

Conductivity of Highly Concentrated Aqueous Electrolyte Solutions: Ammonium Nitrate-Water System

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Conductivity of ammonium nitrate-water system has been determined for the water/salt mole ratio (R) varying between 1.2 to 3.0 and at temperature between 298 to 345 K. At a given R , variation of conductivity (κ) with temperature (T) could be expressed by an equation of the type $\kappa = A + BT$, where A and B are empirical constants. Temperature-dependence of conductivity has been interpreted in terms of free-volume model of liquid transport. Conductivity-composition isotherms exhibited concavity to composition axis, indicating weak ordering tendency of the system.

TRANSPORT properties of highly concentrated aqueous solutions of polyvalent cationic electrolytes, where the water content is insufficient to satisfy more than the first coordination sheath around the cations, have been reported^{1,4}. Investigation in uni-univalent electrolytes, in similar concentration range, have received insufficient attention inspite of their importance from theoretical considerations⁵. Campbell *et al.*⁶ studied the conductivity of dilute 1:1 electrolyte solutions, particularly with a view to testing the validity of modified Robinson and Stokes^{7,8} equation. Scatchard and Prentiss⁹ reported conductivity of 6×10^{-4} to 1.4 molal solutions of NH_4NO_3 at 10°. Measurements in concentrated NH_4NO_3 solutions at limited temperatures have also been reported by Dubeau and Sisi¹⁰. Peleg¹¹, on the basis of extensive association equilibria studies in highly concentrated ammonium nitrate solutions, proposed an extension of the applicability of quasi-lattice model¹² to concentrated electrolyte solutions, taking into consideration the anionic hydration. As a part of extensive study of transport behaviour of highly concentrated aqueous electrolyte solutions and hydrated molten salts, in progress in our laboratory¹³ conductivity measurements of $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ system are presented in this paper.

Materials and Methods

A Beckman conductivity bridge (model RC-18A) based on Wheatstone bridge principle, provided with a Wagner ground and CRT null detector, was employed. A decade capacitance (C_p) box (Radart, type 745-A) was connected in parallel with the resistance (R_p) in the balancing arm of the bridge and resistances of the ratio arms were matched. Considering the cell as a series combination of a resistance (R_s) and a capacitance (C_s)^{14,15}, it follows from ac theory that at balance, cell resistance¹⁶ is $R_s = R_p[1 - (2\pi f R_p C_p)^2 + \dots]$... (1)

where f is the ac frequency in Hz. All measurements were made at ac frequency of 1 kHz.

Other details have been given in an earlier publication¹⁷.

A dip-capillary type cell, made of pyrex glass, was used. Cell constant was determined using 1.0 and 0.1N KCl solutions at 25° using conductivity data of Jones and Prendergast¹⁸. For the small temperature range employed, the dilation correction to cell constant was negligible.

Ammonium nitrate (Analar, BDH), was vacuum desiccated for several days. To a known amount of salt in the cell, calculated volume of triply distilled water (conductivity[†] 1.0×10^{-6} S cm^{-1}) was added and the vessel was kept in a thermostat at 50° for 4-5 hr during which a clear solution was obtained. Concentration unit used is moles of water per mole of ammonium nitrate (R). At a given composition, several sets of data were taken at different temperatures, both in heating and cooling cycles.

Results and Discussion

Temperature-conductivity data — Conductivity of $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ system at R varying between 1.2 to 3.0 in the temperature range, limited by solubility and rapid loss of water, were obtained. Representative data at different compositions are presented in Table 1. At a given composition, variation of conductivity with temperature was least square fitted into a linear equation

$$\kappa = A + BT \quad \dots (2)$$

using IBM 360/44 data processing system. The empirical constants A and B , characteristics of a given composition, are given in Table 2. The temperature coefficient of conductivity, B , is seen to increase with R . At all compositions, the Arrhenius plots of conductivity (Fig. 1) were nonlinear; the activation energy E_κ (also Table 2) increased with decrease in temperature, indicating the inadequacy of Arrhenius type equation to the system. At a given temperature E_κ decreased with increase in R .

Equivalent conductivity (Λ) of $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ system were evaluated using available density data¹³; values for representative data are also listed

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† Conductance is in SI unit.

