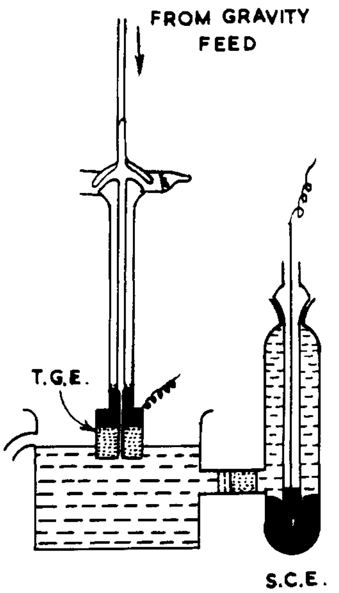

Figure 1. The tubular graphite electrode assembly.

The various values can be divided into three categories as far as their limit of accuracy is concerned.

Category 1. In cases of compounds **1–24,** which do not cause any filming of the electrode (the successive waves almost exactly superimposing on one another), the voltammograms yield ideal values of limiting currents which do not vary by more than ±3% even when different electrodes are used. The values of diffusion coefficients in such cases can be safely taken as sufficiently authentic with a maximum variation of ±5%.

Category 2. In cases of compounds **25–47,** which do cause filming of the electrode surface (the successive waves not superimposing on one another), the voltammograms do not yield ideal values of limiting currents. On account of some surface coverage concurrent with anodic oxidation, the values of the limiting current are likely to be a little smaller than the ideal values. The values of diffusion coefficients for these substances may thus be taken to be slightly on the lower side than the ideal values. The maximum variation of the magnitude of these values, of course, does not exceed ±5%.

Category 3. In cases of compounds **48–59,** which, apart from causing electrode filming, also exhibit distinct maxima, the voltammograms do not yield correct values of limiting currents because of the arbitration involved in computing the limiting current (with reference to the position of the maximum). The variation in the values of diffusion coefficients in such cases is, evidently, greater than ±5%.

It is interesting to note that inspite of the above limitations, the values of diffusion coefficients of the various organic substances are seen to lie fairly close to the generally accepted range of (0.6–0.7) $\times 10^{-5}$ $cm^2\ s^{-1}$ (*8*). Not only that, the values also compare favorably with the few reported in literature, keeping in view the wide differences in the nature of the media used by different investigators.

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Densities and Molar Volumes of the Ammonium Nitrate–Water System

Ramesh C. Sharma and Harish C. Gaur*
Department of Chemistry, University of Delhi, Delhi-110007, India

The densities of the ammonium nitrate–water system for water varying between 1.2 and 3.0 mol per mole of the nitrate (R) have been determined. At a given R, density (ρ) is a linear function of temperature. Variation of ρ with R can be expressed by an equation of the type $\rho = a + bR + cR^2$, where a, b, and c are empirical constants. Molar volume of the ammonium nitrate–water system exhibits ideal behavior.

The intermediate range of concentration between anhydrous molten electrolytes and dilute aqueous electrolyte solutions, although important from a theoretical view point (*1–3, 5, 7, 8, 10–12, 14, 15, 17*), has not been extensively studied. Densities of highly concentrated aqueous ammonium nitrate solutions, needed for calculations of structurally important properties, molar volumes, partial molar volumes, and equivalent conductance, etc., are reported in this paper. Data were obtained in the temperature range 295–345 K, limited by solubility and rapid loss of water due to evaporation.

Experimental Section

The densitometer (Figure 1) was essentially of the type used by Husband (*6*) and McAuley (*9*), modified to accommodate a wider range of temperatures. Briefly, it consisted of a calibrated bulb (volume 25–30 cm^3) joined to a graduated capillary on one side (volume 1 cm^3), and a 1-mm bore capillary with three small bulbs (volume *c* 0.5 cm^3 each) connected to a 10-mm tube on the other. The volumes of the main and small bulbs between fiducial points 1 to 5 were determined using triple-distilled water and distilled mercury at seven temperatures in the range 4–50 °C. Using the literature density data (*4*), average volumes at 30 °C between points 1 and 2, 3, 4, 5 were 24.404, 24.089, 23.879, and 23.654 ± 0.005 cm^3, respectively.

