Densities, Viscosities, and Conductivities of Mixtures of Selected Organic Cosolvents with the Lewis Basic Aluminum Chloride + 1-Methyl-3-ethylimidazolium Chloride Molten Salt

Ronald L. Perry, Kevin M. Jones, William D. Scott, Qing Liao, and Charles L. Hussey*

Department of Chemistry, University of Mississippi, University, Mississippi 38677

The densities, kinematic viscosities, and specific conductances of mixtures of the organic cosolvents acetonitrile, benzene, and dichloromethane with the Lewis basic room-temperature chloroaluminate molten salt aluminum chloride + 1-methyl-3-ethylimidazolium chloride ($AlCl_3$ + MeEtimCl) were determined at 25 °C. Cosolvents were added to melts containing 49.00 and 44.40 mol % (m/o) $AlCl_3$. Polynomial equations were fitted to the results as a function of the mass fraction of the cosolvent. The addition of relatively small amounts of these cosolvents causes a significant decrease in viscosity and a large increase in the conductivity of basic melts.

Introduction

Mixtures of anhydrous aluminum chloride and the quaternary ammonium chloride salt 1-methyl-3-ethylimidazolium chloride (MeEtimCl), which melts at about 85 °C, comprise a family of room-temperature molten salts with adjustable Lewis acidity. The physical and chemical properties of the $AlCl_3$ + MeEtimCl system have been reviewed extensively (Carlin and Wilkes, 1994; Hussey, 1994; Osteryoung, 1986). The phase transitions, densities, electrical conductivities, and viscosities of a number of $AlCl_3$ + 1,3-dialkylimidazolium chloride mixtures, including those derived from MeEtimCl have been reported (Fannin et al., 1984). The $AlCl_3$ + MeEtimCl molten salt system has been widely used as an electrochemical solvent and has potential applications as an electrolyte for high-energy batteries and for the electroplating of aluminum and aluminum alloy films. It is also of interest as a solvent for the liquefaction of coal. However, the modest electrical conductivities and/or the high viscosities of the $AlCl_3$ + MeEtimCl melt at room temperature are obstacles to these applications.

Several studies have been reported in which the addition of various organic liquids or "co-solvents" to room-temperature chloroaluminates was explored (Moy and Emmenegger, 1992; Papageorgiou and Emmenegger, 1993; Robinson et al., 1979; Zawodzinski and Osteryoung, 1989). It was found that the addition of small quantities of aromatic hydrocarbon cosolvents such as benzene (Robinson et al., 1979) or 1,2-dichlorobenzene (Papageorgiou and Emmenegger, 1993) to acidic melts resulted in mixtures with lower viscosities and higher conductivities than the neat molten salt. The origin of this effect is not completely understood, but it is generally believed that the cosolvent acts to decrease ion-pairing between the anionic and cationic constituents of the molten salt. Despite the many advantages to be gained by adding cosolvents to room-temperature chloroaluminate melts, no systematic investigation of the influence of these additives on the viscosity and conductivity of these melts has been reported. In this paper, we report the densities, kinematic viscosities, and specific conductances of mixtures of the organic cosolvents acetonitrile (ϵ_r (20 °C) = 37.5), benzene (ϵ_r (20 °C) = 2.28), and dichloromethane (ϵ_r (20 °C) = 9.08) with two different compositions of the Lewis basic $AlCl_3$ + MeEtimCl melt, one containing 49.00 mol % (m/o) $AlCl_3$ or $x_2 = 0.4900$ and the other containing 44.40 m/o $AlCl_3$ or $x_2 = 0.4440$.

Experimental Section

Materials. Aluminum chloride (Fluka, puriss) was sublimed three times under vacuum before use. MeEtimCl was synthesized and purified according to standard procedures (Wilkes et al., 1982). Acetonitrile (Aldrich, HPLC grade) was dried over 3A molecular sieves, distilled from CaH_2, passed through a column of activated alumina, and stored over fresh 3A sieves before use. Benzene (Aldrich, HPLC grade) and dichloromethane (Aldrich, HPLC grade) were stored over 3A sieves before use. The $AlCl_3$ + MeEtimCl melt reacts vigorously with atmospheric moisture. Therefore, it was necessary to prepare the melt and melt + cosolvent samples in dry nitrogen- or argon-filled gloveboxes. Samples were stored in the glovebox in tightly capped vials with Teflon-lined closures. Density, viscosity, and conductivity measurements were performed under conditions that precluded contact between the samples and the atmosphere, except where noted. The melt compositions reported herein are expressed as the mole fraction of $AlCl_3$, x_2, in the $AlCl_3$ + MeEtimCl mixture. Cosolvent + melt mixtures are designated by the mass fraction, w_1, or mole fraction, x_1, of solvent in the cosolvent (1) + $AlCl_3$ (2) + MeEtimCl (3) mixtures.

