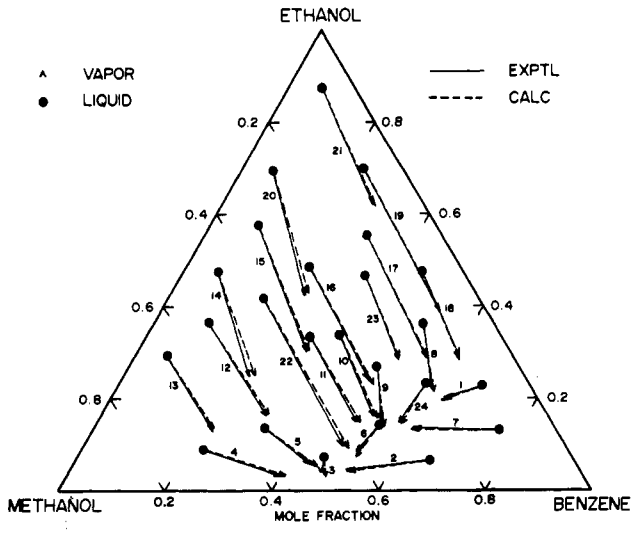

Figure 2. Equilibrium tie lines. Calculated results were obtained from the extended UNIQUAC model.

rameters were used to calculate ternary VLE for the present system without introducing any ternary parameters. Both models gave the errors of the same order of magnitude in the ternary predictions of VLE data as shown in Table IV.

Figure 2 shows the tie lines connecting the liquid and vapor mole fractions in equilibrium, indicating that the system does not involve a ternary azeotrope.

Glossary

a_{ij}	UNIQUAC or extended UNIQUAC binary interaction parameter related to τ_{ij}
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular geometric area parameter for pure component i
q_i'	molecular interaction area parameter for pure component i
q_i^*	correction factor of interaction for pure component i
r_i	molecular volume parameter for pure component i
R	gas constant
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
θ_i'	area fraction of component i in residual contribution to the UNIQUAC activity coefficient
τ_{ij}	UNIQUAC or extended UNIQUAC binary parameter
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at its saturation pressure
Φ_i	segment fraction of component i

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; benzene, 71-43-2.

Literature Cited

(1) Hall, D. J.; Mash, C. J.; Pemberton, R. C. *NPL Rep. Chem.* (*U.K., Natl. Phys. Lab., Div. Chem. Stand.*) **Jan 1979**, *No. 95*, 1-32.
(2) Hwang, S.-C.; R. L., Jr. *J. Chem. Eng. Data* **1977**, *22*, 319-25.
(3) Ohta, T.; Koyabu, J.; Nagata, I. *Fluid Phase Equilib.* **1981**, *7*, 65-73.
(4) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; pp 107, 145, 147.
(5) Hayden, J. G.; O'Connel, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209-16.
(6) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236-41.
(7) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980; Chapters 3, 4, 6, Appendices C, D.
(8) Nagata, I. *Thermochim. Acta* **1982**, *56*, 43-57.

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Specific Conductivity of NaCl–$AlCl_3$ and NaCl–$AlCl_3$–Al_2S_3 Melts

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The specific conductivity of the pure binary NaCl–$AlCl_3$ molten salt system was measured in the temperature range 175–400 °C and with the mole fraction of $AlCl_3$, X_{AlCl_3}, ranging from 0.497 to 0.600. Sulfur, aluminum metal, and sodium chloride were dissolved in the NaCl–$AlCl_3$ solvents at ca. 250 °C, forming polymeric $NaAlSCl_2$. The specific conductivity of these melts was measured in the range $0 < X_{Al_2S_3} < 0.08$. All conductivity data are given as a polynomial function of temperature and composition.

Introduction

It has been shown (*1*) that aluminum metal and elemental sulfur react in alkali tetrachloroaluminate melts in the molar ratio Al:S = 2:3, forming aluminum chlorosulfides. These melts are colorless solutions, possibly containing solute ions like $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ and $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ ($n > 3$ and $m > n$). Such melts are of considerable interest as they are formed during discharge of new galvanic cells based on the Al/S couple and the $NaAlCl_4$ electrolyte (*2*, *3*).

The purpose of the present work was to determine analytical expressions for the specific conductivity of NaCl–$AlCl_3$ melts with and without dissolved aluminum chlorosulfides. There are no previous measurements of the conductivity of NaCl–$AlCl_3$ melts containing aluminum chlorosulfides.

Such information is essential in the optimization of the above-mentioned molten salt batteries. Recently we have published (*4*) the liquid densities of the sodium tetrachloroaluminate melts containing aluminum chlorosulfides.

The conductivity of molten NaCl–$AlCl_3$ has previously been studied and a short review is given by Janz et al. (*5*).