Ammonium nitrate, AnalaR (BDH), was vacuum desiccated at 100 °C. The solution for density measurement was prepared

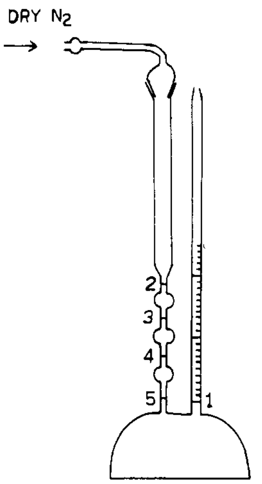

Figure 1. Densitometer.

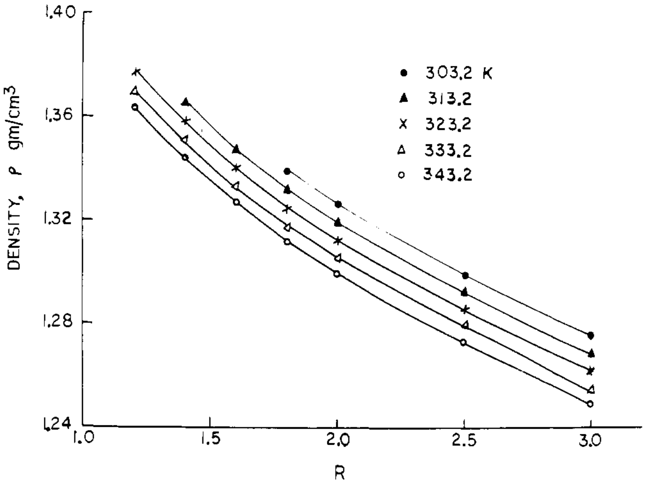

Figure 2. Variation of density with R (moles of water/mole nitrate).

by adding a calculated amount of triple-distilled water to the salt in a stoppered bottle and keeping it at 50 °C for 4–5 h during which a clear solution was obtained. After a given series of experiments, water content of the solution was checked by evaporating a known mass of solution. Loss of water was found to be negligible; in a typical experiment, where the initial water content was 2.00 mol per mole of the nitrate, it was found to be 1.986 after the experiment. For a given composition, several sets of data were taken at different temperatures.

A double-walled water thermostat of 20-l. capacity, provided with a Jumo contact thermometer and a solid state relay system, was used. The temperature was regulated and known with a precision of ±0.05°.

Results and Discussion

The composition units are mole fraction (X) and water to ammonium nitrate mole ratio (R).

Temperature-Density Data. The densities of the ammonium nitrate-water system for R varying between 1.2 and 3.0, at temperatures in the range 298.2–343.2 K are presented in Table I. At given R, density (ρ) variation with temperature could be expressed by the linear equation

$$\rho = A - B(T - 300) \qquad (1)$$

where A and B are empirical constants, characteristic of the composition of the system, and T is temperature on Kelvin scale. A and B (Table II) were evaluated by least-squares fit of the data, using an IBM 360/44 data processing system. B in eq 1 is related to expansion coefficient (α) by the equation,

$$\alpha = B/\rho$$

Table I. Densities of the NH_4NO_3-H_2O System

Moles of water/ mole of nitrate (R)	Temp (T, K)	Density (ρ, g cm^{-3})
1.2	323.2	1.3770
	328.2	1.3732
	333.2	1.3697
	338.2	1.3663
	343.2	1.3631
1.4	313.2	1.3651
	318.2	1.3618
	323.2	1.3585
	328.2	1.3545
	333.2	1.3513
	338.2	1.3478
1.6	303.2	1.3536
	308.2	1.3503
	313.2	1.3469
	318.2	1.3436
	323.2	1.3401
	328.2	1.3365
	333.2	1.3330
	338.2	1.3295
	343.2	1.3260
1.8	303.2	1.3373
	308.2	1.3340
	313.2	1.3311
	318.2	1.3278
	323.2	1.3245
	328.2	1.3214
	333.2	1.3180
	338.2	1.3145
	343.2	1.3114
2.0	303.2	1.3260
	308.2	1.3227
	313.2	1.3190
	318.2	1.3157
	323.2	1.3123
	328.2	1.3091
	333.2	1.3057
	338.2	1.3022
	343.2	1.2988
2.5	298.2	1.3026
	303.2	1.2992
	308.2	1.2958
	313.2	1.2926
	318.2	1.2894
	323.2	1.2860
	328.2	1.2826
	333.2	1.2795
	338.2	1.2762
	343.2	1.2729
3.0	298.2	1.2782
	303.2	1.2750
	308.2	1.2718
	313.2	1.2687
	318.2	1.2653
	323.2	1.2619
	328.2	1.2588
	333.2	1.2553
	338.2	1.2521
	343.2	1.2489

Values of α at different concentrations are of the same order, $(5.13 \pm 0.15) \times 10^{-4}$.