Density. Densities were measured by using a Mettler-Paar Model DMA 40 digital densimeter. This instrument was calibrated according to the manufacturer's recommendations with air and distilled water. The sample chamber of the instrument was maintained at (25.00 ± 0.05) °C with circulating oil from an oil bath. The temperature of the oil bath was controlled with a modified Haake Model E3 thermoregulator. Samples were transported from the glovebox and introduced into the measuring capillary of the densimeter by means of glass syringes fitted with Luer stopcocks. Each data point was the average of not less than four readings. The estimated experimental uncertainty of these measurements was ±0.0001 g cm^{-3}.

Viscosity. Viscosity measurements were carried out in no. 150 and no. 200 Cannon-Fenske viscometers (Cannon Instrument Co., State College, PA). Some measurements were performed with the modified viscometer described in

0021-9568/95/1740-0615$09.00/0

Table 1. Comparison of $AlCl_3$ + MeEtimCl Density, Viscosity, and Conductivity Data at 298.2 K

property	present work	literature[a]	% difference
	$x_2 = 0.4900$		
$\varrho/(g \cdot cm^{-3})$	1.2844	1.2902	−0.45
$10^2\nu/(cm^2 \cdot s^{-1})$	0.1399	0.1544	−9.39
$\kappa/(S \cdot m^{-1})$	1.87	2.02	−7.43
	$x_2 = 0.4440$		
$\varrho/(g \cdot cm^{-3})$	1.2713	1.2722	−0.07
$10^2\nu/(cm^2 \cdot s^{-1})$	0.2690	0.2760	−2.54
$\kappa/(S \cdot m^{-1})$	1.10	1.14	−3.51

[a] Fannin et al., 1984.

Table 2. Densities of Organic Liquid (1) + $AlCl_3$ (2) + MeEtimCl (3) Mixtures at 298.2 K

$x_2^b = 0.4900$			$x_2 = 0.4440$		
w_1^a	x_1	$\varrho/(g \cdot cm^{-3})$	w_1	x_1	$\varrho/(g \cdot cm^{-3})$
CH_3CN					
0.000 00	0.000 00	1.2894	0.000 00	0.000 00	1.2713
0.021 07	0.068 43	1.2730	0.023 01	0.074 70	1.2586
0.059 04	0.176 38	1.2448	0.044 54	0.137 78	1.2373
0.116 70	0.310 78	1.2064	0.107 40	0.292 01	1.1977
0.273 10	0.561 84	1.1056	0.144 70	0.367 06	1.1766
0.382 90	0.679 25	1.0411	0.249 50	0.532 62	1.1096
C_6H_6					
0.000 00	0.000 00	1.2894	0.000 00	0.000 00	1.2713
0.092 60	0.154 71	1.2448	0.152 90	0.245 35	1.2032
0.213 50	0.327 43	1.1902	0.248 80	0.373 66	1.1624
0.337 50	0.477 43	1.1378	0.350 00	0.492 36	1.1219
0.362 60	0.505 01	1.1271	0.386 50	0.531 57	1.1066
0.371 80	0.514 90	1.1242	0.462 70	0.608 02	1.0751
0.432 90	0.577 89	1.1003			
CH_2Cl_2					
0.000 00	0.000 00	1.2894	0.000 00	0.000 00	1.2713
0.105 10	0.162 30	1.2997	0.094 52	0.147 45	1.2826
0.202 40	0.295 09	1.3075	0.186 10	0.274 75	1.2923
0.303 50	0.418 21	1.3147	0.240 90	0.344 60	1.2973
0.367 30	0.489 18	1.3190	0.405 00	0.530 02	1.3111
0.459 20	0.583 46	1.3236	0.492 30	0.616 35	1.3174

[a] w_1 is the mass fraction of cosolvent. [b] x_2 is the mole fraction of $AlCl_3$ in the $AlCl_3$ + MeEtimCl mixture before the addition of cosolvent.

