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Conductivities in Thionyl Chloride

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ABSTRACT

Conductivity measurements in thionyl chloride are reported for dilute solutions of $AlCl_3$, $LiAlCl_4$, and the tetrapropylammonium (Pr_4N) salts Pr_4NCl, Pr_4NClO_4, Pr_4NAlCl_4. The data for electrolyte solutions having concentrations in the range of ~0.01 to 1×10^{-5} mole dm^{-3} were fitted empirically to an equation of the Fuoss-Hsia type. In all cases except for $AlCl_3$ ion pair formation was found to be extensive. $AlCl_3$ solutions in thionyl chloride appear to be complex possibly owing to the formation of complex species such as Al_2Cl_6 and $Al_2Cl_7^-$. The effect of ionic strength on the solubility of LiCl is discussed.

In addition to the interesting general solvent properties of thionyl chloride (1), this solvent has received considerable attention as a cathode depolarizer in primary lithium batteries (2, 3). A number of important physico-chemical properties of electrolytic solutions have been reported (1, 4) including the conductivities of $LiAlCl_4$ solutions (4). In the present paper, the conductivities of dilute solutions (between 0.01 and 1×10^{-5} mole dm^{-3}) of various salts including $LiAlCl_4$ are reported and analyzed in accordance with an ion pairing model. The dielectric constants and densities of the pure solvent over a small temperature range are also reported.

Experimental

Chemicals.—Purified $LiAlCl_4$ was supplied by W. K. Behl of this laboratory and was purified as described previously (3). Fluka purris $AlCl_3$ was sublimed in vacuum and transferred to a dry box while under vacuum. Tetrapropylammonium perchlorate (Pr_4NClO_4) was recrystallized from distilled water, and Pr_4NCl was precipitated from an acetone/ether mixture: both salts were dried in a vacuum at 60 C and stored in the dry box. AR grade LiCl was dried at 110 C and stored in the dry box. Tetrapropylammonium tetrachloroaluminate, Pr_4NAlCl_4, was prepared in the dry box by mixing stoichiometric quantities of $AlCl_3$ and Pr_4NCl followed by addition of the solvent. $SOCl_2$ (MCB/B best grade) was refluxed with P_2O_5 at room temperature for 24-48 hr before distillation: the middle 2/3 of the colorless distillate was retained for use. A Vacuum Atmospheres Corporation dry box with an argon atmosphere was used in this work.

Dielectric constant measurements.—The static dielectric constants at 15°, 25°, and 35°C were measured by the comparison method (5). The cell, which utilized Type 304 stainless steel, consisted of concentric steel electrodes threaded onto a Teflon base which also formed part of a water jacket. The cell capacitances were measured at 1 MHz by a substitution method with a General Radio 1606-B bridge and 722-D and 1422-ME precision capacitors. The cell constants were determined from measurements with air, benzene, and tetrahydrofuran. The cell was filled with $SOCl_2$ in the dry box, sealed with a Teflon stopper, and removed to the laboratory for capacitance measurements at 15°, 25°, and 35° ± 0.1 C.

Conductivity measurements.—These measurements were carried out at 25° ± 0.03 C (uncalibrated thermometer) at 1 kHz using a General Radio 1608-A impedance bridge. Yellow Springs Instrument Company Type 3402 conductivity cells were modified to permit sealing with a 10/20 ST Pyrex stopper, and to permit immersion in a thermostated water bath. Smooth Pt electrodes were used, and the two cells modified for this work had cell constants of the order of 0.1 cm^{-1}. The cell constants were determined with dilute KCl solutions. All solutions were prepared in the dry box at room temperature (22°-26° C), the cells filled and sealed, and removed into the laboratory for the measurements. Solutions were prepared on a volume basis, and corrections to 25 C were made utilizing results from dilatometric measurements on the pure solvent, and in several cases for dilute salt solutions. The error in concentration using solvent densities rather than solution densities is negligible. The major factors influencing the accuracies of the conductivities were the weighing of salts in the dry box (±0.04%) and the determination of final volumes (±0.2%): the accuracy in the reported concentrations is therefore ±0.3%. Due to the use of smooth Pt electrodes and associated instrumentation, the overall accuracy in the molar conductivities is no better than ±3%.