For the molten compound $NaAlCl_4$ (50 mol % $AlCl_3$) the equation

$$\kappa = -0.7966 + 2.7366 \times 10^{-3}T \qquad (1)$$

was derived (*5*) from data given by Yamaguti and Sisido (*6*) in the temperature range between 460 and 545 K (187–272 °C). Here, as in the following, the conductivity κ has the units Ω^{-1}

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cm^{-1} and T is the absolute temperature.

Kryagova (*7*) measured the conductivity of a 50.3 mol % $AlCl_3$ melt as a function of temperature between 190 and 270 °C. Moss (*8*) studied the conductivity of acidic NaCl–$AlCl_3$ mixtures and concluded that the older data (*6*, *7*) were of low precision. Midorikawa (*9*) reported the following expressions for the conductivity of a melt containing 52.3 mol % $AlCl_3$:

$$\kappa = 0.408 + 2.35 \times 10^{-3}(t - 170) \quad (2)$$

or

$$\log \kappa = -499/T + 0.735$$

where t and T are the temperature in degrees Celsius and kelvin in the range of 170–202 °C. Other constants were given for more acidic compositions up to 70 mol % $AlCl_3$.

Howie and Macmillan (*10*) reported the equation for the conductivity

$$\kappa = (-0.1594 + 2.07 \times 10^{-3}t) - (-1.475 \times 10^{-2} + 1.43 \times 10^{-4}t)W + (-4.022 \times 10^{-4} + 5.48 \times 10^{-6}t)W^2 \quad (3)$$

where t is the temperature in degrees Celsius and W is the weight percent of NaCl in the NaCl–$AlCl_3$ melts. The formula should be valid in the range of 15–30 wt % NaCl (corresponding to 50.6–71.3 mol % $AlCl_3$) between 155 and 195 °C.

Carpio et al. (*11*) measured the specific conductivity for NaCl–$AlCl_3$ melts in the temperature range of 160–250 °C. The conductivity for a melt containing 49.75 mol % $AlCl_3$ was 0.375 and 0.565 Ω^{-1} cm^{-1} at 174.4 and 251.0 °C, respectively, and for a melt with 60.0 mol % $AlCl_3$ the conductivity was 0.285 and 0.432 Ω^{-1} cm^{-1} at 178.8 and 249.2 °C, respectively. Carpio et al. (*11*) also gave linear equations of the form $\kappa = -b_1 + b_2t$, where κ is the specific conductivity, b_1 and b_2 are parameters, and t is the temperature in degrees Celsius, but one should be aware that the minus sign has been left out in their equation 7.

For the $NaAlCl_4$ compound at 700 °C a specific conductivity of ca. 1.27 Ω^{-1} cm^{-1} can be calculated from data given by Matiasovsky (*12*).

As may be seen, there is no general expression for the NaCl–$AlCl_3$ melts covering a large range in temperature and composition, although a number of works cover the very basic (nearly pure NaCl) and the very acidic (nearly pure $AlCl_3$) compositions (*13*–*16*).

Experimental Section

The chemicals used were of the same quality as described earlier (*4*). The Pyrex measuring cells (Figure 1) were of a type similar to those used in previous work (*17*). Nine cells were used, and for each cell the composition was changed several times by subsequent additions of chemicals.

Cell constants (of the order of 300 cm^{-1}) were determined in a thermostat at room temperature by using aqueous KCl solutions made in accordance with Jones and Bradshaw (*18*). The measurements were not corrected for the temperature dependence of the cell constant since the error by ignoring this was only approximately 0.1%. The materials that made up a melt were weighed in a nitrogen-filled dry glovebox and the cells were sealed under vacuum. Cells with aluminum and sulfur (always having aluminum in excess) were preequilibrated in a rocking furnace at ca. 250 °C for several days (until completion of reaction, characterized by the visible absence of elemental sulfur).

Other experimental details (furnace, etc.) have been described elsewhere (*19*). Temperature measurements were done with a Pt-100Ω resistor to a precision better than 0.1 °C. The conductivity was measured with a Wheatstone bridge (accuracy 0.1%) as described previously (*17*).

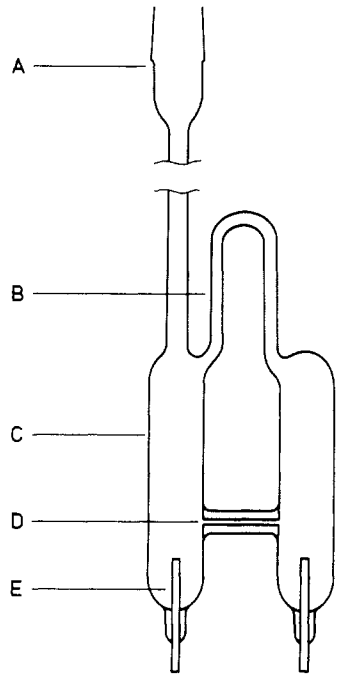

Figure 1. Conductivity cell made of Pyrex glass: (A) conical joint, (B) pressure equilibration tube, (C) cell compartment, (D) capillary tube, and (E) vitreous carbon electrode.