Table 3. Kinematic Viscosities of Organic Liquid (1) + $AlCl_3$ (2) + MeEtimCl (3) Mixtures at 298.2 K

$x_2^b = 0.4900$			$x_2 = 0.4440$		
w_1^a	x_1	$10^2\nu/(cm^2 \cdot s^{-1})$	w_1	x_1	$10^2\nu/(cm^2 \cdot s^{-1})$
CH_3CN					
0.0000	0.0000	13.99	0.0000	0.0000	26.90
0.0117	0.0388	12.59	0.0092	0.0308	23.31
0.0211	0.0685	10.32	0.0169	0.0556	20.61
0.0395	0.1231	8.47	0.0293	0.0938	16.89
0.0492	0.1501	7.72	0.0445	0.1377	13.60
0.0590	0.1763	6.77	0.0708	0.2071	9.80
0.0990	0.2727	4.96	0.0909	0.2553	8.02
0.1167	0.3108	4.18	0.1074	0.2920	6.81
0.1938	0.4507	2.57	0.1241	0.3269	5.83
0.2721	0.5606	1.82	0.1447	0.3671	4.58
0.3039	0.5984	1.61	0.1724	0.4166	4.03
0.3829	0.6793	1.32	0.2029	0.4660	3.35
0.4524	0.7382	1.08	0.2495	0.5326	2.54
			0.3223	0.6198	1.79
			0.4000	0.6956	1.35
C_6H_6					
0.0000	0.0000	13.99	0.0000	0.0000	26.90
0.0206	0.0364	12.39	0.0318	0.0559	21.86
0.0344	0.0601	11.53	0.0599	0.1030	18.19
0.0493	0.0851	10.77	0.0906	0.1521	15.50
0.0628	0.1073	10.15	0.1292	0.2109	12.53
0.0791	0.1335	9.59	0.1510	0.2426	11.23
0.0929	0.1552	9.11	0.1781	0.2807	9.95
0.1059	0.1752	8.56	0.2114	0.3256	8.61
0.1432	0.2306	7.54	0.2305	0.3505	7.86
0.1700	0.2686	6.65	0.2609	0.3887	6.95
0.2300	0.3488	5.38	0.3071	0.4439	5.69
0.2850	0.4169	4.56	0.3300	0.4701	5.13
0.3580	0.5000	3.68	0.3535	0.4962	4.79
			0.4015	0.5472	4.37
CH_2Cl_2					
0.0000	0.0000	13.99	0.0000	0.0000	26.90
0.0164	0.0268	12.70	0.0222	0.0363	23.04
0.0419	0.0673	11.03	0.0331	0.0537	21.18
0.0821	0.1286	8.73	0.0608	0.0969	17.54
0.1057	0.1632	7.85	0.0925	0.1445	14.25
0.1416	0.2139	6.49	0.1289	0.1969	11.27
0.1762	0.2608	5.57	0.1787	0.2650	8.60
0.2143	0.3103	4.66	0.1817	0.2689	8.28
0.2390	0.3413	4.27	0.2108	0.3068	7.19
0.2600	0.3669	3.88	0.2403	0.3439	6.17
0.2942	0.4074	3.36	0.2745	0.3853	5.15
0.3220	0.4393	3.05	0.2994	0.4145	4.62
0.3661	0.4879	2.57	0.3502	0.4717	3.70
0.3990	0.5227	2.28	0.3987	0.5235	2.93
0.4270	0.5514	2.07	0.4557	0.5811	2.31

[a] w_1 is the mass fraction of cosolvent. [b] x_2 is the mole fraction of $AlCl_3$ in the $AlCl_3$ + MeEtimCl mixture before the addition of cosolvent.

a previous publication from this laboratory (Sanders et al., 1986). This viscometer was filled and hermetically sealed in a glovebox, attached to a vertical turntable, and completely immersed in a water bath. Another modified viscometer used during this study was fabricated by attaching female 12/5 spherical joints to the open ends of a commercial viscometer. Vacuum stopcocks with matching male 12/5 spherical joints were mated to the viscometer and held in place with clamps. This modified viscometer was filled with sample and sealed in the glovebox. After removal from the glovebox, it was partially submerged in a temperature-regulated water bath to a level approximately 2 cm below the joints. The stopcocks were connected to small Drierite desiccant-filled canisters with rubber tubing. The viscometer was opened to the atmosphere through the dessicant when data were collected. There was no statistical difference in the results obtained with the different viscometers and methods. The viscometers were calibrated with acetonitrile, distilled water, ethanol (McCormick), 1-butanol (Baker, reagent grade), and freshly distilled ethylene glycol (Baker, reagent grade). Reference data for these compounds were taken from the *Handbook of Chemistry and Physics*, 65th ed. Each data point was the average of no less than five runs. Efflux times were recorded to 0.01 s with a digital stopwatch. The temperature of the water bath was maintained at (25.00 ± 0.05) °C with a Braun Model 1420 Thermomix immersion controller. The estimated experimental uncertainty of these measurements was ±0.01 $cm^2\ s^{-1}$.