Results and Data Analyses

The static dielectric constants at 15°, 25°, and 35°C are, respectively, 9.65, 9.25, and 8.77D. These results were fitted by least squares to the following smoothing equation

$$\epsilon/D = -3.88 + 3903/(T/K) \qquad [1]$$

For the densities of pure $SOCl_2$, dilatometric measurements at 15°, 20°, 25°, and 35° C were fitted by least squares to the following smoothing equation

$$d/\mathrm{kg\ m^{-3}} = 1.6284 - 0.00191(t - 25) \qquad [2]$$

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The experimental conductivity data for $LiAlCl_4$, $AlCl_3$, Pr_4NClO_4, Pr_4NCl, Pr_4NAlCl_4 (Λ) were calculated from the electrolytic conductivities, κ, after correcting for the solvent conductance: at 25°C the electrolytic conductivity of the solvent is $\kappa(SOCl_2) = 5 \times 10^{-9}$ S cm^{-1} (6). The conductivity data were analyzed using the following equation (7)

$$\Lambda = \Lambda^{\infty} - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) + J_2(\alpha c)^{3/2} - \Lambda\alpha c y_{\pm}^2/(K^{\circ}_D y_n) \quad [3]$$

The Onsager and Fuoss-Onsager constants S and E were calculated using the present value for the dielectric constant of $SOCl_2$ and a value of 0.626 cp for the viscosity at 25°C (6). The remaining terms in Eq. [3] are defined as follows: α is the degree of dissociation of the neutral ion pair; c is the total molar concentration of the salt; Λ^{∞} is the molar conductivity at infinite dilution; $y_{\pm}$ is the mean molar activity coefficient and y_n is the activity coefficient for the neutral ion pair; J_1 and J_2 are constants which were evaluated empirically by least squares; and K°_D is the dissociation constant for the ion pair defined by

$$K^{\circ}_D = \alpha^2 c y_{\pm}^2/[(1-\alpha)y_n] \quad [4]$$

Initial attempts to evaluate activity coefficients by emf measurements on cells without transport failed. In spite of reports (1b) that metals such as Ag, Ni, Mo respond thermodynamically to Cl^-, attempts to utilize these electrodes in various combinations, and in combinations with Li and Ag, AgCl electrodes, lead to irreproducible results. The mean molar activity coefficients were therefore calculated from the Davies equation (8)

$$\log y_{\pm} = -AI^{1/2}/[1 + I^{1/2}] + 0.3AI \quad [5]$$

where I is the ionic strength,[1] and A is the Debye-Hückel factor. At the present time the only justification for the use of Eq. [5] for $SOCl_2$ solutions is that the Davies equation has previously been successfully used in aprotic solvents of varying dielectric constants (9, 10). Since $SOCl_2$ has a low dielectric constant, it is anticipated that salting out coefficients would be significantly more important than in aqueous solutions, and in the present calculations, it is assumed that the activity coefficient for the neutral ion pair is given by

$$\log y_n = 0.3AI \quad [6]$$

For the concentrations employed in the present study, the y_n values as calculated from this equation are close to unity and have a small effect on the magnitudes of K°_D and Λ^{∞}. Equation [6] was incorporated into the present calculations.

Equation [3] was solved by evaluating J_1 and J_2 by least squares (11). Both K°_D and Λ^{∞} were varied until the error σ_{Λ} was minimized. σ_{Λ} is defined by

$$\sigma_{\Lambda} = \{\Sigma(\Lambda_{obs} - \Lambda_{calc})^2/(N-3)\}^{1/2} \quad [7]$$

where N is the number of data points in each experiment. The results are summarized in Table VI, and the associated results for α and y have been included in Tables I-V. Two, or three at the most, data points for concentrations of the order of 0.1 mole dm^{-3} are not reported in the tables. The reason these points were omitted from the present analyses is that their inclusion gave rise to abnormally large σ_{Λ} values which is undoubtedly due to the formation of triple ions according to (4, 6)

$$MX + X^- = MX_2^- \quad [8a]$$

$$MX + M^+ = M_2X^+ \quad [8b]$$

The conductivity data for the binary $AlCl_3$-$SOCl_2$ system could not be analyzed by the present method, and the possible reasons for this are discussed below.

