is almost constant over the entire concentration range. A steady increase in the specific conductance can be observed for KCl, RbCl, and CsCl solutions in AlCl₃ (1 *m*)-PC. Small minima can be observed at low concentrations of LiCl and CsCl. A comparison of the specific conductance of the alkali metal chlorides shows that the specific conductance increases as we pass along the alkali metal series from Li to Cs. Despite the fact that Li is the smallest ion, its chloride solutions have the lowest conductance, while Rb and Cs, which are large ions, have the highest. These observations can be explained on the basis of ionic equilibrium, solvation, and viscosity considerations.

Our measurements yield a value of 6.9×10^{-3} ohm⁻¹ cm⁻¹ for the specific conductance of a 1 *m*, i.e., 1.263 *M*, solution of AlCl₃, as compared to Boden's¹⁴ low-frequency value of 9×10^{-3} ohm⁻¹ cm⁻¹ for a 1 *M* solution of AlCl₃ in PC. However, the present results are in better agreement

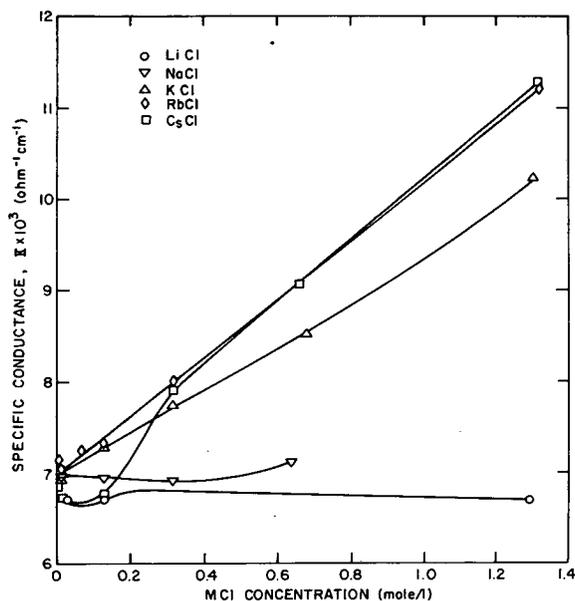


Figure 1. Specific conductance of the alkali metal chlorides in AlCl_3 (1 m)-PC solution at 25°.

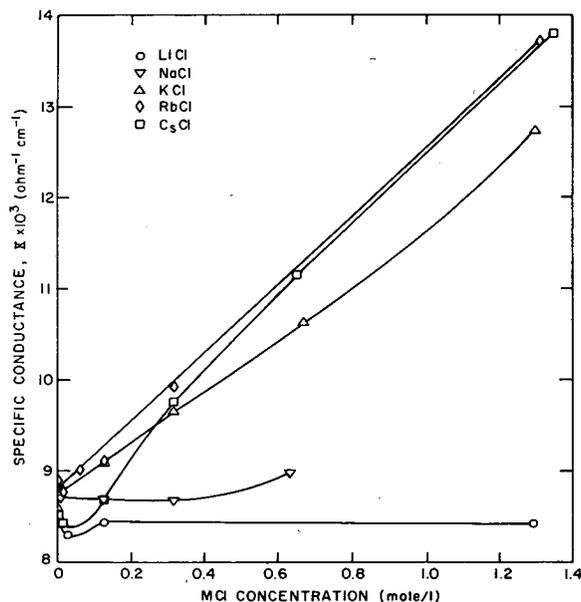
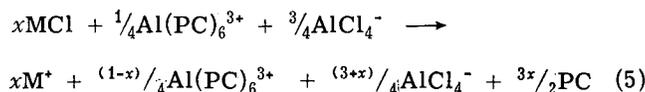


Figure 2. Specific conductance of the alkali metal chlorides in AlCl_3 (1 m)-PC solution at 35°.

with the value $6.96 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ reported by Keller³ for 1 M AlCl_3 solution in PC at 25°. Extrapolation of the conductance curve of Breivogel and Eisenberg¹⁵ results in a somewhat smaller value of approximately $6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. Chilton and Cook¹⁶ report a specific conductance of approximately 7.1×10^{-3} for AlCl_3 (1 M) at 25°. The specific conductance of LiAlCl_4 (1 m) at 25° was measured in the present work as $6.7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The molarity of this solution is 1.26 M . Keller, *et al.*,³ reports a value of 6.58×10^{-3} for saturated solution of LiCl in AlCl_3 (1 M) in PC at 25°, in good agreement with the present results. In addition, Keller's data confirm the present observation that the addition of LiCl to AlCl_3 (1 m) solution reduces the conductance of the resultant solution. Eisenberg, *et al.*'s, conductance measurements of LiAlCl_4 in PC¹⁵ were

restricted to concentrations of up to 0.6 M . However, crude extrapolation of their data to 1 M gives a value of approximately $7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°. The temperature coefficient of the specific conductance of AlCl_3 (1 m) solution in PC can be calculated from the data at 25 and 35°. Our value of $0.15 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{K}^{-1}$ is in reasonable agreement with $dk/dT = 0.17 \times 10^{-3}$, calculated after Keller, *et al.*³ The temperature coefficient of the specific conductance of LiAlCl_4 (1 m) in PC is $0.17 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{K}^{-1}$, again in good agreement with a value of 0.18×10^{-3} , after Keller, *et al.*³ In general, good agreement was found between the present results of AlCl_3 and LiAlCl_4 solutions in PC, and the corresponding results found in the literature. This agreement also should lend credibility to the data obtained for the rest of the alkali metal chloride- AlCl_3 system. Unfortunately, the latter results cannot be compared to earlier results obtained elsewhere; previous work was restricted to the LiCl - AlCl_3 system.

