Density of Solutions of Ammonium Nitrate and Tetramethylammonium Nitrate in Nitric Acid

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WITHIN the last decade, numerous studies have been reported on various physicochemical properties of solutions of oxides of nitrogen and alkali nitrate salts in nitric acid. However, the densities of alkali nitrate–nitric acid solutions have been studied only in a cursory fashion—that is, data have been obtained over limited ranges of conditions to provide values needed to develop correlations involving the other measured properties. The only recent studies which have treated densities of nitric acid systems in detail have been those of Mason, Petker, and Vango (*6*) and Antipenko, Beletskaya, and Korleva (*1*), which were concerned with the HNO_3-NO_2-H_2O system, and that of Potier and Potier (*7*) which dealt with the KNO_3-HNO_3-H_2O system.

Because the density has been generally treated as a secondary property, the precision and extent of the measurements have not been great enough to develop useful correlations with solute concentration. In this study, the densities of solutions of ammonium nitrate and tetramethylammonium nitrate in nitric acid have been measured for a wide range of composition and over two temperature ranges, from about 5° to 25° C. and from −43° to −25° C. The over-all experimental error, estimated to be about 0.0003 in the density, is sufficiently small so that one may calculate partial molar volumes of both components and examine their dependence on concentration and temperature.

The density of solutions of NH_4NO_3 and $(CH_3)_4NNO_3$ in nitric acid was measured by the hydrostatic method. The partial molar volume of both solutes went through a minimum near 1 molal concentration. This effect was attributed to the disruptive effect of NO_3^- on the solvent structure. A peak in the partial molar volume near 0.2 molal was attributed to the self-dissociation of nitric acid. For both solutes, the temperature coefficient of the density became less negative with increasing molality. For NH_4NO_3, the partial molar volume showed a negative temperature dependence. For $(CH_3)_4NNO_3$ no effect of temperature was found.

EXPERIMENTAL WORK

Apparatus. The density was measured by determining the loss in weight of a sinker of known volume on immersion. This method, which has been extensively used (*9*), gives high precision whenever fairly large samples of solution can be used under essentially open conditions. In this study, a borosilicate glass tube about 24 cm. long and 35 mm. in diameter was used to contain the test solution; the tube was fitted with a ground-glass joint and cap. About 100 cc. of solution were used for each determination. The sinker was made of 96% silica glass tubing with mercury sealed inside. It was suspended from one arm of an analytical balance by a platinum wire 0.003 inch in diameter, the wire extending down through a hole in the bottom of the balance. In making a determination, the sample was fitted with a cap having a hole 2.5 mm. in diameter through which the suspension wire passed. The sample tube was kept immersed in a bath to the level of the ground-glass joint, so that the sample itself was sufficiently far below the bath level that no temperature gradient existed through the sample. The temperature of the bath was controlled to ±0.02° C. and measured with a platinum resistance therometer. For the low-temperature determinations, an alcohol bath cooled by dry ice was used.

Each of the sinkers had a volume of about 13.7 cc. This was determined as a function of temperature from the loss in weight on immersion in freshly boiled and cooled distilled water. The uncertainty in the volume was about 0.0001 cc., corresponding to an uncertainty in the density of about 1×10^{-5} gram per cc.

Materials. Reagent grade ammonium nitrate was dried in an oven before use. A sample of tetramethylammonium nitrate was obtained from the Dow Chemical Co., Pittsburg, Calif., and was dried over P_2O_5 for at least 1 week before use.

The nitric acid used was prepared by the action of 100% sulfuric acid on potassium nitrate in a vacuum system, a method similar to that described by Stern and Kay (*10*). Stored under vacuum at dry ice temperature, the product was a snow-like mass which, on melting under vacuum, gave a colorless liquid.

The density of the pure nitric acid was determined as a function of temperature. The most careful of recent determinations (*2, 10*) indicate that the density should be given to within ±0.0003 gram per cc. by the equation

$$\rho = 1.5492 - \left\{\begin{matrix} 0.00182 \\ 0.00183 \end{matrix}\right\} t \qquad (1)$$

where t is temperature in ° C.