Results and Discussion

NaCl–AlCl₃. The conductivity of pure solvent NaCl–$AlCl_3$ melts was measured vs. composition and temperature as shown in Table I. It is seen that the conductivity decreases with X_{AlCl_3} (addition of $AlCl_3$) and increases with temperature, which is to be expected. The composition range was limited since the liquidus curve rises very rapidly with temperature for X_{AlCl_3} below ca. 0.50.

Due to the high volatility of aluminum chloride, the gas phase over acidic melts contains various amounts of Al_2Cl_6, such that the actual formal mole fraction of $AlCl_3$ in the melt, X_{AlCl_3}, is slightly lower than the weight-based one. The question of correcting X_{AlCl_3} for the loss of $AlCl_3$ to the gas phase was investigated in all experiments by estimating the gas volume in the cells and using (sometimes by extrapolation) the vapor pressure data by Viola et al. (*20*) for determining the amount of lost $AlCl_3$.

Only those experiments were considered as needing correction in which the uncorrected conductivity deviated more than 0.1% from the conductivity, calculated from a preliminary polynomial equation (see later). According to this criterion, the correction had to be applied only when the X_{AlCl_3} error is on the order of 0.02%, i.e., in the experiments 2-2, 2-3, 8-2, 8-3, and 8-4, as indicated in Table I.

The conductivity data from the literature and our results are compared in Table II. It is seen that Kryagova's results (*7*) without question are erroneous. The rest of the literature data generally scatter up to approximately 10% and are in accordance with our results on this level of precision. We are unable to explain the deviations among the results of the different experimentalists, but they may be due to impurities and inaccuracies in the composition of the melts.

NaCl–AlCl₃–Al₂S₃. Sulfur, NaCl, and excess of aluminum metal were added to almost neutral NaCl–$AlCl_3$ melts (i.e., X_{AlCl_3} = ca. 0.50) according to the reactions

$$2Al + 3S \rightarrow Al_2S_3 \quad (4)$$

$$Al_2S_3 + NaAlCl_4 + 2NaCl \rightarrow 3NaAlSCl_2 \quad (5)$$

When equilibrated, these melts were usually clear and colorless. For high concentrations of polymerized (*1*) "$NaAlSCl_2$", the

Table I. Conductivity of NaCl-$AlCl_3$ Melts with the Initial (Weighed) Mole Fraction of $AlCl_3$, X, Given[a]

expt 1-1, X = 0.50000		expt 1-2, X = 0.51001		expt 2-1, X = 0.50029		expt 2-2, X = 0.52024[b]		expt 2-3, X = 0.55072[b]	
t	κ	t	κ	t	κ	t	κ	t	κ
174.45	0.443	174.69	0.423	174.01	0.439	174.47	0.396	174.66	0.341
199.97	0.515	200.27	0.491	199.13	0.508	199.56	0.461	199.58	0.397
225.18	0.583	225.73	0.558	224.03	0.575	224.66	0.524	224.79	0.452
249.90	0.647	250.52	0.619	249.31	0.641	249.92	0.584	250.08	0.506
274.72	0.707	275.36	0.678	274.66	0.704	275.08	0.641	275.42	0.557
300.44	0.766	300.70	0.735	299.63	0.761	300.03	0.695	300.28	0.604
325.30	0.819	325.61	0.788	324.93	0.816	325.21	0.746	325.35	0.651
350.94	0.870	351.17	0.838	349.97	0.867	349.97	0.795	350.43	0.694
375.75	0.917	375.37	0.884	375.03	0.914	400.00	0.887		
400.71	0.959	401.42	0.928	400.32	0.957				

expt 3-1, X = 0.49951		expt 4-1, X = 0.49725		expt 5-1, X = 0.49851		expt 6-1, X = 0.49851		expt 7-1, X = 0.49851	
t	κ	t	κ	t	κ	t	κ	t	κ
174.50	0.438	174.29	0.435	174.26	0.435	172.40	0.442	174.85	0.439
199.35	0.508	198.91	0.503	199.26	0.505	197.05	0.512	199.09	0.508
224.55	0.577	224.55	0.569	224.52	0.573	224.63	0.586	224.39	0.578
249.75	0.643	249.31	0.634	249.48	0.638	250.34	0.652	249.65	0.643
275.00	0.703	274.72	0.696	274.69	0.701	275.41	0.714	274.71	0.706
299.69	0.761	300.08	0.750	299.58	0.759	300.06	0.771	299.98	0.765
326.18	0.819	325.95	0.810	324.65	0.814	325.28	0.817	324.94	0.820
350.29	0.868	349.40	0.858	349.54	0.865	350.33	0.878	349.96	0.872
375.32	0.915	374.22	0.905	374.63	0.913	375.35	0.926	374.78	0.919
399.62	0.959	399.85	0.951	399.71	0.957	401.08	0.970	399.95	0.964
		176.90	0.511						