TABLE 1 — CONDUCTIVITY DATA OF AMMONIUM NITRATE-WATER SYSTEM

Temp. (T, K)	Conductivity S cm ⁻¹	Molar volume* cm ³	Equiv. cond. S cm ² equiv. ⁻¹	Temp. (T, °K)	Conductivity S cm ⁻¹	Molar volume* cm ³	Equiv. cond. S cm ² equiv. ⁻¹
R = 1.2				R = 2.0			
323.2	0.3574	73.81	26.38	298.2	0.3402	87.34	29.71
328.2	0.3800	74.02	28.13	303.2	0.3666	87.56	32.10
333.2	0.4032	74.20	29.92	308.2	0.3908	87.78	34.30
338.2	0.4253	74.39	31.64	313.2	0.4163	87.96	36.62
343.2	0.4482	74.56	33.42	318.2	0.4410	88.17	38.88
R = 1.4				R = 2.5			
313.2	0.3430	77.09	26.44	323.2	0.4667	88.41	41.26
318.2	0.3667	77.26	28.33	328.2	0.4927	88.64	43.67
323.2	0.3900	77.45	30.21	333.2	0.5174	88.87	45.98
328.2	0.4131	77.69	32.09	338.2	0.5433	89.11	48.41
333.2	0.4370	77.87	34.03	343.2	0.5680	89.35	50.75
338.2	0.4602	78.07	35.39	R = 3.0			
343.2	0.4837	78.27	37.86	298.2	0.3721	95.98	35.71
R = 1.6				303.2	0.3987	96.24	38.37
303.2	0.3227	80.40	25.95	308.2	0.4250	96.50	41.01
308.2	0.3461	80.61	27.90	313.2	0.4515	96.73	43.67
313.2	0.3703	80.81	29.92	318.2	0.4775	96.96	46.30
318.2	0.3948	81.01	31.98	323.2	0.5041	97.22	49.01
323.2	0.4191	81.22	34.04	328.2	0.5307	97.49	51.74
328.2	0.4427	81.44	36.05	333.2	0.5575	97.76	54.50
333.2	0.4667	81.65	40.18	338.2	0.5831	98.01	57.15
343.2	0.5144	82.08	42.22	343.2	0.6094	98.27	59.89
R = 1.8				R = 3.0			
303.2	0.3486	84.01	29.29	298.2	0.3897	104.80	40.84
308.2	0.3730	84.21	31.41	303.2	0.4170	105.10	43.83
313.2	0.3977	84.44	33.58	308.2	0.4439	105.38	46.78
318.2	0.4221	84.64	35.73	313.2	0.4710	105.64	49.76
323.2	0.4466	84.87	37.90	318.2	0.4978	105.91	52.72
328.2	0.4715	85.10	40.12	323.2	0.5250	106.21	55.76
333.2	0.4955	85.32	42.28	328.2	0.5525	106.48	58.83
338.2	0.5209	85.54	44.56	333.2	0.5788	106.76	61.79
343.2	0.5438	85.74	46.63	338.2	0.6058	107.06	64.86
				343.2	0.6315	107.32	67.77

*From density data (ref. 13).

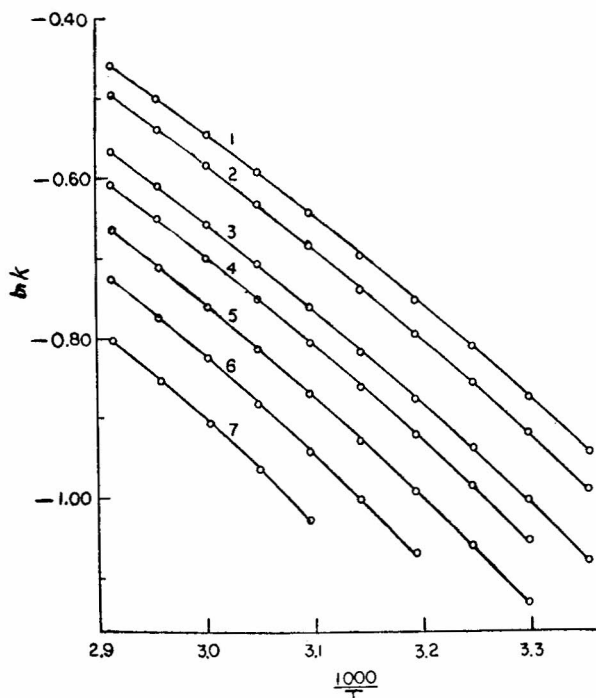


Fig. 1 — Arrhenius plots of conductivity [Water/ammonium nitrate mole ratio (R) for curve (1) 1.2; (2) 1.4; (3) 1.6; (4) 1.8; (5) 2.0; (6) 2.5; (7) 3.0

in Table 1. Temperature-dependence of equivalent conductivity also showed inadequacy of Arrhenius type equation. On the other hand, the data can be adequately fitted into a three-parameter Vogel-Tammann-Fulcher (VTF) equation¹⁹ which has

$$\Lambda = A'T - \frac{1}{2} \exp \left[-\frac{B'}{T-T_0} \right] \quad \dots(3)$$

been proposed using free volume model²⁰ and also the cooperative rearrangement theory²¹ of liquid transport. A' and B' are empirical constants and T_0 is the temperature at which free volume of the system ceases or where configurational entropy of the system becomes zero. This equation has been successfully used for systems with glass-forming tendency and which show considerable supercooling. NH₄NO₃-H₂O system has feeble tendency to supercool and the measurements at temperatures well below room temperature were not possible. For such a system, precise evaluation of T_0 by graphical method was not possible. Computer calculation of T_0 were made by least square fitting of $\Lambda-T$ data in Eq. 3. The computer was programmed to select the T_0 values at an interval of 1° over a specified temperature range (50-300°K). For each value of T_0 , a least square fitted value of A' , B' and standard deviation were printed out. T_0 for best fit was adopted. Alternatively, T_0 was evaluated