In the present study, four independent determinations were made under a variety of experimental conditions. Each determination consisted of six to eight data points obtained at different temperatures on a single sample of acid. Two different sinkers were used. Three of the determinations were made between 5° and 25° C., and the fourth was done between −5° and −32° C. Different samples were used which had been prepared from different lots of reagents.

The four results obtained for pure nitric acid are shown in the first part of Table I, which gives coefficients for the relation

$$\rho = \rho_0 - at \qquad (2)$$

where ρ_0 is the density of 0° C. The standard deviation of the data from each line was about 5×10^{-5} gram per cc. Values of both ρ_0 and $d\rho/dt$ are slightly lower than those given in Equation 1. However, the density at 25° C. agrees with that obtained from Equation 1 to within 5×10^{-4} gram per cc. It is also seen that there is no change in ρ_0 if the measurements are made below 0° C. but that $d\rho/dt$ is slightly higher at the lower temperatures. Detailed discussion of the discrepancy in the coefficients is complicated by the fact that a wide spectrum of density values has been reported over the last decade, corresponding to ρ_0 values both higher and lower than 1.5492. However, the fact that all ρ_0 values obtained in this study are consistent to within ±0.0002 indicates that any change of density with composition greater than about ±0.0002 should be caused by the solute and not by fluctuation in the density of the acid.

Table I. Summary of Experimental Results

Molality	ρ_0, G./Cc.	$-a$, G./(Cc.) (° C.)
Pure Nitric Acid		
0	1.5480	0.001798
0^a	1.5482^a	0.001829^a
0	1.5484	0.001805
0	1.5480	0.001799
Ammonium Nitrate–Nitric Acid		
0.02754	1.5491	0.001766
0.05778	1.5500	0.001782
0.2759	1.5511	0.001716
0.5145	1.5548	0.001642
0.8484	1.5625	0.001553
1.125	1.5699	0.001502
1.416	1.5751	0.001443
1.721	1.5795	0.001408
1.876	1.5825	0.001386
2.260	1.5874	0.001344
2.695	1.5922	0.001309
3.331	1.5969	0.001235
Tetramethylammonium Nitrate–Nitric Acid		
0.05875	1.5443	0.001797
0.1293	1.5392	0.001741
0.2207	1.5289	0.001707
0.4000	1.5144	0.001634
0.4138^a	1.5116^a	0.001690^a
0.5877	1.4998	0.001549
0.6458^a	1.4965^a	0.001587^a
0.6713^a	1.4942^a	0.001585^a
0.8453	1.4837	0.001481
1.039	1.4720	0.001426
1.330	1.4564	0.001364
1.635^a	1.4419^a	0.001349^a
0.761	1.4350	0.001251
2.072	1.4188	0.001201

[a] Determination below 0° C.

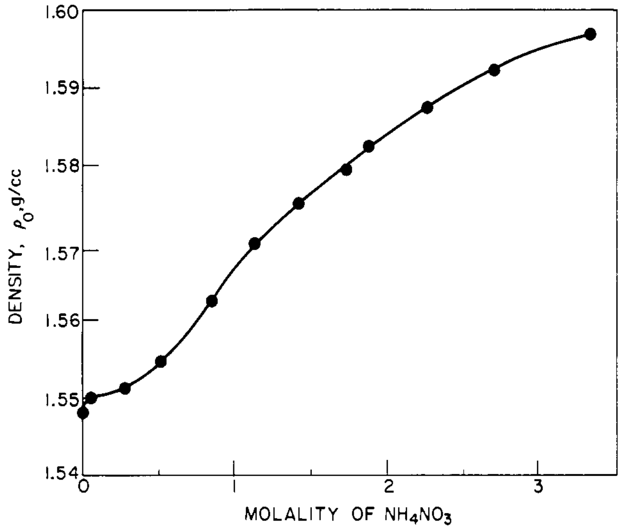

Figure 1. Density of ammonium nitrate–nitric acid solutions at 0° C.

Procedure. The mixtures were made up at room temperature by weight with the sample tube capped during weighings. After a mixture had been made, the sinker was lowered into the tube and the solid cap replaced by one with a small hole. The assembly was immersed in the bath and the suspension connected to the balance. The position of the tube was adjusted so that about ¾ inch of wire was beneath the surface; no correction was necessary for this immersion, since a similar length of wire had been immersed during calibration of the sinker. For equilibration at any temperature, 15 to 20 minutes were allowed; the adequacy of such an interval was shown by the absence of drift in the weights. Data points were taken at 2° to 3° intervals, and between points the bath temperature was changed at a rate of about 1° every 10 minutes.

