Conductivity and Viscosity of Molten Mixtures of Aluminum Nitrate Decahydrate with Hydrates of Calcium, Cadmium, Magnesium, and Zinc Nitrates

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Conductivity and viscosity of molten mixtures of aluminum nitrate decahydrate with hydrates of calcium, cadmium, magnesium, and zinc nitrates have been measured as a function of temperature and composition. Both conductivity and fluidity exhibit a non-Arrhenius temperature dependence for all the compositions and have been described in terms of three-parameter equations. The deviations from ideal behavior in transport properties have been interpreted considering ion-ion, ion-water, and water-water interactions.

Introduction

The extensive supercooling and glass-forming tendencies of molten hydrated salts provide media specially suited for low-temperature electrochemical investigations. Various aspects of physicochemical behavior of such systems have been reported (*1-5*). In continuation of our studies on the behavior of molten hydrated salts (*6-8*), the results of conductivity and viscosity measurements on molten mixtures of aluminum nitrate decahydrate with hydrates of calcium, cadmium, magnesium, and zinc nitrates are reported in this paper.

Experimental Section

AnalaR (BDH) grade chemicals were used. Water of hydration was determined by volumetric titration using EDTA with an accuracy of ±0.02 mol/mol of cation. The average number of moles of water of hydration per mole of the salt (R) was 10.03 for aluminum nitrate, 3.99 for calcium nitrate, 4.12 for cadmium nitrate, 6.02 for magnesium nitrate, and 6.10 for zinc nitrate. Mixtures were prepared by adding calculated amounts of the salts, melted, and matured for 3 h. Details regarding the conductivity bridge, conductivity cell, and viscometer have been described earlier (*8*).

A liquid-paraffin thermostat of 20-L capacity was used. Temperature was controlled and known with a precision of ±0.05 °C. Data were recorded in both heating and cooling cycles at ca. 5-10-deg intervals.

Results and Discussion

Conductivity, κ (S cm^{-1}), and viscosity, η (cP), of molten mixtures of $Al(NO_3)_3 \cdot 10H_2O$ with (Ca, Cd, Mg, Zn)$(NO_3)_2 \cdot RH_2O$ have been measured over available composition and temperature ranges limited by solubility and thermal stability. The constants of polynomial equations of the type

$$\kappa = A + B(T - 300) + C(T - 300)^2 \quad (1)$$

$$\ln \eta = A' + B'/(T - 273.2) + C'/(T - 273.2)^2 \quad (2)$$

were obtained by a least-squares method and are presented in Tables I and II, along with standard errors (SE). Both

Table I. Constants of the Equation κ (S cm^{-1}) = $A + B(T - 300) + C(T - 300)^2$ for the Conductivity Data of the $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$ mole fractn	temp range, K	$10A$	10^3B	10^5C	10^3SE
	$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 3.99H_2O$				
0.3984	303-354	0.0871	0.5138	1.0619	0.045
0.5311	305-353	0.0769	0.4668	0.9814	0.098
0.6573	303-353	0.0664	0.3987	0.9423	0.081
0.7282	313-353	0.0605	0.4020	0.8807	0.041
0.8049	303-353	0.0447	0.2970	0.8254	0.120
0.8606	303-353	0.0436	0.2683	0.8064	0.046
0.9114	303-353	0.0506	0.3358	0.7671	0.103
0.9591	303-353	0.0481	0.3061	0.7697	0.058
1.0000	281-353	0.0538	0.3491	0.7310	0.223
	$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.12H_2O$				
0.1155	308-353	0.1048	0.6052	1.2445	0.404
0.2022	308-353	0.1139	0.6936	1.1556	0.094
0.3280	308-353	0.1077	0.7019	1.1254	0.420
0.4097	308-353	0.1164	0.6705	1.1048	0.115
0.5143	303-353	0.1160	0.6748	1.0482	0.146
0.7050	303-353	0.1238	0.6638	1.0319	0.146
0.7944	303-353	0.1168	0.6501	0.9686	0.112
0.8966	303-353	0.1160	0.6639	0.8780	0.197
1.0000	313-353	0.1132	0.7284	0.7567	0.145
	$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$				
0.1005	328-353	0.1128	0.7398	1.0651	0.373
0.2017	313-353	0.1246	0.7213	1.0403	0.119
0.3030	318-353	0.1241	0.6854	1.0178	0.124
0.3926	323-353	0.1244	0.7446	0.9080	0.069
0.4896	337-353	0.0497	0.9783	0.6433	0.039
0.6021	345-355	0.1299	0.7188	0.8025	0.061
	$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.10H_2O$				
0.1518	308-363	0.1288	0.7579	1.1873	0.159
0.2879	313-363	0.1621	0.7221	1.3480	0.982
0.4008	302-353	0.1454	0.8294	1.2126	0.191
0.4836	298-353	0.1406	0.7896	1.2075	0.333
0.5343	293-353	0.1365	0.7782	1.2067	0.344
0.7246	303-353	0.1905	0.9606	1.2095	0.149
0.8902	303-353	0.2464	1.1559	1.1081	0.301
0.9418	303-353	0.2485	1.1076	1.1576	0.169
1.0000	308-353	0.2654	1.2690	0.9598	0.288