[1] For 1:1 electrolytes, $I = \alpha c$.

Table I.* The $LiAlCl_4$-$SOCl_2$ system at 25°C

10^4c	Λ	α	$y_{\pm}$	y_n
93.68	7.28	0.147	0.357	1.012
61.00	7.76	0.152	0.427	1.008
38.15	9.52	0.165	0.494	1.006
14.80	12.37	0.209	0.606	1.003
11.58	13.97	0.225	0.631	1.002
10.72	14.42	0.230	0.639	1.002
7.806	16.38	0.253	0.669	1.002
6.134	17.49	0.273	0.690	1.001

* In Tables I-V, the experimental data are c/mole dm^{-3} and Λ S-cm^2 mole^{-1}. The quantities α, $y_{\pm}$, and y_n were calculated as described in the text.

Table II. The $AlCl_3$-$SOCl_2$ system at 25°C

10^4c	Λ
68.87	0.49
22.19	1.27
11.58	2.21
5.89	4.13

Table III. The $(C_3H_7)_4NClO_4$-$SOCl_2$ system at 25°C

10^4c	Λ	α	$y_{\pm}$	y_n
14.23	25.71	0.310	0.552	1.004
8.223	30.70	0.353	0.616	1.003
7.110	32.34	0.367	0.631	1.002
4.106	38.67	0.424	0.686	1.002
3.510	39.93	0.442	0.700	1.001
2.085	48.18	0.506	0.744	1.001
1.666	57.85	0.599	0.794	1.001
0.640	67.30	0.671	0.828	1.000
0.510	68.56	0.703	0.841	1.000
0.258	80.59	0.792	0.877	1.000

Table IV. The $(C_3H_7)_4NCl$-$SOCl_2$ system at 25°C

10^4c	Λ	α	$y_{\pm}$	y_n
29.69	35.15	0.463	0.357	1.012
15.27	40.83	0.485	0.466	1.006
7.907	48.06	0.533	0.559	1.004
4.916	53.12	0.580	0.618	1.002
2.321	63.64	0.665	0.701	1.001
1.840	64.96	0.692	0.723	1.001
0.968	76.28	0.768	0.780	1.001
0.481	84.45	0.843	0.832	1.000

Table V. The $(C_3H_7)_4NAlCl_4$-$SOCl_2$ system at 25°C

10^4c	Λ	α	$y_{\pm}$	y_n
29.22	23.97	0.369	0.400	1.009
19.23	25.07	0.385	0.465	1.006
11.46	31.08	0.419	0.538	1.005
5.864	37.72	0.481	0.620	1.002
2.899	45.94	0.561	0.694	1.001
1.727	52.09	0.627	0.742	1.001
1.154	59.67	0.680	0.775	1.001
0.721	65.97	0.741	0.810	1.000

An attempt was also made to evaluate the solubility of LiCl, c_{satd}, in the pure solvent. The solubility is given by

$$c_{satd} = [LiCl]_{sln} + [Li^+] \quad [9a]$$

and in terms of equilibrium constants

$$c_{satd} = K^{\circ}_{s0}/(K^{\circ}_D y_n) + (K^{\circ}_{s0})^{1/2}/y_{\pm} \quad [9b]$$

where K°_{s0} is the thermodynamic solubility product constant for LiCl. $[Li^+]$ can be calculated from the electrolytic conductivity of a saturated LiCl solution, and c_{satd} is obtained from Eq. [9b]. $SOCl_2$ was saturated with LiCl in the dry box at 22°-26°C for 72 hr with occasional shaking. Storage of these solutions for more than 7 days results in slight decomposition which is indicated by the appearance of a light green color. The conductivity cell containing excess solid LiCl was filled in the dry box, removed to the laboratory, and

Table VI.* Results of analyses based on Eq. [3]