Experimental Results. Density-temperature data were obtained for each solute up to concentrations of about 22% by weight. The data were fitted to straight lines of the form of Equation 2. The constants for Equation 2, determined by least squares, are given in Table I. Values of the standard deviation in ρ from Equation 2 were usually less than 5×10^{-5} gram per cc., giving the effect of errors in the measurement of weight and temperature.

Values of ρ_0 obtained are shown plotted in Figures 1 and 2 for each solute. (To avoid crowding, the point at $m = 0.02754$ described in Table I is not shown in Figure 1.) For tetramethylammonium nitrate solutions, the value of ρ_0 extrapolated from below 0° C. agrees with ρ_0 values extrapolated from cold water temperatures over the whole measured composition range to within a few units in the fourth decimal place. However, there is a slight increase in the magnitude of $d\rho/dt$ at low temperatures, an increase which is consistent with the expectation that the magnitude of the temperature coefficient of the specific volume should increase with temperature for a liquid. For ammonium nitrate solutions no low temperature measurements were made.

Because of the complicated shape of the density-molality curves, it was not practical to smooth the data by least-squares treatment. However, by drawing smooth curves through values of ρ_0 and a, for measurements in a single temperature range, one could estimate the over-all experimental error. The average deviation of ρ_0 from such curves was about 3×10^{-4} gram per cc.; the deviation in a was about 5×10^{-6} gram/(cc.) (° C.). Theoretical and experimental analysis of possible sources of experimental error showed that the value to be expected had the same magnitude as the observed deviation in ρ_0. Sources of error considered included fluctuations in the density of the pure acid, uncertainties in the composition, surface forces involving the suspension wire, and slow changes in density caused by thermal decomposition and water absorption.

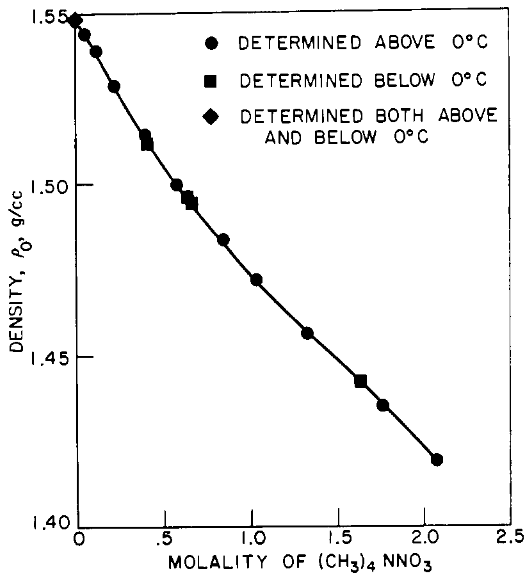

Figure 2. Density of tetramethylammonium nitrate–nitric acid solutions at 0° C.

TREATMENT OF DATA

The partial molar volume of the solute, $\bar{v}_2$, was obtained from density-composition data by the equation (5)

$$\bar{v}_2 = \frac{M_2}{\rho} - \frac{(1000 + mM_2)}{\rho^2}\frac{d\rho}{dm} \quad (3)$$

where M_2 is the molecular weight of the solute and m is the molality of the solution. Calculation of $\bar{v}_2$ was done by using experimental values of ρ and graphically estimated values of $d\rho/dm$, for the data obtained above 0° C. The results are plotted in Figures 3 and 4. The important features of the plots were not affected by the uncertainty in $d\rho/dm$, but arose from the general behavior of the density-molality data. For ammonium nitrate $\bar{v}_2$ is about one third as great as for tetramethylammonium nitrate; this represents the fact that tetramethylammonium nitrate combines the properties of relatively high molecular weight and extremely low density. For both solutes, $\bar{v}_2$ shows a broad minimum near 1 molal concentration and a sharp peak near 0.2 molal.