equivalent conductivity, Λ (S cm^2 equiv^{-1}), and fluidity, ϕ (cP^{-1}), exhibit a non-Arrhenius temperature dependence for all the compositions. Three-parameter Vogel-Tammann-Fulcher (VTF) equations of the type

$$\Lambda = A_\Lambda \exp\left(-\frac{B_\Lambda}{T - T_{0,\Lambda}}\right) \quad (3)$$

$$\phi = A_\phi \exp\left(-\frac{B_\phi}{T - T_{0,\phi}}\right) \quad (4)$$

based on a free-volume model and cooperative rearrangement theory describe adequately the temperature dependence of Λ and ϕ. Parameters A_Λ, A_ϕ, B_Λ, B_ϕ, $T_{0,\Lambda}$, and $T_{0,\phi}$ are constants characteristic of the system. T_0, the zero mobility temperature, is the temperature at which the molten system looses

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Table II. Constants of the Equation $\ln \eta = A + B/(T - 273.2) - C/(T - 273.2)^2$ for the Viscosity Data of the $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$ mole fractn	temp range, K	A	$10^{-3}B$	$10^{-4}C$	10SE
$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 3.99H_2O$					
0.3984	303–354	0.5585	0.2250	0.2721	0.184
0.5311	318–353	0.3221	0.2501	0.3439	0.145
0.6573	313–353	0.3221	0.2564	0.3716	0.165
0.7282	318–353	0.0982	0.2887	0.4320	0.106
0.8049	313–353	0.2655	0.2915	0.4111	0.059
0.8606	313–353	0.2854	0.2949	0.4163	0.159
0.9114	313–353	0.2816	0.2798	0.3890	0.081
1.0000	313–353	0.4589	0.2472	0.3118	0.146
$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.12H_2O$					
0.1155	313–353	0.1115	0.2695	0.3978	0.126
0.2022	318–353	0.0419	0.2719	0.4174	0.102
0.3280	313–353	0.0778	0.2608	0.3946	0.031
0.4097	308–353	0.2845	0.2269	0.3011	0.128
0.5143	303–353	0.4038	0.2124	0.2617	0.231
0.7050	303–353	0.3551	0.2088	0.2586	0.205
0.7944	308–353	0.1522	0.2282	0.3122	0.114
0.8966	303–353	0.4248	0.2026	0.2462	0.227
1.0000	313–353	0.1405	0.2304	0.3270	0.065
$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$					
0.1005	323–353	0.1958	0.2643	0.4064	0.055
0.2017	313–353	0.2516	0.2506	0.3712	0.104
0.3030	318–353	0.1274	0.2657	0.4203	0.063
0.3926	323–353	0.0819	0.2685	0.4371	0.061
0.4896	337–353	0.2588	0.2319	0.3051	0.070
$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.10H_2O$					
0.1518	308–353	0.2916	0.2299	0.3083	0.178
0.2879	313–353	0.0327	0.2469	0.3619	0.097
0.4008	302–353	0.2882	0.2107	0.2607	0.227
0.4836	313–353	−0.6766	0.2493	0.3585	0.059
0.5343	313–353	−0.0468	0.2508	0.3684	0.049
0.7246	303–353	0.0551	0.2009	0.2543	0.238
0.8902	303–353	0.0576	0.1848	0.2825	0.257
0.9418	303–353	−0.0394	0.1861	0.2876	0.286
1.0000	308–353	−0.1354	0.1873	0.2529	0.234