Salt	J_1	$-J_2$	$\Lambda^\infty(\sigma)$	$10^6 K^\circ_D(\sigma)$	σ_Λ
$LiAlCl_4$	7.649×10^4	3.531×10^6	75.5 (1.7)	3.0 (0.1)	0.28
Pr_4NClO_4	1.015×10^5	2.142×10^5	106.2 (1.2)	6.0 (0.2)	0.72
Pr_4NCl	1.302×10^6	9.768×10^5	106.6 (1.3)	15.0 (0.6)	0.82
Pr_4NAlCl_4	8.411×10^4	8.149×10^4	97.0 (2.0)	10.0 (0.5)	0.88

* All data are for 25°C. Λ^∞ units are $S\ cm^2\ mole^{-1}$, and K°_D units are mole dm^{-3}.

placed in the water bath at about 33°C for 10 min. Reducing the temperature to 25°C and measuring the conductivity gave an electrolytic conductivity for the solution of $\kappa(\text{sln}) = 1.65 \times 10^{-7}\ S\ cm^{-1}$; correcting for the electrolytic conductivity of the solvent, $\kappa(\text{LiCl}) = 1.60 \times 10^{-7}\ S\ cm^{-1}$. The concentration of dissociated LiCl, c' (note $c' = [Li^+]$), was calculated from the Onsager equation

$$1000\kappa(\text{LiCl})/c' = [\Lambda^\infty - S(c')^{1/2}]/[1 + y_\pm{}^2 c'/(K^\circ_D y_n)] \quad [10]$$

$\Lambda^\infty(\text{LiCl})$ is obtained from the data in Table VI, *i.e.*, $\Lambda^\infty(\text{LiCl}) = \Lambda^\infty(LiAlCl_4) + \Lambda^\infty(Pr_4NCl) - \Lambda^\infty(Pr_4NAlCl_4) = 85.1\ S\ cm^2\ mole^{-1}$. Since at high dilutions α values are generally quite large (*i.e.*, $\simeq$ 0.9), K°_D is rather insensitive to the final c_{satd} and it is found that c_{satd} is almost constant (within experimental error) from $K^\circ_D \doteq 0.1$ to 1×10^{-5} mole dm^{-3}. Values of $K^\circ_D = 1 \times 10^{-6}$ mole·dm^{-3} or smaller results in significantly increasing c_{satd} values. In light of the smallest K°_D value of 3×10^{-5} mole dm^{-3} for $LiAlCl_4$ found in the present work, and the value of $K^\circ_D = 1 \times 10^{-5}$ mole dm^{-3} for $(CH_3)_4NOC_6H_2(NO_2)_3$ (picrate) reported by Beronius and Brändström (15) in water saturated methylene chloride ($\epsilon = 9.53D$), the present assumed value of $K^\circ_D(\text{LiCl}) = 1 \times 10^{-5}$ in $SOCl_2$ seems a reasonable lower estimate. Solving for c' by an iterative method, the following are obtained (note $K^\circ_{s0} = (\alpha c_{satd} y_\pm)^2$)