expt 8-1, X = 0.49851		expt 8-2, X = 0.53520[b]		expt 8-3, X = 0.57636[b]		expt 8-4, X = 0.60045[b]	
t	κ	t	κ	t	κ	t	κ
171.48	0.441	173.66	0.371	173.37	0.300	173.56	0.268
197.87	0.517	198.28	0.431	197.43	0.349	197.60	0.312
225.40	0.592	225.46	0.494	224.50	0.402	224.69	0.361
252.44	0.659	250.07	0.549	249.21	0.450	249.40	0.404
277.30	0.721	276.55	0.605	274.41	0.496	274.57	0.446
302.26	0.778	301.47	0.652	299.42	0.540	299.75	0.487
327.46	0.832	326.98	0.702	325.14	0.580	325.42	0.525
352.76	0.883	349.22	0.743				
376.76	0.929						
402.91	0.974						

[a] The temperature t is in degrees Celsius, and κ is the conductivity in Ω^{-1} cm^{-1}. Expt refers to an experiment; e.g., expt 1-2 is cell 1 with the second composition. [b] Corrected for $AlCl_3$ lost to the gas phase.

Table II. Selected Literature Data on Conductivities of NaCl-$AlCl_3$ Melts in Comparison to the Results Obtained Here

		κ, Ω^{-1} cm^{-1}							
								present work	
X_{AlCl_3}	temp, °C	ref 5 and 6	ref 7	ref 8	ref 9	ref 10[a]	ref 11	obsd	calcd[j]
0.500	175	0.430[a]				0.407	0.377[c]	0.433	0.455
0.500	200	0.498[a]	0.436[b]			0.477	0.440[c]	0.515	0.520
0.500	250	0.635[a]	0.532[b]			0.617	0.564[c]	0.647	0.640
0.500	300	0.772[a]				0.757	0.689[a,c]	0.766	0.754
0.500	400	1.046[a]				1.037	0.939[a,c]	0.959	0.958
0.520	175			0.378[e]	0.420	0.369		0.396	0.397
0.520	200		0.262[d]	0.434[e]	0.479	0.431		0.461	0.460
0.520	250		0.378[d]		0.596[a]	0.556		0.584	0.582
0.520	300				0.714[a]	0.681		0.695[f]	0.695
0.520	400				0.949[a]	0.931		0.887[f]	0.899
0.600	175			0.263		0.255	0.280	0.268[f,g]	0.218[g]
0.600	200		0.170[h]	0.305		0.296	0.322	0.312[f,i]	0.279[i]
0.600	250		0.300[h]			0.378	0.437[a]	0.404[f]	0.405
0.600	300					0.460	0.541[a]	0.487[f]	0.520

[a] Calculated values by interpolation or extrapolation. [b] X_{AlCl_3} = 0.503. [c] X_{AlCl_3} = 0.498. [d] X_{AlCl_3} = 0.518. [e] X_{AlCl_3} = 0.525. [f] Corrected for $AlCl_3$ evaporation. [g] 173.6 °C. [h] X_{AlCl_3} = 0.594. [i] 197.6 °C. [j] Model 2A.

viscosity and surface tension increased significantly, judging from visual observations when shaking the melts.

Addition of sufficient $AlCl_3$ to melts containing "$NaAlSCl_2$" gave a white precipitate, probably "AlSCl" according to the reaction

$$NaAlSCl_2 + AlCl_3 \rightarrow NaAlCl_4 + AlSCl \quad (6)$$

The formation of this precipitate limits the range of X_{AlCl_3} in which useful experiments can be done and is the reason that NaCl is needed in reaction 5.