Table III. Constants of the Equation Λ (S cm² equiv⁻¹) = $\Lambda_A \exp(-B_A/T - T_{0,A})$ for the Equivalent Conductivity–Temperature Data for the $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$ mole fractn	temp range, K	$\ln \Lambda_A$	B_A	$T_{0,A}$	10SE
$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 3.99H_2O$					
0.3984	303–354	5.4292	568.44	202.15	0.019
0.5311	305–353	6.3126	562.66	203.56	0.041
0.6573	303–353	5.2830	577.63	203.62	0.034
0.7282	313–353	5.0915	542.11	207.80	0.013
0.8049	303–353	5.0944	569.12	208.77	0.038
0.8606	303–353	5.1205	595.03	205.80	0.032
0.9114	303–353	4.8638	533.34	209.67	0.030
0.9591	303–353	4.7283	512.02	212.45	0.056
1.0000	281–353	4.9647	573.97	203.92	0.069
$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.12H_2O$					
0.1155	308–353	5.8420	627.86	194.89	0.045
0.2002	308–353	5.4530	531.36	203.56	0.020
0.3280	308–353	5.5779	566.27	200.22	0.069
0.4097	308–353	5.4799	560.17	199.14	0.021
0.5143	303–353	5.3542	540.53	200.86	0.019
0.7050	303–353	5.4029	577.21	194.72	0.035
0.7944	303–353	5.1515	527.06	200.85	0.035
0.8966	303–353	5.0054	510.83	201.71	0.022
1.0000	313–353	4.7476	460.82	206.75	0.012
$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$					
0.1005	328–353	5.5425	559.13	198.89	0.064
0.2017	313–353	5.4090	535.99	199.70	0.030
0.3030	318–353	5.5451	586.00	198.10	0.024
0.3926	323–353	5.8732	548.47	195.59	0.048
0.4896	337–353	6.3418	873.20	158.66	0.092
$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.10H_2O$					
0.1518	308–353	5.4821	524.16	202.93	0.027
0.2879	313–353	5.5200	532.19	199.65	0.132
0.4008	302–353	5.5376	529.78	200.84	0.023
0.4836	298–353	5.5996	552.34	198.71	0.046
0.5343	293–353	5.4366	511.93	204.84	0.040
0.7246	303–353	5.6429	564.57	191.70	0.012
0.8902	303–353	5.5649	537.58	189.30	0.015
0.9418	303–353	5.6758	576.57	184.14	0.019
1.0000	308–353	5.3112	500.53	191.50	0.030

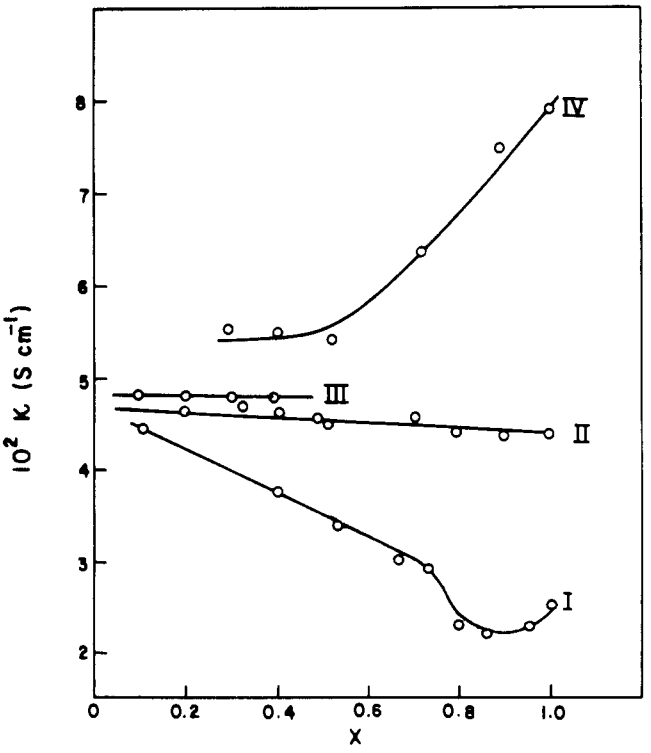

Figure 1. Conductivity (κ) vs mole fraction of $M(NO_3)_2 \cdot RH_2O$ isotherms at 333.2 K for $Al(NO_3)_3 \cdot 10H_2O + M(NO_3)_2 \cdot RH_2O$ systems: (I) for Ca-, (II) for Cd-, (III) for Mg-, and (IV) for Zn-containing mixtures.