Composition-Density Data. At a given temperature, variation of ρ with R was not linear; typical variation at five temperatures is shown in Figure 2. Data could be fitted into the equation

$$\rho = a + bR + cR^2 \qquad (2)$$

Values of empirical constants a, b, and c, which are functions of temperature and the limited range of concentration employed,

Table II. Empirical Parameters of the Least-Squares Fit Equations for the Densities of NH_4NO_3–RH_2O Systems ($\rho = A - B(T - 300)$)

Moles of water (R)	Temp range (T, K)	A (g cm^{-3})	10^3 B (g cm^{-3} K)	Std. Dev	Data points
1.2	320–345	1.392 68	0.687 42	0.000 12	44
1.4	315–345	1.374 50	0.694 81	0.000 23	52
1.6	300–345	1.356 08	0.704 01	0.000 44	52
1.8	300–345	1.340 33	0.654 36	0.000 39	56
2.0	300–345	1.327 88	0.676 19	0.000 49	60
2.5	295–345	1.301 50	0.673 13	0.000 32	75
3.0	295–345	1.277 36	0.660 06	0.000 29	91

Table III. Empirical Parameters of the Least-Squares Fit Equations for the Molar Volumes of NH_4NO_3–H_2O Systems ($\bar{V} = A' + B'(T - 300)$)

Moles of water (R)	Temp range (T, K)	A' (cm^3 mol^{-1})	B' (cm^3 mol^{-1} K^{-1})	Std. dev
1.2	320–345	33.1605	1.7069	0.003
1.4	315–345	31.8939	1.6678	0.004
1.6	300–345	30.8654	1.6455	0.010
1.8	300–345	29.9569	1.5498	0.009
2.0	300–345	29.1259	1.5045	0.015
2.5	295–345	27.4472	1.4518	0.008
3.0	295–345	26.2312	1.3877	0.006

Table IV. Empirical Parameters of the Density-Concentration Equations for the Ammonium Nitrate–Water System ($\rho = a + bR + cR^2$)

Temp (K)	a	$b \times 10$	$c \times 10$	Std. dev
323.2	1.484 14	0.614 16	−4.770 17	0.0012
328.2	1.487 06	0.385 16	−4.572 49	0.0012
333.2	1.457 36	1.205 25	−5.208 67	0.0014
338.2	1.526 27	−1.049 73	−5.469 28	0.0009
343.2	1.502 00	−0.405 26	−3.959 04	0.0010

are given in Table III. The first coefficient, a, in eq 2 cannot be taken as the density at $R = 0$, i.e., of ammonium nitrate.

Temperature–Molar Volume Data. At a given composition, molar volumes ($\bar{V}$) at different temperatures were calculated using *mean* molecular mass, $M (= X_1M_1 + X_2M_2$ where X_1, X_2 are the mole fractions and M_1, M_2 molecular masses of the two components), and the observed density. Plots of $\bar{V}$ vs. T (Figure 3) are linear. Data could be adequately fitted into the equation

$$\bar{V} = A' + B'(T - 300) \tag{3}$$

The parameters A' and B' are listed in Table IV. B' is the molar expansivity of the solution. It exhibits a smooth change over the concentration range employed, indicating absence of any significant structural change on dilution.

Composition–Molar Volume Data. A typical trend of variation of molar volume with mole fraction of ammonium nitrate at two temperatures is shown in Figure 4. It is seen to be linear, the maximum deviation from linearity in large scale plots (not shown) being *c* 0.25%. The system may thus be considered as ideal, at least to a first approximation, over the concentration range employed.