The compositions of the sulfide-containing melts are shown in Table III and are based on the mole fraction of the formal "Al_2S_3" compound, $X_{Al_2S_3}$, since the identities of the compounds formed actually are unknown. Also shown in Table III is the

Table III. Initial Mole Fractions, Calculated from the Weighing Data, for the Conductivity Measurements on $NaCl-AlCl_3-Al_2S_3$ Melts

expt no.	X_{AlCl_3}	$X_{Al_2S_3}$	solv ratio[a]
0-1	0.494 56	0.003 647	1.0001
0-2	0.485 36	0.009 325	0.9973
0-3	0.476 09	0.015 617	0.9979
0-4	0.460 95	0.026 035	1.0000
0-5	0.457 11	0.029 169	1.0041
0-6	0.419 38	0.054 024	1.0023
4-2	0.491 57	0.003 858	0.9893
4-3	0.490 22	0.006 590	1.0004
4-4	0.484 53	0.010 594	1.0018
4-5	0.473 90	0.017 514	1.0007
5-2	0.450 14	0.034 466	1.0089
5-3	0.407 79	0.062 350	1.0077
5-4	0.413 67	0.061 732	1.0369
5-5	0.435 55	0.059 427	1.1511
6-2	0.432 42	0.041 117	0.9709
6-3	0.446 80	0.040 075	1.0352
6-4	0.455 25	0.039 463	1.0747
6-5	0.463 36	0.038 875	1.1137
6-6	0.483 66	0.037 405	1.2169
7-2	0.378 75	0.079 751	0.9893
7-3	0.392 59	0.077 975	1.0647

[a] Molar ratio of remaining $AlCl_3$ to remaining NaCl after a hypothetical complete formation of "$NaAlSCl_2$" according to reaction 5.

molar ratio of the remaining $AlCl_3$ to the remaining NaCl after a hypothetical complete formation of "$NaAlSCl_2$". This ratio is near 1.0, showing that all the melts might be considered as "$NaAlSCl_2$" dissolved in roughly equimolar $NaCl-AlCl_3$ solvents (exact condition: $X_{NaCl} = 0.500 + {}^1/_2X_{Al_2S_3}$). No gas-phase correction of X_{AlCl_3} was made in Table III due to lack of vapor pressure data over the melts considered here, but since the evaporation loss of $AlCl_3$ is estimated to be small, this is not considered of importance. The measured specific conductivities are given in Table IV. The conductivity decreases almost linearly with increasing amounts of Al_2S_3 and increases almost linearly with temperature.

Polynomials. A convenient way to represent the experimental data is to combine the results, obtained at different temperatures and compositions, into an empirical equation which fits the observations as closely as possible. General polynomial expressions like

$$\kappa = a + bt + ct^2 + dX_{AlCl_3} + eX_{AlCl_3}^2 + fX_{AlCl_3}^3 + gX_{Al_2S_3} + hX_{Al_2S_3}^2 \quad (7)$$

where $a-h$ are fitting parameters, were tried with success.

The fitting was done by using standard least-squares regression methods (*21*), independently for the pure $NaCl-AlCl_3$ system, for the sulfide-containing melts and for all our data. The parameters for the most satisfactory analytical expressions (models) are shown in Table V for these different groups of data. By statistical analysis of the importance of the individual parameters in the models, using the SAS procedure RSQUARE CP (*22*), it was concluded that the terms with e, f, and h in eq

Table IV. Conductivity of $NaCl-AlCl_3-Al_2S_3$ Melts for the Compositions in Table III

expt 0-1		expt 0-2		expt 0-3		expt 0-4		expt 0-5		expt 0-6	
t	κ	t	κ	t	κ	t	κ	t	κ	t	κ
176.60	0.426	162.50	0.363	162.50	0.343	162.50	0.312	176.60	0.329	176.60	0.279
		176.60	0.403	176.60	0.383	176.60	0.350				
						188.40	0.388				

expt 4-2		expt 4-3		expt 4-4		expt 4-5		expt 5-2	
t	κ	t	κ	t	κ	t	κ	t	κ
173.75	0.424	175.09	0.414	174.39	0.403	174.42	0.378	174.31	0.329
198.69	0.495	199.56	0.482	199.13	0.472	199.40	0.448	199.35	0.399
223.92	0.562	225.12	0.552	224.93	0.537	224.60	0.516	225.55	0.470
249.36	0.627	249.78	0.616	249.56	0.602	249.56	0.582	249.50	0.537
274.89	0.688	275.42	0.678	274.97	0.665	274.66	0.645	274.72	0.603
299.55	0.746	300.28	0.736	300.03	0.724	299.55	0.705	299.89	0.665
325.50	0.803	326.03	0.793	325.95	0.781	324.65	0.762	324.76	0.724
350.26	0.856	350.57	0.844	350.54	0.833	349.49	0.814	349.66	0.778
375.78	0.899	375.32	0.892	375.37	0.882	374.60	0.861	374.68	0.831
401.10	0.944	400.76	0.937	400.76	0.929	399.68	0.907	399.80	0.880