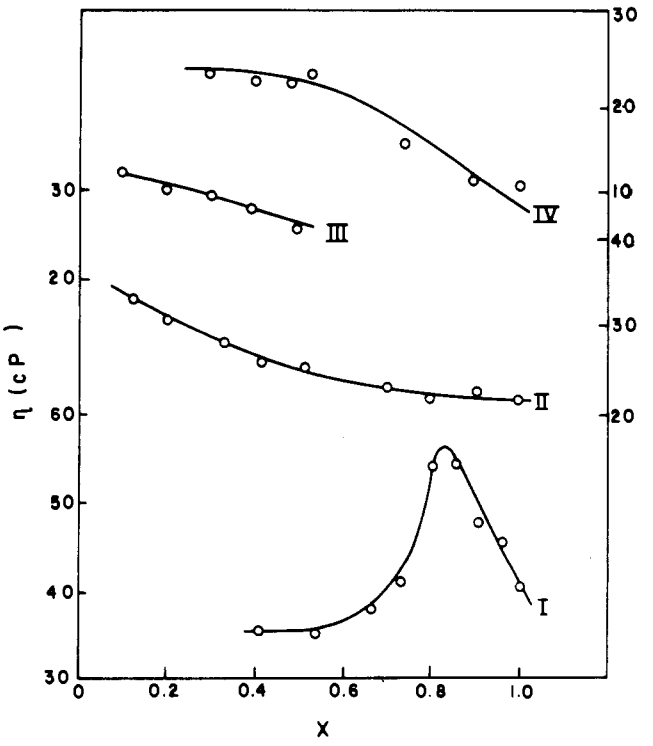

Figure 2. Viscosity (η) vs mole fraction of $M(NO_3)_2 \cdot RH_2O$ isotherms at 333.2 K for $Al(NO_3)_3 \cdot 10H_2O + M(NO_3)_2 \cdot RH_2O$ systems: (I) for Ca-, (II) for Cd-, (III) Mg-, and (IV) for Zn-containing mixtures.

Table IV. Constants of the Equation ϕ (cP^{-1}) = $A_\phi \times \exp(-B_\phi/T - T_{0,\phi})$ for the Fluidity-Temperature Data for the $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$ mole fractn	temp range, K	ln A_ϕ	B_ϕ	$T_{0,\phi}$	10SE
$M(NO_3)_2 \cdot RH_2O$ = $Ca(NO_3)_2 \cdot 3.99H_2O$					
0.3984	303-354	1.2367	619.81	204.41	0.036
0.5311	313-353	0.9180	534.95	213.35	0.057
0.6573	313-353	1.3113	633.42	205.30	0.054
0.7282	318-353	1.2745	627.84	207.31	0.038
0.8049	313-353	1.1909	636.50	210.26	0.033
0.8606	313-353	1.5122	716.16	203.20	0.032
0.9114	313-353	1.0874	598.98	212.40	0.016
0.9591	317-353	1.3640	676.42	203.54	0.060
1.0000	313-353	0.8023	573.72	210.27	0.081
$M(NO_3)_2 \cdot RH_2O$ = $Cd(NO_3)_2 \cdot 4.12H_2O$					
0.1155	313-353	1.6417	716.93	193.79	0.041
0.2002	318-353	1.4926	666.61	197.41	0.024
0.3280	313-353	1.8981	782.02	183.73	0.060
0.4097	308-353	1.2535	580.02	204.16	0.027
0.5143	303-353	1.5299	647.54	197.42	0.032
0.7050	303-353	1.6107	656.11	195.09	0.049
0.7944	303-353	1.4541	614.11	198.24	0.025
0.8966	303-353	1.3197	586.36	201.69	0.020
1.0000	313-353	1.1714	545.22	204.91	0.014
$M(NO_3)_2 \cdot RH_2O$ = $Mg(NO_3)_2 \cdot 6.02H_2O$					
0.2017	313-353	1.6320	735.39	187.12	0.062
0.3030	318-353	1.7565	778.33	181.99	0.035
0.3926	323-353	1.3616	657.32	193.57	0.027
0.4896	337-353	1.5352	700.44	187.00	0.029
$M(NO_3)_2 \cdot RH_2O$ = $Zn(NO_3)_2 \cdot 6.10H_2O$					
0.1518	308-353	1.4815	648.01	197.14	0.048
0.2879	313-353	1.6399	669.17	193.41	0.043
0.4008	302-353	1.7117	666.96	194.56	0.047
0.4836	313-353	1.5123	602.69	202.41	0.022
0.5343	313-353	1.5767	629.76	199.34	0.023
0.7246	303-353	2.1521	728.97	183.59	0.036
0.8901	303-353	2.1560	704.04	179.35	0.027
0.9418	303-353	2.3937	772.86	172.91	0.038
1.0000	308-353	1.9450	652.45	182.54	0.058

its fluid behavior. The constants of eqs 3 and 4 were found by an iterative method (Tables III and IV).