TABLE 2 — EMPIRICAL PARAMETERS OF THE LEAST SQUARE FIT EQUATIONS FOR THE SPECIFIC CONDUCTANCE OF AMMONIUM NITRATE-WATER SYSTEM

Water/salt mole ratio (R)	Temp. range (T, K)	Data points	A S cm ⁻¹	B × 10 ² S cm ⁻¹ K ⁻¹	Std dev.	Activation energy (kJ mole ⁻¹)
1.2	320-345	13	-1.1114	0.4544	0.0012	10.88-9.96
1.4	310-345	19	-1.1262	0.4691	0.0008	11.18-9.50
1.6	300-345	25	-1.1327	0.4801	0.0011	11.39-9.13
1.8	300-345	25	-1.1363	0.4900	0.0007	10.76-8.83
2.0	295-345	28	-1.1724	0.5072	0.0008	10.05-8.75
2.5	295-345	28	-1.1984	0.5267	0.0005	10.51-8.54
3.0	295-345	29	-1.2166	0.5388	0.0005	10.26-8.33

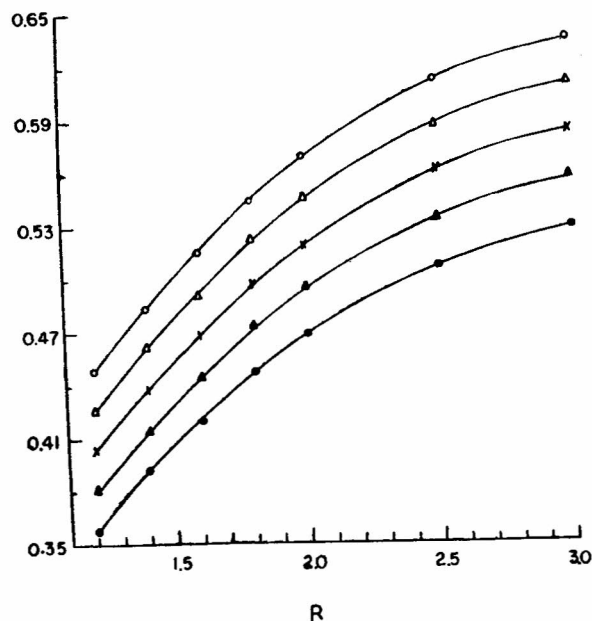


Fig. 2 — Composition-conductivity isotherms [Temperatures for curve (●) 323.2; (▲) 328.2; (×) 333.2; (△) 338.2; (○) 343.2K]

by considering equivalent 'activation energy' equation of the free volume model, in the form

$$E_{\text{corr}} = P + Q \left[\frac{T}{T - T_0} \right]^2 \quad \dots(4)$$

E_{corr} being related to the experimentally determinable parameters E_x and α , the mean expansion coefficient, by the relation (5)

$$E_{\text{corr}} = E_x + \alpha RT^2 + \frac{1}{2} RT \quad \dots(5)$$

For the applicability of free volume model, E_{corr} should be a linear function of $\left[\frac{T}{T - T_0} \right]^2$, passing

through origin. Computer calculation of T_0 using Eq. 4 was also made. T_0 's (Table 3), by both methods, agreed within $\pm 5^\circ$. It may also be seen that T_0 decreased with 'mean cationic potential'²²

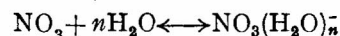
$\left(\sum \frac{N_i z_i}{r_i}, N_i, \text{ mole fraction; } z_i, \text{ ionic charge and } r_i, \text{ radius of species } i \right)$, as predicted by the free volume model.

Composition-conductivity data — At a given temperature, κ is seen to increase with R_0 (Fig. 2). The

TABLE 3 — ZERO FREE VOLUME TEMPERATURE OF THE AMMONIUM NITRATE-WATER SYSTEM

R	Zero free volume temperature (T_0) (°K) using	
	$\Lambda - T$ fitting	$E_{\text{corr}} - (T/T - T_0)^2$ fitting
1.2	138	144
1.4	130	134
1.6	126	129
1.8	122	122
2.0	119	117
2.5	115	113
3.0	110	108

rate of change of κ with R , $(\partial \kappa / \partial R)_T$, decreasing with increase in R , tending to a limiting value at $R \gg 3$. Peleg, from association equilibria studies suggested that at $R \leq 1$, only cationic hydration occurred; at $R > 1$, anionic hydration, first suggested by Keenan²³, would be predominant. Since the energy required for hydration of anion is small relative to that for the cations, it is reasonable to consider an equilibrium between hydrated and unhydrated anions,



With increase in R , formation of weak field anions would be favoured. This will result in a decrease in Coulombic interactions and consequently increase in κ , as observed.

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