expt 5-3		expt 5-4		expt 5-5		expt 6-2		expt 6-3	
t	κ	t	κ	t	κ	t	κ	t	κ
174.47	0.249	174.69	0.249	174.79	0.268	173.12	0.307	175.82	0.327
199.37	0.315	199.31	0.315	199.39	0.333	197.22	0.373	200.48	0.395
221.86	0.375	221.73	0.388	224.58	0.401	224.25	0.447	227.92	0.473
249.67	0.451	249.65	0.453	249.79	0.467	249.02	0.513	253.52	0.542
274.86	0.519	274.88	0.519	274.88	0.532	274.21	0.578	278.48	0.608
299.69	0.581	299.87	0.583	299.87	0.596	299.33	0.640	302.79	0.669
324.93	0.644	324.91	0.643	324.91	0.662	325.08	0.702	325.34	0.729
349.86	0.702	349.93	0.702	349.91	0.714	349.13	0.757	353.45	0.785
374.74	0.757	374.86	0.757	374.83	0.763	373.86	0.809	378.37	0.838
399.94	0.808	399.95	0.809	399.90	0.820	400.16	0.863	403.58	0.886

expt 6-4		expt 6-5		expt 6-6		expt 7-2		expt 7-3	
t	κ	t	κ	t	κ	t	κ	t	κ
174.71	0.322	174.69	0.326	174.66	0.335	173.39	0.199	173.26	0.207
198.96	0.390	198.90	0.394	199.12	0.407	197.22	0.260	197.92	0.268
226.14	0.465	226.14	0.469	226.20	0.480	222.33	0.326	225.15	0.340
250.95	0.532	250.98	0.536	250.87	0.544	247.05	0.391	249.76	0.406
276.16	0.597	276.13	0.602	277.33	0.610	272.32	0.457	276.13	0.475
301.38	0.660	301.33	0.665	301.78	0.674	297.45	0.521	300.57	0.536
326.98	0.726	326.98	0.725	326.19	0.730	322.56	0.584	326.47	0.609
351.13	0.782	349.68	0.776	352.73	0.788	347.59	0.645	351.90	0.670
375.78	0.836	374.43	0.829	376.82	0.833	372.53	0.700	375.55	0.731
402.07	0.886	399.43	0.879	403.17	0.879	397.78	0.756	402.07	0.783

Table V. Coefficients for Empirical Polynomials for the Specific Conductivity of NaCl–$AlCl_3$–Al_2S_3 Melts

model no.	group of data	a,[e] Ω^{-1} cm^{-1}	X_{AlCl_3}, Ω^{-1} cm^{-1}	$X_{NaCl}-0.5$, Ω^{-1} cm^{-1}	t, Ω^{-1} cm^{-1} °C^{-1}	$t-175$, Ω^{-1} cm^{-1} °C^{-1}	t^2, Ω^{-1} cm^{-1} °C^{-2}	$(t-175)^2$, Ω^{-1} cm^{-1} °C^{-2}	$X_{Al_2S_3}$, Ω^{-1} cm^{-1}	SD,[c] Ω^{-1} cm^{-1}	r^2 [d]
1[a]	pure NaCl–$AlCl_3$	1.2887 (278)[b]	−2.4326 (505)		$2.2405 (212) \times 10^{-3}$					0.016	0.9922
2	pure NaCl–$AlCl_3$	1.1937 (319)	−2.4620 (467)		$3.071 (168) \times 10^{-3}$		$-1.470 (300) \times 10^{-6}$			0.015	0.9935
2A	pure NaCl–$AlCl_3$	0.45512 (326)		2.4620 (467)		$2.5568 (666) \times 10^{-3}$		$-1.470 (300) \times 10^{-6}$		0.015	0.9935
3	all data	0.9898 (402)	−1.9345 (761)		$2.3983 (228) \times 10^{-3}$				−5.254 (136)	0.028	0.9788
3	only sulfide	−0.2157 (442)	0.4411 (878)		$2.4644 (136) \times 10^{-3}$				−2.100 (130)	0.013	0.9957
4	all data	0.8808 (441)	−1.9737 (734)		$3.376 (193) \times 10^{-3}$		$-1.730 (340) \times 10^{-6}$		−5.307 (131)	0.027	0.9806
4	only sulfide	−0.3532 (285)	0.4073 (540)		$3.6492 (741) \times 10^{-3}$		$-2.094 (130) \times 10^{-6}$		−2.1777 (800)	0.008	0.9984
4A	all data	0.43176 (386)		1.9737 (734)		$2.7707 (762) \times 10^{-3}$		$-1.730 (340) \times 10^{-6}$	−5.307 (131)	0.027	0.9806
4A	only sulfide	0.42495 (163)		−0.4073 (540)		$2.9163 (293) \times 10^{-3}$		$-2.094 (130) \times 10^{-6}$	−2.1777 (800)	0.008	0.9984
5	only sulfide	−0.1520 (116)			$3.6742 (863) \times 10^{-3}$		$-2.133 (150) \times 10^{-6}$		−2.7466 (313)	0.009	0.9978
5A	only sulfide	0.42569 (189)				$2.9278 (341) \times 10^{-3}$		$-2.133 (150) \times 10^{-6}$	−2.7466 (313)	0.009	0.9978

[a] This means that the first model is $\kappa = 1.2887 - 2.4326 X_{AlCl_3} + 2.2405 \times 10^{-3} t$. [b] I.e., 1.2887 ± 0.0278. [c] Standard deviation. [d] Coefficient of determination, defined in, e.g., ref 19. [e] Constant.