Conductivity. Conductivity data were obtained with a Yellow Springs Instrument Co. no. 3403 dip-type conductivity cell and a Stanford Research Systems Model SR720 LCR meter. A drive voltage of 100 mV was used in the *C−R* series mode for all measurements. The conductivity cell was equipped with platinized platinum−iridium electrodes and had a nominal cell constant of 100 m^{-1}. It could be sealed airtight into a no. 15 ACE-Thred adapter tube (ACE Glass) with a Teflon bushing and Viton O-ring; the plain end of this tube had been closed previously by glass blowing. The cell was filled and sealed in a glovebox and then equilibrated in the water bath described above prior to resistance measurements. The cell resistances were found to vary as much as 35% over the frequency range extending from 100 Hz to 10 kHz. However, plots of cell resistance versus the inverse square root of the frequency were linear, and the intercepts of such plots were used to

Table 4. Conductivities of Organic Liquid (1) + $AlCl_3$ (2) + MeEtimCl (3) at 298.2 K

$x_2^b = 0.4900$			$x_2 = 0.4440$		
w_1a	x_1	$\kappa/(S \cdot m^{-1})$	w_1	x_1	$\kappa/(S \cdot m^{-1})$
		CH_3CN			
0.000 00	0.000 00	1.87	0.000 00	0.000 00	1.10
0.011 63	0.038 60	2.00	0.021 11	0.068 83	1.32
0.021 48	0.069 70	2.24	0.059 87	0.179 19	1.63
0.064 43	0.190 32	2.96	0.106 38	0.289 81	2.40
0.090 63	0.253 80	3.40	0.141 33	0.360 69	2.95
0.120 54	0.318 70	3.89	0.180 80	0.430 70	3.43
0.152 06	0.379 67	4.39	0.220 17	0.491 82	3.99
0.181 42	0.430 66	4.81	0.259 66	0.545 93	4.59
0.209 42	0.474 81	5.24	0.301 93	0.597 21	5.23
0.240 34	0.519 18	5.65	0.339 34	0.637 77	5.67
0.267 31	0.554 60	5.98	0.377 38	0.675 08	6.15
0.300 75	0.594 80	6.20	0.421 62	0.714 19	6.39
0.329 42	0.626 39	6.34	0.460 56	0.745 33	6.93
		C_6H_6			
0.000 00	0.000 00	1.87	0.000 00	0.000 00	1.10
0.015 98	0.028 29	1.88	0.025 75	0.045 44	1.16
0.030 34	0.053 14	1.90	0.051 48	0.089 06	1.30
0.061 86	0.105 75	2.14	0.080 11	0.135 59	1.35
0.091 64	0.153 20	2.25	0.113 80	0.187 86	1.48
0.122 62	0.200 41	2.34	0.140 28	0.227 15	1.56
0.150 78	0.241 52	2.47	0.170 78	0.270 59	1.68
0.180 21	0.282 77	2.56	0.200 49	0.311 15	1.74
0.212 28	0.325 83	2.60	0.230 45	0.350 40	1.82
0.242 18	0.364 33	2.71	0.261 75	0.389 74	1.89
0.269 89	0.398 66	2.79	0.290 51	0.424 47	1.94
0.302 32	0.437 30	2.81	0.332 18	0.472 57	2.04
0.329 95	0.468 97	2.85			
		CH_2Cl_2			
0.000 00	0.000 00	1.87	0.000 00	0.000 00	1.10
0.015 04	0.024 57	1.88	0.025 96	0.042 30	1.21
0.030 23	0.048 90	1.97	0.051 27	0.082 19	1.45
0.062 73	0.099 43	2.27	0.083 19	0.130 69	1.63
0.090 36	0.140 79	2.38	0.113 82	0.175 46	1.87
0.134 38	0.203 89	2.56	0.140 85	0.213 61	2.09
0.149 53	0.224 84	2.66	0.169 32	0.252 46	2.18
0.182 89	0.269 67	2.89	0.202 23	0.295 78	2.47
0.210 24	0.305 14	3.02	0.233 01	0.334 81	2.64
0.239 36	0.341 71	3.06	0.262 01	0.370 37	2.74
0.268 83	0.377 54	3.16	0.290 46	0.404 15	2.82
0.301 35	0.415 73	3.36	0.320 25	0.438 39	2.97
0.330 92	0.449 31	3.42	0.349 96	0.471 45	3.03