For neither solute are the extent and precision of the data sufficiently great to justify quantitative discussion of the behavior of $\bar{v}_2$ with change in composition. In particular, the value of $d\rho/dm$ for ammonium nitrate at $m = 0$ is no better than a crude estimate. Nevertheless, the details in the density-molality curves leading to the general features of the $\bar{v}_2$ – molality curves involve changes much greater than the estimate of experimental error.

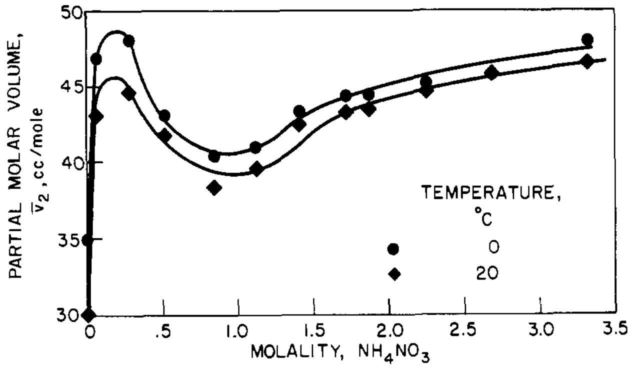

Figure 3. Partial molar volume of ammonium nitrate in nitric acid

The partial molar volume of the solvent $\bar{v}_2$ was obtained by the corresponding relation

$$\bar{v}_1 = \frac{M_1}{\rho} + \frac{M_1}{\rho^2}\left(m + \frac{m^2M_2}{1000}\right)\frac{d\rho}{dm} \qquad (4)$$

where M_1 is the solvent molecular weight. The values obtained, about 41 cc. per mole for each solute, do not vary much with composition. This behavior is in accord with the fact that $\bar{v}_1$ and $\bar{v}_2$ are related, at constant temperature, by the expression

$$\frac{d\bar{v}_1}{dm} = -\frac{mM_1}{1000}\frac{d\bar{v}_2}{dm} \qquad (5)$$

Near a molality of 1, $mM_1/1000$ is about 0.05; thus the magnitude of $d\bar{v}_2/dm$ is much greater than $d\bar{v}_1/dm$.

With regard to the effects of temperature, $\bar{v}_2$ for ammonium nitrate shows a negative temperature coefficient of about 0.05 cc./(mole) (° C.), whereas for tetramethylammonium nitrate, no temperature effect is found. For $\bar{v}_1$, however, positive temperature coefficients of about 0.05 cc./(mole) (° C.) are found for both solutes. This behavior is reasonable, because $d\bar{v}_1/dt$ and $d\bar{v}_2/dt$ are relatively independent of each other. Thus, from the equations defining the partial molar volume, one has the relation

$$n_1\frac{d\bar{v}_1}{dt} + n_2\frac{d\bar{v}_2}{dt} = \frac{dV}{dt} \qquad (6)$$

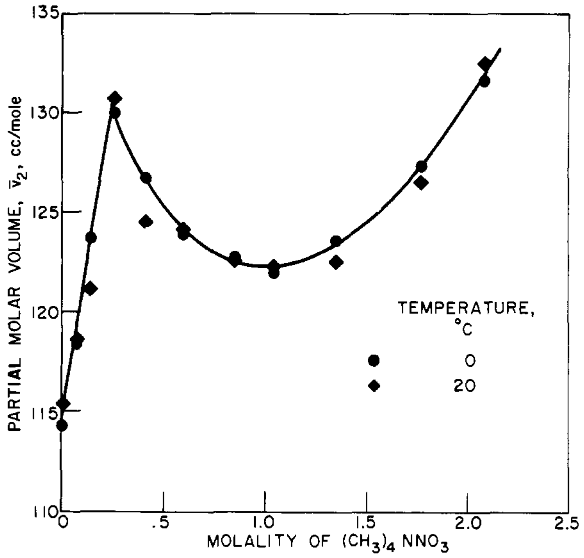

Figure 4. Partial molar volume of tetramethylammonium nitrate in nitric acid

where the n's are mole numbers and V is the total volume. Equation 6 applies if the temperature is not constant. On expressing V in terms of molecular weights, mole numbers and density and replacing mole numbers by functions of molality, one obtains

$$\frac{d\bar{v}_1}{dt} = -\left[0.0630\ m\frac{d\bar{v}_2}{dt} + \left(\frac{63.02 + 5.43m}{\rho^2}\right)\frac{d\rho}{dt}\right] \qquad (7)$$

In Equation 7, for molalities near 1, $d\bar{v}_1/dt$ must equal about 0.05 for any values of $d\bar{v}_2/dt$ smaller than about 0.1, since it depends almost entirely on ρ and $d\rho/dt$. Values of $d\bar{v}_1/dt$ calculated by Equation 4 and, more directly, by Equation 7 agree within 10%.