Figure 2. Conductivity of NaCl–$AlCl_3$ melts. The X,t positions of the experimental observations are indicated on the surface calculated from the polynomial expression of κ (model 2A).

Figure 3. Conductivity of NaCl–$AlCl_3$–Al_2S_3 melts, with $X_{NaCl} \sim 0.5000 + {}^1/_2 X_{Al_2S_3}$. The X,t positions of the experimental observations are indicated on the surface calculated from the polynomial expression of κ (model 5A). The conductivity further depends slightly on X_{AlCl_3} (as given by, e.g., model 4A) because X_{AlCl_3} is only made approximately equal to $0.5000 - {}^3/_2 X_{Al_2S_3}$.

7 were of no significance; the rest of the terms were significant, and of these the first-order temperature term is dominating. Two of the good models are visualized in Figures 2 and 3. It should be noted that the fact that X_{NaCl} is only made approximately equal to $0.5000 + {}^1/_2 X_{Al_2S_3}$ means that the conductivity in principle depends also on X_{AlCl_3}, and hence the three-dimensional picture in Figure 3 is not completely sufficient. The effect, however, is small.

As can be seen from Table V, the uncertainty in the a parameter is smaller when the temperature and mole fraction dependences are based on 175 °C and 0.5000 than when developed from the usual 0 °C and 0.0000. This is, of course, due to the inherent uncertainty in the regression line slope in conjunction with the distance to the reference point. A comparison of model 2A with the literature results (Table II) shows acceptable agreement.

The best model for all data and for the sulfide-containing measurements is our model 4A, while the best model for the conductivity of pure NaCl–$AlCl_3$ melts is model 2A.

Registry No. NaCl, 7647-14-5; $AlCl_3$, 7446-70-0; Al_2S_3, 1302-81-4.

Literature Cited

(1) Berg, R. W.; von Winbush, Sc; Bjerrum, N. J. *Inorg. Chem.* **1980**, *19*, 2688–98.
(2) Rédey, L.; Porubszky, I.; Molnár, I. *Power Sources* **1975**, *5*, 559–72.
(3) Koura, N. *J. Electrochem. Soc.* **1980**, *127*, 1529–31.

(4) Berg, R. W.; Hjuler, H. A.; Bjerrum, N. J. J. Chem. Eng. Data 1983, 28, 253-5.
(5) Janz, G. J.; Tomkins, R. P. T.; Allen, C. B.; Downey, J. R.; Gardner, G. L.; Krebs, U.; Singer, S. K. J. Phys. Chem. Ref. Data 1975, 4, 871-83.
(6) Yamaguti, Y.; Sisido, S. J. Chem. Soc. Jpn. 1938, 59, 1311-20.
(7) Kryagova, A. I., Zh. Obshch. Khim. 1939, 9, 2061-6.
(8) Moss, R. H. "Doctoral Dissertation Series No. 12730"; University Microfilms: Ann Arbor, MI, 1955; pp 1-57.
(9) Midorikawa, R. J. Electrochem. Soc. Jpn. 1956, 24, 23-7.
(10) Howie, R. C.; Macmillan, D. W. J. Inorg. Nucl. Chem. 1971, 33, 3681-6.
(11) Carpio, R. A.; Kibler, F. C.; King, L. A.; Brockner, W.; Tørklep, K.; Øye, H. A. Ber. Bunsenges. Phys. Chem. 1981, 85, 31-8.
(12) Matlasovsky, K.; Fellner, P.; Chrenkova-Paucirova, M.; Bräutigam, G.; Emons, H. H. Electrochim. Acta 1980, 25, 195-200.
(13) Kinosz, D. L.; Haupin, W. E. "Proceedings of the International Symposium on Molten Salts"; Pemsler, J. P., Braunstein, J., Nobe, K., Eds.; Electrochemical Society: Princeton, NJ, 1976; pp 375-87.
(14) Cho, K. Denki Kagaku oyobi Kogyo Butsuri Kagaku 1978, 46, 614-6.
(15) Biltz, W.; Klemm, W. Z. Anorg. Allg. Chem. 1926, 152, 267-94.
(16) Borisoglebskii, Yu. V.; Vetyukov, M. M.; Stekolshchikov, M. V. Zh. Prikl. Khim. (Leningrad) 1977, 50, 539-41; J. Appl. Chem. USSR (Engl. Transl.) 1977, 50, 520-2.
(17) Poulsen, F. W.; Bjerrum, N. J. J. Phys. Chem. 1975, 79, 1610-4.
(18) Jones, G.; Bradshaw, B. C. J. Am. Chem. Soc. 1933, 55, 1780-800.
(19) Berg, R. W.; Hjuler, H. A.; Bjerrum, N. J. J. Chem. Eng. Data 1983, 28, 251-3.
(20) Viola, J. T.; King, L. A.; Fannin, A. A.; Seegmiller, D. W. J. Chem. Eng. Data 1978, 23, 122-5.
(21) Statistical Analysis System, Procedure GLM, SAS Institute Inc., SAS Circle, Box 8000, Cary, NC 27511, version May 1979.
(22) Reference 21, Procedure RSQUARE CP.