[a] w_1 is the mass fraction of cosolvent. [b] x_2 is the mole fraction of $AlCl_3$ in the $AlCl_3$ + MeEtimCl mixture before the addition of cosolvent.

obtain the cell resistance at infinite frequency (Braunstein and Robbins, 1971). The specific conductances of the samples were calculated from these resistances and the cell constant. Measurements were performed at 0.10, 0.12, 1.0, and 10 kHz. The conductivity cell was calibrated with 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, and 0.20 mol dm^{-3} aqueous KCl solutions according to IUPAC recommended procedures (Spiro, 1986). The conductivities of these solutions were calculated from the Chiu–Fuoss equation (Chiu and Fuoss, 1968). Each data point was the average of no fewer than 30 individual readings. Given the appreciable frequency dependence of the cell resistance, the experimental uncertainty of these measurements was estimated to be approximately ±0.01 S m^{-1}.

Results and Discussion

The experimental densities, ϱ, kinematic viscosities, ν, and specific conductances, κ, of the pure $AlCl_3$ + MeEtimCl melt measured in this study at 25 °C are compared to literature values (Fannin et al., 1984) in Table 1. The present results are in reasonable agreement with previously published values; with the exception of the ν and κ values for $x_2 = 0.4900$, which differ by 9.4% and 7.4%, respectively. The factors that lead to the observed differences are not known; however, they may simply reflect slight differences in x_2, which is reported to two significant figures in the literature ((Fannin et al., 1984), but known to no less than four significant figures in the present study.

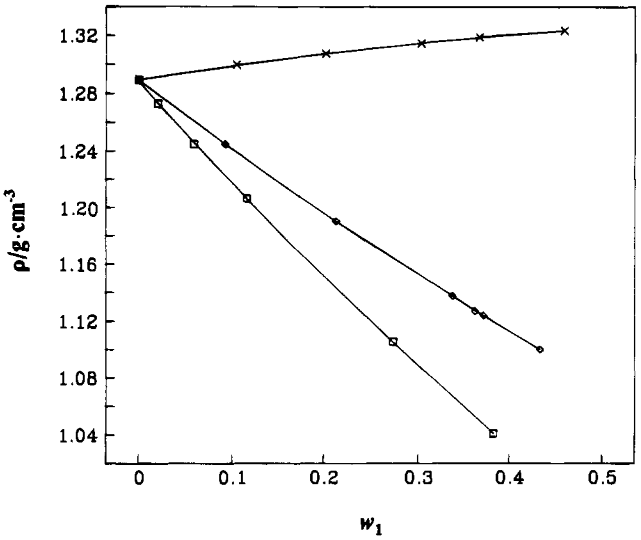

Figure 1. Variation of the density, ϱ, of the $x_2 = 0.4900$ $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 1 and the fitted parameters in Table 5.

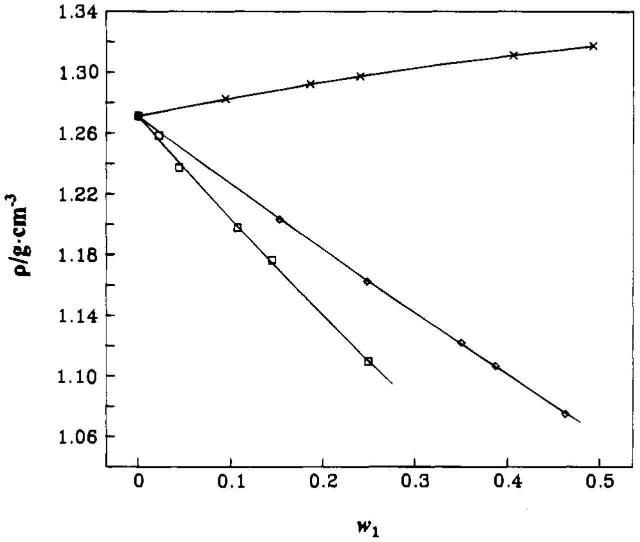

Figure 2. Variation of the density, ϱ, of the $x_2 = 0.4440$ $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 1 and the fitted parameters in Table 5.

Experimental ϱ, ν, and κ results for cosolvent + $AlCl_3$ + MeEtimCl mixtures are listed in Tables 2–4, respectively. The data in these tables are grouped according to the x_2 of the $AlCl_3$ + MeEtimCl melt *before* the addition of cosolvent.