Highly concentrated aqueous electrolyte solutions, where the water content is insufficient to satisfy more than the first coordination sheath for the ions, have generally been discussed in terms of a reference state (*13*), e.g., the melting point of the component with higher molecular mass, the implication being that a basic microscopic reference lattice structure of this component may be considered to predominate over the whole range of concentration and temperature. This consideration leads molar volume of the solution to be a function of temperature (T) and the mole fraction of component with lower molecular mass, in this case water (X_{H_2O}). Thus

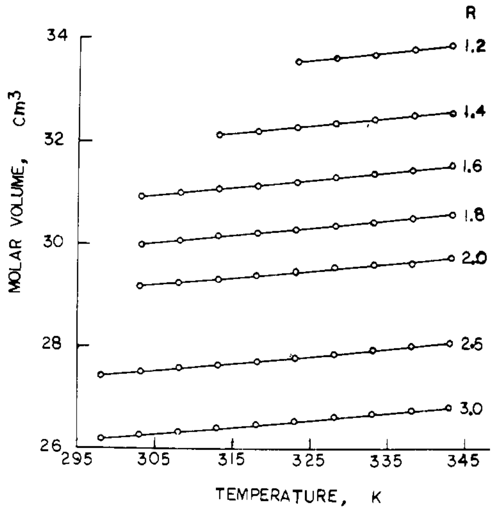

Figure 3. Variation of molar volume with temperature.

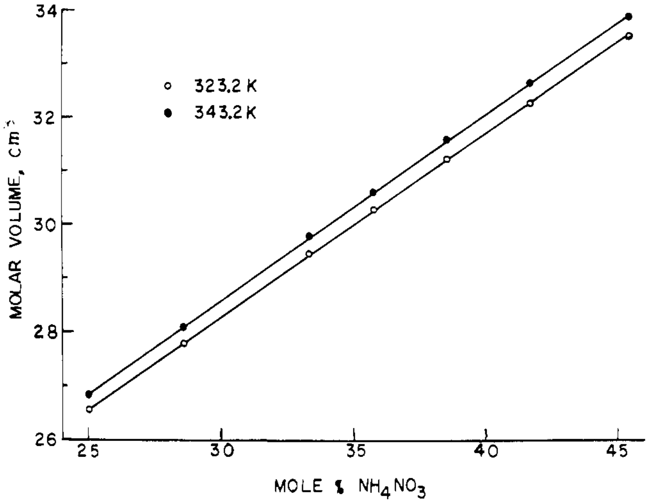

Figure 4. Molar volume–composition isotherms.

$$\bar{V} = f(T, X_{H_2O}) \tag{4}$$

and

$$d\bar{V} = \left(\frac{\partial \bar{V}}{\partial T}\right)_{X_{H_2O}} dT + \left(\frac{\Delta \bar{V}}{\Delta X_{H_2O}}\right)_T dX_{H_2O} \tag{5}$$

$(\partial \bar{V}/\partial T)_{H_2O}$, the rate of change of molar volume with temperature, at a fixed composition, is equal to coefficient B' of eq 3. To evaluate $(\partial \bar{V}/\partial X_{H_2O})$, one can start by expressing molar volume in terms of partial molar volumes of the components.

$$\bar{V} = X_{H_2O}\bar{V}_{H_2O} + X_{NH_4NO_3}\bar{V}_{NH_4NO_3} \tag{6}$$

from which

$$\left(\frac{\partial \bar{V}}{\partial X_{H_2O}}\right)_T = \bar{V}_{H_2O} + X_{H_2O}\left(\frac{\partial \bar{V}_{H_2O}}{\partial X_{H_2O}}\right)_T - \bar{V}_{NH_4NO_3} + X_{NH_4NO_3}\left(\frac{\partial \bar{V}_{NH_4NO_3}}{\partial X_{H_2O}}\right)_T \tag{7}$$

since $(\partial X_{NH_4NO_3}/\partial X_{H_2O}) = -1$.