$$c_{satd} = 2.2 \times 10^{-6}\ \text{mole dm}^{-3} \text{ and}$$

$$K^\circ_{s0} = 3.3 \times 10^{-12}\ \text{mole}^2\ \text{dm}^{-12}$$

Discussion and Conclusions

The data in Table VI demonstrate that the salts studied are all highly associated. The only other study on ion association by conductivity methods is that of Venkatasetty and Ebner (4) in which values of $\Lambda^\infty = 16.5\ S\ cm^2\ mole^{-1}$ and $K^\circ_D = 1.61 \times 10^{-3}$ mole dm^{-3} were reported. They analyzed conductivity data from a simplified form of the Fuoss-Shedlovsky equation (12), and neglected to include activity coefficients. These authors also report $K_3/\Lambda_3{}^\infty = 1.21 \times 10^{-3}\ dm^3\ S^{-1}\ cm^{-2}$. By means of Walden's rule, $\Lambda_3{}^\infty$ for the triple ion can be estimated from $\Lambda^\infty(LiAlCl_4)/3$: using the present value for $\Lambda^\infty(LiAlCl_4)$, the molar conductivity for the triple ions given in Eq. [8] at infinite dilution is 25.8 $S\ cm^2\ mole^{-1}$ which gives a value of 0.03 $mole^{-1}\ dm^3$ for the triple ion formation constant K_3. Since the conductivity data of Venkatasetty and Ebner appear (only graphical data are given in their paper) similar to the present data, the differences in our results for Λ^∞ and K°_D must be due to the method of treament of the data. For $K_D < 10^{-3}$, the Fuoss-Shedlovsky plots become insensitive to Λ^∞, and the K_D values are even more uncertain (7, 13). In addition, the neglect of activity coefficients is not justified (the Debye-Hückel "A" factor = 12.64 $mole^{-1/2}\ dm^{3/2}$ at 25°C). The major problem encountered in the present work involves the estimation of activity coefficients. In a previous study (11), it was found that the empirical solution of Eq. [3] using Eq. [4]-[6] can reproduce previously published Λ^∞ and K°_D values for K°_D ranging from 1 to 1×10^{-5} mole dm^{-3}, and in solvents having dielectric constants ranging from 78.3D (water) to 9.53D (83 mass% p-dioxane in water). Generally, the analysis of the conductivity equation [3] by more elaborate methods (7) employs the following relation for the activity coefficients

$$\log y_\pm = -A(\alpha c)^{1/2}/[1 + BR(\alpha c)^{1/2}] \quad [11]$$

The activity coefficients listed in Tables I-V can be reproduced by Eq. [11] by taking values of the ion association distance, R, around 0.4 nm. However if R is equated (14) to the Bjerrum critical distance q ($q = z^2e^2/(2\epsilon kT) = 3.0$ nm for 1:1 electrolytes in $SOCl_2$ at 25°C), then the calculated activity coefficients differ significantly from those given in Tables I-V, *e.g.*, for concentrations of the order of 0.01 mole dm^{-3}, Eq. [11] results in $y_\pm$ values about twice as great as those calculated from Eq. [5], and this difference decreases to around 10% at concentrations of the order of 1×10^{-4} mole dm^{-3}.

The analysis of the conductivity data for $AlCl_3$ solutions in terms of the simple dissolution reaction

$$AlCl_3 + SOCl_2 = SOCl^+ + AlCl_4^-$$

$$K^\circ_D = (SOCl^+)(AlCl_4^-) \quad [12]$$

was not successful, *i.e.*, σ_Λ values were generally large and insensitive to values of K°_D. This inability to fit the data to this simple dissolution mechanism is attributed to both the experimental error and to the probability that dissolution is more complex and involves such species as Al_2Cl_6, $Al_2Cl_7^-$, etc.

The solubility of LiCl in $SOCl_2$ plays an important role in the stability of lithium-$SOCl_2$ primary batteries (2). The solubility for the binary system is described by Eq. [9b], and in the presence of an excess of "neutral" electrolyte, *i.e.*, one which does not yield Cl^- or Li^+ ions, the solubility is given to a good approximation by

$$c_{satd} = (K^\circ_{s0})^{1/2}/y_\pm \quad [13]$$

Equation [13] demonstrates the need for reliable activity coefficient data at high concentrations of the neutral salt. For example if Eq. [5] is used to approximate $y_\pm$ at higher concentrations, the solubility of LiCl reaches a maximum of 0.005 mole dm^{-3} at ionic strengths of around 0.4-0.5 mole dm^{-3}; this is three orders of magnitude greater than the solubility in the binary system. In solutions containing a large excess of a salt which yields a common ion, say $LiAlCl_4$, the solubility of LiCl is given approximately by

$$c_{satd} = K^\circ_{s0}/\{y_\pm{}^2[Li^+]\} \quad [14]$$

In highly concentrated $LiAlCl_4$ solutions, say 1.5 mole dm^{-3}, c_{satd} will still be significantly larger than it would be in the pure binary system because $[Li^+]$ will be small as the major species in solution are the ion pair and the triplet Li_2Cl^+. Taking $K_3 \simeq 0.03\ mole^{-1}\ dm^3$, the concentration of Li_2Cl^+ is about 0.3 mole dm^{-3}, and by Eq. [14], the solubility of LiCl should increase significantly.

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