Linear polynomial expressions of the form

$$\varrho/(g \cdot cm^{-3}) = \sum_{i=0}^{n} a_i (w_1)^i \qquad (1)$$

were fitted to the density data using linear regression techniques. The adjustable parameters resulting from these fits are collected in Table 5. Plots of ϱ versus w_1 are shown in Figures 1 and 2. The solid lines in these figures were calculated from eq 1 and the fitted parameters listed in Table 5. In all cases, the squares of the correlation

Table 5. Fitted Parameters for Eqs 1–3

system	a_0	a_1	a_2	a_3	$S_{y/x}$	R^2
Equation 1 (Density)						
$x_2 = 0.4900$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2886	−0.7352	0.2333		9.13×10^{-4}	0.9999
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2894	−0.4929	0.1290		3.08×10^{-4}	1.0000
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2895	0.1017	−0.0594		2.02×10^{-4}	0.9998
$x_2 = 0.4440$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2715	−0.7015	0.2167		2.98×10^{-3}	0.9985
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2710	−0.4494	0.0591		8.16×10^{-4}	0.9999
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.2714	0.1224	−0.0593		2.00×10^{-4}	0.9999
Equation 2 (Kinematic Viscosity)						
$x_2 = 0.4900$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	2.6355	−13.2773	27.9522	−24.5482	2.62×10^{-2}	0.9994
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	2.6158	−4.7257	2.9857		1.24×10^{-2}	0.9992
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	2.6399	−6.0668	5.2790	−3.6764	6.28×10^{-3}	0.9999
$x_2 = 0.4440$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	3.2865	−16.4191	37.2027	−37.2195	2.50×10^{-2}	0.9994
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	3.2841	−6.3933	4.5223		1.79×10^{-2}	0.9992
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	3.2968	−7.5654	7.0920	−5.1331	7.59×10^{-3}	0.9999
Equation 3 (Specific Conductance)						
$x_2 = 0.4900$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.9017	−2.6105	33.8211	−26.9605	7.19×10^{-2}	0.9985
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.8642	−1.1008	10.6796	−10.0688	2.64×10^{-2}	0.9960
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.8600	−0.8695	10.9811	−8.2625	4.61×10^{-2}	0.9947
$x_2 = 0.4440$						
CH_3CN (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.1466	−3.5427	27.4500	−14.2021	1.04×10^{-1}	0.9980
C_6H_6 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.1003	−0.4580	6.3564	−4.7859	1.79×10^{-2}	0.9976
CH_2Cl_2 (1) + $AlCl_3$ (2) + MeEtimCl (3)	1.1046	−1.6183	16.1538	−13.2813	3.79×10^{-2}	0.9976

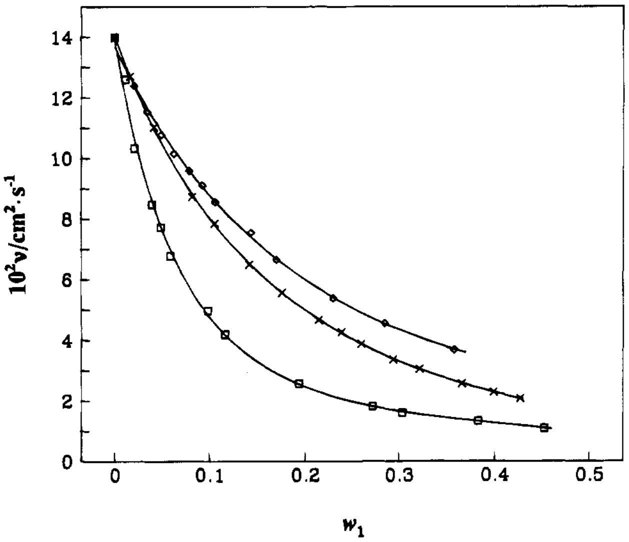

Figure 3. Variation of the kinematic viscosity, ν, of the x_2 = 0.4900 $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 2 and the fitted parameters in Table 5.