Conductivity and viscosity composition isotherms for the binary mixtures of $Al(NO_3)_3 \cdot 10H_2O$ with (Ca, Cd, Mg, Zn)$(NO_3)_2 \cdot RH_2O$ are shown in Figures 1 and 2. Addition of $Ca(NO_3)_2 \cdot 4H_2O$ to the $Al(NO_3)_3 \cdot 10H_2O$ melt causes preferential orientation of the NO_3^- ion—the common anion—toward the $Al(H_2O)_n^{3+}$ ion due to its higher cationic potential (0.91) relative to that of the $Ca(H_2O)_n^{2+}$ ion (0.53) (*9*). Water released from the hydration sphere of the Al^{3+} ions occupies new sites in the hydration sphere of the Ca^{2+} ions, decreasing their mobility and consequently κ. The observed increase in κ beyond 83 mol % may be due to a saturation of these interactions. As expected, an opposite trend is observed in viscosity composition isotherms for this system.

Small variations in κ and η on addition of $Cd(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ to the $Al(NO_3)_3 \cdot 10H_2O$ melt are attributed to small changes in $Al(H_2O)_n^{3+}$–NO_3^- interactions. Cadmium and magnesium ions have been found to form contact ion pairs in concentrated solutions (*10*, *11*), because of which they would not alter the NO_3^- ion equilibrium in the mixture to a large extent. $Al(NO_3)_3 \cdot 10H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ mixtures do not show much change in κ up to 53 mol % of the divalent salt. A decrease in κ due to $Al(H_2O)_n^{3+}$–NO_3^- interactions may be counterbalanced by an increase in κ due to water released from the hydration sphere of the Al^{3+} ions. A saturation effect of these interactions may be responsible for an increase in κ and a decrease in η on addition of zinc salt beyond this composition. Studies are in progress to provide further insight into these systems.

Literature Cited

(1) Angell, C. A. *J. Electrochem. Soc.* **1965**, *112*, 1224.
(2) Moynihan, C. T.; Fratiello, A. *J. Am. Chem. Soc.* **1967**, *89*, 5546.
(3) Braunstein, J.; Orr, L.; Macdonald, W. *J. Chem. Eng. Data* **1967**, *12*, 415.
(4) Islam, N.; Ismail, K. *J. Phys. Chem.* **1975**, *79*, 2180.
(5) Jain, S. K. *J. Chem. Eng. Data* **1973**, *18*, 397.
(6) Ramana, K. V.; Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1985**, *30*, 449.
(7) Ramana, K. V.; Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1986**, *31*, 288.
(8) Ramana, K. V.; Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1990**, *35*, 293.
(9) Moynihan, C. T. in *Ionic Interactions*; Petrucci, S., Ed.; Academic Press: New York, 1971; Vol. 1.
(10) Davis, A. R.; Plane, R. A. *Inorg. Chem.* **1968**, *7*, 2565.
(11) Chang, T. G.; Irish, D. E. *J. Phys. Chem.* **1973**, *77*, 52.

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Equilibrium Phase Behavior of the Poly(ethylene glycol)/Potassium Phosphate/Water Two-Phase System at 4 °C

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The two-phase liquid–liquid equilibria behavior of the system composed of poly(ethylene glycol), potassium phosphate, and water at 4 °C is presented. The effect of poly(ethylene glycol) molecular weight on phase separation at pH 7 was investigated by utilizing poly(ethylene glycol) of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000. By varying the ratio of monobasic to dibasic potassium phosphate and maintaining the poly(ethylene glycol) molecular weight at 3400, the effect of pH on phase equilibria was studied over the pH range 6–9.2.

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Introduction

When poly(ethylene glycol) (PEG) is mixed with potassium phosphate and water at an appropriate pH and temperature, two phases are produced, the top phase being rich in PEG and the bottom phase containing primarily phosphate. As discovered by Albertsson (*1*, *2*), the phases of the system offer different physical and chemical environments and are delicate enough to be used for the purification of biological materials. However, in order to gain a fundamental understanding of phase separation and select an appropriate PEG/potassium phosphate/water system for purification purposes, phase equilibrium data are ultimately needed.

The main source of phase equilibrium data for the PEG/potassium phosphate/water system is that of Albertsson (*1*).

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