For an ideal system the molar volume is a linear function of the mole fraction of either component,

$$\bar{V} = E + FX_{H_2O} = (E + F) - FX_{NH_4NO_3} \tag{8}$$

Table V. Computer Calculated Partial Molar Volumes of Ammonium Nitrate and Water ($\bar{V} = E + FX_{H_2O}$)

Temp (K)	$\bar{V}_{NH_4NO_3}$, cm^3 mol^{-1}	$\bar{V}_{H_2O}$, cm^3 mol^{-1}
323.2	52.29_7	18.00_3
328.2	52.46_0	18.04_8
333.2	52.54_8	18.13_1
338.2	52.69_2	18.16_8
343.2	52.81_6	18.22_1

Hence the partial molar volumes of both components, $\bar{V}_{NH_4NO_3}$ and $\bar{V}_{H_2O}$, are constant over the concentration range of ideal behavior. From this it follows that the derivatives $(\partial \bar{V}_{H_2O}/\partial X_{H_2O})$ and $(\partial \bar{V}_{NH_NO_3}/\partial X_{H_2O})$ in eq 7 would be zero. Equation 7 then reduces to

$$\left(\frac{\partial \bar{V}}{\partial X_{H_2O}}\right)_T = \bar{V}_{H_2O} - \bar{V}_{NH_4NO_3} \qquad (9)$$

Partial molar volumes were evaluated by least-squares fit of molar volume and mole fraction data in eq 8; the evaluated values are given in Table V. Partial molar volumes of water at the reported temperatures are in good agreement with the molar volumes at corresponding temperatures.

The change in the molar volume could thus be found out using eq 5, which, for convenience, may be rewritten in terms of changes in molar volume with temperature ($\Delta \bar{V}_T$) and concentration ($\Delta \bar{V}_{X_{H_2O}}$)

$$d\bar{V} = \int_{T}^{T_0} \Delta V_T dT + \int_{x=0}^{x=x} \Delta \bar{V}_{x_{H_2O}} dX_{H_2O} \qquad (10)$$

Using this, the effect of the two integral terms in eq 10 on the molar volume change can then be considered beyond the reference state (*16*), the effect of temperature exhibiting a decrease in ΔV_T with the increase of X_{H_2O}. The change is smooth over the range of concentration employed. $\Delta V_{X_{H_2O}}$ increases with the temperature, typical values at 323.2, 333.2, and 343.2 K being 34.28, 34.42, and 34.58 cm^3. At a given temperature $\Delta V_{X_{H_2O}}$ is reasonably constant (deviation 0.25%) confirming that NH_4NO_3–H_2O system is ideal over the range of concentration employed.

By extending the composition–molar volume isotherms (not shown in Figure 4), the *extrapolated* molar volume of NH_4NO_3 was of the same order as those evaluated from eq 8. These are, however, more than those expected at the corresponding temperatures and could arise due to unusual behavior which the system may show at $R < 1.2$.

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Isobaric Vapor–Liquid Equilibrium of Binary Mixtures of 1-Propanol + Chlorobenzene and 1-Butanol + Chlorobenzene

K. Venkateswara Rao,* A. Raviprasad, and C. Chiranjivi
Department of Chemical Engineering, Andhra University, Waltair, India

Vapor–liquid equilibrium data are obtained for the binary mixtures of 1-propanol–chlorobenzene and 1-butanol–chlorobenzene at atmospheric pressure. These systems show positive deviations from Raoult's law and form minimum boiling azeotropes. The experimental data are correlated satisfactorily by the three-suffix Margules equations and tested for thermodynamic consistency by the Herington test. Both the systems form symmetrical solutions.

As a part of the continuing study of phase equilibria involving alcohols, vapor–liquid equilibrium data at 760 ± 1 mmHg are measured for the two binary systems 1-propanol + chlorobenzene and 1-butanol + chlorobenzene. These systems are chosen as a part of our general study to obtain additional information on azeotropic behavior of the solutions of various organic liquids with alcohols.

Experimental Section

Purity of Chemicals. 1-Propanol, 1-butanol, and chlorobenzene (all Analytical Grade) are further purified by distilling in a laboratory packed distillation column. The physical properties of the chemicals are given in Table I. These values compare well with the values given in literature (*7*).

Analytical Method. Vapor and liquid samples are analyzed at 30 °C by means of refractive index using an Abbe's refractometer with an accuracy of ±0.0005. The composition of the vapor and liquid samples for each system is determined from the standard plot of refractive index vs. composition prepared from samples of known composition. The boiling temperatures are measured using a standard mercury-in-glass thermometer having an accuracy of ±0.1 °C.

Equilibrium Still. The equilibrium still used for determining the vapor–liquid equilibrium data is of the vapor recirculatory type of Jones, Schoenborn, and Colburn, as modified by Ward (*6*).