The addition of x moles of alkali metal chloride, MCl , to AlCl_3 (1 m) solution in PC is accompanied by the following reaction



The number of charge carriers increases by $0.5x$ mol, and therefore, purely on this basis, the specific conductance should increase. The equivalent conductances of all the species are not known. The equivalent conductance of LiAlCl_4 in PC is reported as $34.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$.¹⁵ The equivalent ionic conductance of Li^+ in PC is $7.30 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$. Hence the estimated equivalent conductance of AlCl_4^- is relatively quite high: $27.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ (see Table I for comparison). The equivalent ionic conductances of the alkali metal ions in PC increases from Li^+ to Cs^+ , despite the fact that the ionic crystal radius of Li^+ is the smallest, and that of Cs^+ the largest. This reversed trend was observed in most aprotic solvents as well as in water, and is caused by the tightly held sheath of solvent molecules attracted by the intense electric field of the small ion. The equivalent ionic conductances of Li^+ , Na^+ , and K^+ in PC are 7.30, 9.40, and 12.0, respectively (see Table I), and it is expected that the equivalent ionic conductances of Rb^+ and Cs^+ are even higher. The solvated radius of ions in nonaqueous solvents is discussed by Della Monica and Senatore.²⁰ The radii of the solvated metal ions increase from Li^+ to Cs^+ in most solvents (methanol, formamide, N,N -dimethylformamide, dimethylacetamide, pyridine, acetonitrile, and sulfolane). The same trend was observed by Yao and Bennion²¹ in DMSO. Mukherjee, Boden, and Lindauer⁵ report equivalent conductances for Li^+ and K^+ in PC of 7.30 and 11.97, respectively.

The addition of MCl to AlCl_3 solution in PC results in two effects: addition of M^+ ions, and a conversion of $\text{Al}(\text{PC})_6^{3+}$ to AlCl_4^- ions. On the basis of the discussion so far, both effects tend to increase the conductance, and the increase is larger as we move along the alkali metal series from Li to Cs . The equivalent conductance of $\text{Al}(\text{PC})_6^{3+}$ is not known since extrapolation to infinite dilution of AlCl_3 in PC is tenuous (because of the minimum at low concentrations) and therefore quantitative analysis is not possible.

Viscosities of electrolytic solutions have been used as an indication of the degree of structure within the solvent. In aqueous solutions the effects are generally ascribed to the

ability of the various ions to increase or decrease the structure of water over that of the pure solvent. Small ions, such as lithium, are structure makers, while large simple ions, such as cesium, are structure breakers. This is the reason why the viscosities of aqueous alkali metal solutions decrease as the cations change along the series from Li^+ to Cs^+ . According to this consideration, the effect should not be observed for solvents exhibiting only a small tendency for structuring. However, Criss and Mastroianni²² discuss this aspect, and show that even in structureless solvents, the B_η coefficients in the Jones-Dole equation²³

$$\eta/\eta_0 = 1 + A_\eta C^{1/2} + B_\eta C \quad (6)$$

decrease with an increase in the size of the ion presumably because of structuring of the solvent by the smaller cations. In the present system, the original solution is AlCl_3 (1 *m*)-PC and not pure PC. This solution possesses a large degree of order to begin with. The addition of LiCl to this solution destroys the previous order by converting $\text{Al}(\text{PC})_6^{3+}$ to AlCl_4^- , but the small Li^+ ion is a structure maker, and therefore the viscosity increases. On the other hand, the addition of CsCl , for example, destroys the initial order, but the large Cs^+ ion is a poor order maker, and it is predicted, therefore, that the increase in the viscosity with concentration will be small or even reversed in the case of RbCl and CsCl solutions in AlCl_3 -PC.

Evidence that in PC viscosity varies with the size of the cation can be found in the viscosity measurements of Mukherjee and Boden.⁴ The B_η coefficient decreases in the order $\text{LiClO}_4 > n\text{-Bu}_4\text{NClO}_4 > \text{Et}_4\text{NClO}_4$, in agreement with the size of the solvated cations.

The minimum in the conductance curve for LiCl in AlCl_3 (1 *m*)-PC can be the result of ionic association of LiCl in PC.^{4,24-26} The association constant for LiCl was estimated to be 557 from conductance measurements,⁴ and as 59 from emf measurements.²⁵ The minimum in the conductance curve of CsCl in AlCl_3 (1 *m*)-PC can be the result of a combination of the opposing factors which determine the conductance of the solution.

The minimum in the plot of the equivalent conductance of AlCl_3 in PC was observed by several workers.^{3,15,16} There is no conclusive explanation for this behavior at low concentration. An attempt to explain the minimum on the basis of the water content of the solvent seems questionable because the minimum was observed by three independent laboratories and the water contents were probably dif-

ferent. Moreover, if we assume that the minimum is the result of the water content, we can extrapolate to infinite dilution, neglecting the minimum, and obtain the molar conductance at infinite dilution, $\Lambda_0 = 18 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The equivalent conductance of AlCl_4^- was estimated before at 27.2, and according to this, the equivalent ionic conductance of $\text{Al}(\text{PC})_6^{3+}$ would be

$$\Lambda_{\text{Al}(\text{PC})_6^{3+}}^0 = \frac{4}{3}(18) - 27.2 = -3.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1} \quad (7)$$

Thus it seems that the minimum in the equivalent conductance of AlCl_3 is not due to impurities, but is probably a genuine feature associated with multiple ionic equilibria.

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