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Transport Properties of Lithium Nitrate and Calcium Nitrate Binary Solutions in Molten Acetamide

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Viscosity and electrical conductivity were measured for eutectic binary mixtures of $LiNO_3$– and $Ca(NO_3)_2$–CH_3CONH_2 in the range of 290–329 K. The complex behavior of these solutions is discussed as aggregation phenomena of solvated ions.

Introduction

Some experimental evidence exists for the complexity of electrolytic solutions in molten acetamide. Cryoscopic measurements (*1–3*) showed that solute–solvent interactions become very important with decreasing temperature (i.e., with increasing electrolyte concentration). Around the eutectic concentration (when the electrolyte is an alkali metal salt of strong acids) the mixture supercools and in some cases (sodium salt) the crystallization does not occur at all even if the mixture is stirred and crystalline nuclei are added. These supercooled liquids exhibit viscoelastic behavior (*4*) and high ultrasonic losses (*5*, *6*) in the megahertz region that can be related to aggregation phenomena of solvated ions. In this note we present the results of measurements of viscosity and electrical conductivity performed on $LiNO_3$– and $Ca(NO_3)_2$–CH_3CONH_2 binary mixtures.

Experimental Section

Conductivity. The electrical conductivity was measured with a H. Tinsley and Co. Ltd. electrolytic bridge and a Phylips conductivity cell, checked by means of potassium chloride solutions. The cell constant was calculated by using the mean values of specific conductivity of KCl solutions given by Kohlrausch and Jones (*7*).

Viscosity. The viscosity coefficient was measured by means of a Hoeppler viscosimeter previously described (*8*), using the ball which gives a falling time in the range suggested by the manufacturer. The density was measured with a conventional pycnometric method with a Lauda ultrathermostat (±0.05 K). The chemicals employed are Fluka CH_3CONH_2 and Carlo Erba RPE $LiNO_3$ and $Ca(NO_3)_2$. The salts were dried under dynamic vacuum at 180 °C. Acetamide was purified by sublimation and dried under dynamic vacuum at room temperature.

Table I. Viscosity Values (η) as a Function of T

T, K	η, cP	T, K	η, cP
$LiNO_3$ (1)–CH_3CONH_2 (2), x_2 = 0.7960			
289.5	656.2	297.7	303.7
291.9	498.2	300.6	279.8
293.8	385.4	304.1	184.1
$Ca(NO_3)_2$ (1)–CH_3CONH_2 (2), x_2 = 0.8760			
314.3	191.8	323.3	101.2
317.3	145.8	326.8	84.0
320.8	117.8		

Table II. Specific Electrical Conductivity (χ) as a Function of T

T, K	$10^4\chi$, Ω^{-1} cm^{-1}	T, K	$10^4\chi$, Ω^{-1} cm^{-1}
$LiNO_3$ (1)–CH_3CONH_2 (2), x_2 = 0.7960			
289.6	4.45	296.3	7.36
291.7	5.25	299.5	9.14
294.0	6.25	302.4	11.08
$Ca(NO_3)_2$ (1)–CH_3CONH_2 (2), x_2 = 0.8760			
313.8	9.42	323.5	15.58
316.5	10.80	326.8	18.00
319.6	12.86		

Results and Discussion

The experimental results of viscosity are given in Table I and shown in Figure 1 as an Arrhenius plot. Specific electrical conductivity is given in Table II. In Figure 2 the trend of equivalent conductivity Λ vs. temperature is shown as an Arrhenius plot.

From these results, the following observations may be made: (1) The Ca^{2+} solutions have larger equivalent conductivities than the corresponding Li^+ solutions. (2) The slope in the plot of ln Λ vs. $1/T$ is higher for Ca^{2+} solutions. (3) Viscosity is higher for Ca^{2+} solutions. (4) The slope in a plot of ln η vs. $1/T$ is higher for Li^+ solutions.

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