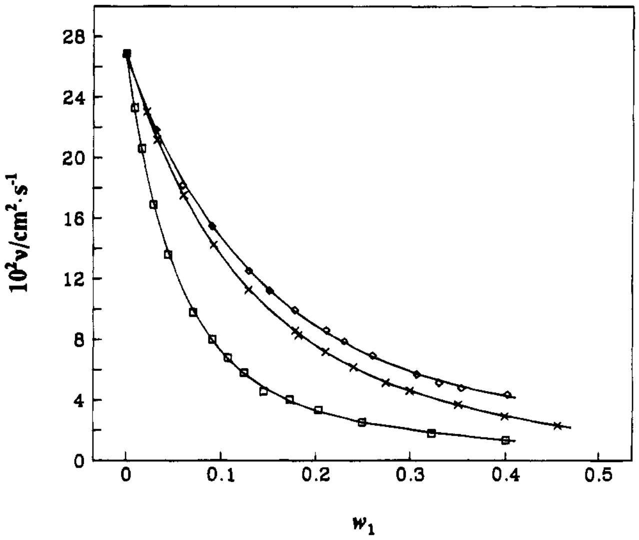

Figure 4. Variation of the kinematic viscosity, ν, of the x_2 = 0.4440 $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 2 and the fitted parameters in Table 5.

coefficients, R^2, in Table 5 indicate that eq 1 provides an excellent representation of the experimental density data.

Polynomial expressions of the form

$$\ln(10^2\nu/(\mathrm{cm}^2\cdot\mathrm{s}^{-1})) = \sum_{i=0}^{n} a_i(w_1)^i \tag{2}$$

were fitted to the experimental viscosity data given in Table 3. The adjustable parameters resulting from these fits are given in Table 5. Plots of ν versus w_1 are shown in Figures 3 and 4; the solid lines in these plots were calculated from eq 2 and the a_i values given in Table 5. These plots and the values of R^2 in Table 5 indicate that eq 2 provides an excellent representation of the experimental viscosity data.

A number of different correlating expressions for representing the w_1 dependence of κ were investigated. Polynomials of the type

$$\kappa/(\mathrm{S}\cdot\mathrm{m}^{-1}) = \sum_{i=0}^{n} a_i(w_1)^{i/2} \tag{3}$$

were found to provide a good fit to the experimental results. The adjustable parameters and R^2 values resulting from these fits are collected in Table 5. The solid lines in Figures 5 and 6 were calculated by using eq 3 and the appropriate parameters in this table.

Examination of Figures 3–6 indicates that the addition of cosolvents to basic $AlCl_3$ + MeEtimCl results in consid-

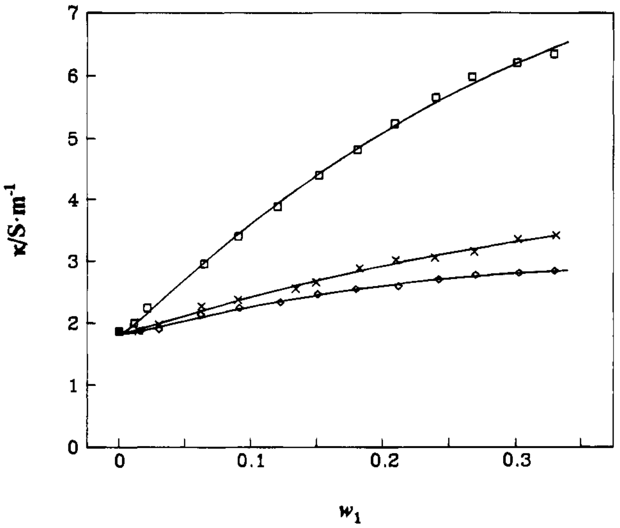

Figure 5. Variation of the specific conductance, κ, of the x_2 = 0.4900 $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 3 and the fitted parameters in Table 5.

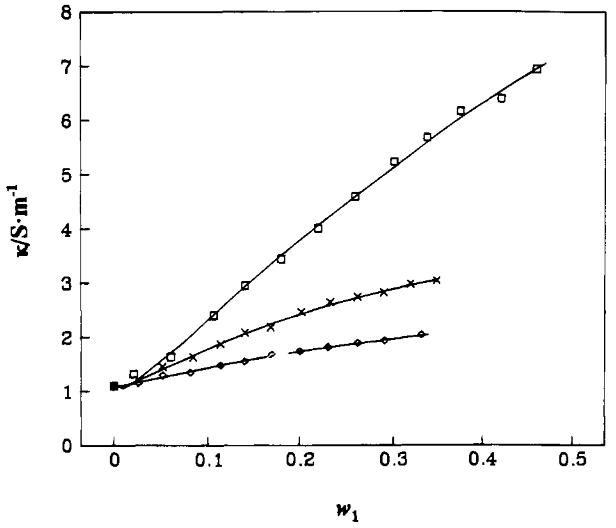

Figure 6. Variation of the specific conductance, κ, of the x_2 = 0.4440 $AlCl_3$ (2) + MeEtimCl (3) melt with the mass fraction, w_1, of cosolvent (1): (□) acetonitrile, (◇) benzene, (×) dichloromethane. The solid lines were calculated with eq 3 and the fitted parameters in Table 5.

erable improvements in both the viscosity and conductivity of this molten salt. For example, the addition of 12 mass % acetonitrile to the x_2 = 0.4900 melt causes the viscosity to decrease by about 70% and the conductivity to double. Furthermore, the magnitude of these improvements parallels the dielectric constant of the cosolvent, with the greatest effect seen for acetonitrile (ϵ_r (20 °C) = 37.5) and the least effect seen for benzene (ϵ_r (20 °C) = 2.28). This result lends further credence to the supposition that the organic cosolvents "solvate" the constituent ions of the molten salt, resulting in a decrease in the aggregation of these ions.

Acknowledgment

The authors wish to express their appreciation to Dr. John S. Wilkes for the use of the facilities of the Frank J. Seiler Research Laboratory at the USAF Academy to conduct density measurements.

Literature Cited

Braunstein, J; Robbins, G. D. Electrolytic Conductance Measurements and Capacitive Balance. *J. Chem. Educ.* **1971**, *48*, 52–59.

Carlin, R. T.; Wilkes, J. S. Chemistry and Speciation in Room-Temperature Chloroaluminate Molten Salts. In *Chemistry of Nonaqueous Solutions: Current Progress*; Mamantov, G. M., Popov, A. I., Eds.; VCH: New York, 1994; pp 277–306.

Chiu, Y-C.; Fuoss, R. M. Conductance of the Alkali Halides. XII. Sodium and Potassium Chlorides in Water at 25°. *J. Phys. Chem.* **1968**, *72*, 4123–4129.

Fannin, A. A., Jr.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; and Williams, J. L. Properties of 1,2-Dialkylimidazolium Chloride-Aluminum Chloride Ionic Liquids. 2. Phase Transitions, Densities, Electrical Conductivities, and Viscosities. *J. Phys. Chem.* **1984**, *88*, 2614–2621.

Hussey, C. L. The Electrochemistry of Room-Temperature Haloaluminate Molten Salts. In *Chemistry of Nonaqueous Solutions: Current Progress*; Mamantov, G. M., Popov, A. I., Eds.; VCH: New York, 1994; pp 227–275.

Moy, R.; Emmenegger, F.-P. Co-Solvents for Chloroaluminate Electrolytes. *Electrochim. Acta* **1992**, *37*, 1061–1068.

Osteryoung, R. A. Organic Chloroaluminate Ambient Temperature Molten Salts. In *Molten Salt Chemistry: An Introduction and Selected Applications*; Mamantov, G., Marassi, R., Eds.; NATO ASI Series C: Mathematical and Physical Sciences; Reidel: Dordrecht, The Netherlands, 1986; Vol. 202, pp 329–364.

Papageorgiou, N.; Emmenegger, F.-P. The Effect of Cosolvents and Additives on the Electrochemical Properties of [$(Me)_3PhN$][Al_2Cl_7] Melts. *Electrochim. Acta* **1993**, *38*, 245–252.

Robinson, J.; Bugle, R. C.; Chum, H. L.; Koran, D.; Osteryoung, R. A. ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide–Alkylpyridinium Halide Molten Salts and Their Benzene Mixtures. *J. Am. Chem. Soc.* **1979**, *101*, 3776–3779.

Sanders, J. R.; Ward, E. H.; Hussey, C. L. Aluminum Bromide–1-Methyl-3-ethylimidazolium Bromide Ionic Liquids. I. Densities, Viscosities, Electrical Conductivities, and Phase Transitions. *J. Electrochem. Soc.* **1986**, *133*, 325–328, 1526.

Spiro, M. Conductance and Transference Determinations. In *Physical Methods of Chemistry*, 2nd ed.; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Vol. II, Chapter 8.

Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis. *Inorg. Chem.* **1982**, *21*, 1263–1264.

Zawodzinski, T. A., Jr.; Osteryoung, R. A. Donor–Acceptor Properties of Ambient-Temperature Chloroaluminate Melts. *Inorg. Chem.* **1989**, *28*, 1710–1715.

Received for review September 28, 1994. Accepted February 16, 1995.® Financial support for this work was provided by the National Science Foundation, Grant No. CHE-9411165.

JE940206D

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.