DISCUSSION OF RESULTS

The peak in $\bar{v}_2$ near 0.2 molal probably represents the effect of self-dissociation of nitric acid in the presence of very low concentrations of NO_3^- ions. It seems reasonable to suppose that the equilibrium mixture of nitric acid with its dissociation products should have a lower density than undissociated HNO_3 if dissociation takes place in the generally accepted fashion (*8*)

$$2HNO_3 \rightleftarrows H_2O + NO_2^+ + NO_3^-$$

From consideration of the behavior of the density-molality curves as the molality approaches zero, one can estimate that, if the density of "equilibrium" nitric acid at 0° C. is 1.5482 grams per cc., the density of the species HNO_3 is about 1.5503. This value is arrived at by, in the case of ammonium nitrate, extrapolating the curve to zero molality ignoring the downward break near 0.05 molal. For tetramethylammonium nitrate, the extrapolation is done ignoring the decrease in slope which occurs from about 0.15 molal. In both cases, the extrapolated value for zero molality is the same within ±0.0001 gram per cc.

The minima in $\bar{v}_2$ observed near 1 molal are most simply explained by the interaction of NO_3^- ions (produced by the nearly complete dissociation of the salts) with the solvent, which is associated through hydrogen bonds. Since the NO_3^- ion tends to form strong complexes with two molecules of HNO_3 (*3*), one can explain the minima in $\bar{v}_2$ on the assumption that solute addition tends to break up the structure of the solvent through reactions such as

$$(HNO_3)_{a+b} + (a/2)\, NO_3^- \rightarrow (a/2)\, NO_3^- \cdot (HNO_3)_2 + b\, HNO_3 \qquad (8)$$

leading to a net decrease in volume. One might expect a further weakening of the solvent structure if the addition of solute lowers the dielectric constant of the solution. At low solute concentration, reactions such as Equation 8 will facilitate the formation of ion-solvent complexes on further addition of solute and lead to a decrease in $\bar{v}_2$ with concentration. At high concentrations, there will be the more usual increase in $\bar{v}_2$ with molality as the concentration of solvent molecules available for ion-solvent association decreases, and repulsion between ions becomes more important. Results similar to the minima near 1 molal had been previously reported by Klemenc and Rupp (*4*) for the HNO_3-NO_2 system and, more recently, by Potier and Potier (*7*) for HNO_3-KNO_3 solutions.

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Porous Structure of Catalyst Materials

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THE POROUS STRUCTURE of catalyst materials and of catalyst supports has received continuous attention for some years. In the proceedings of a recent conference on porous materials (*8*), interest in catalyst materials as porous bodies was made evident. In another review (*14*), the relevance of the porous structure of the catalyst not only to catalyst activity but also to catalyst selectivity was developed extensively.

To study porous structure in greater detail, various schemes have been developed whereby the adsorption and/or desorption isotherms can be translated into "pore size distributions." In the one case (*4, 6*), sorption data are interpreted as describing the lengths associated with straight-sided cylindrical pores of a given size. In this way, the data can also be related to the area (or the volume) associated with pores of radius up to and including a certain size. In the other case (*7, 11, 13*), the sorption data are related to a physical model which represents a pore as a slit between two flat parallel plates.

The physical model is, no doubt, strictly correct in neither case. In fact, an exhaustive study of any particular porous body would almost certainly require both adsorption and desorption measurements, mercury porosimeter measurements (*12*), etc. For example, as shown by deBoer and Everett (*8*), the "shape" of the whole isotherm, including the hysteresis loop, can tell a good deal about what kind of geometry can be attributed to the pore structure—viz., "blind" pores, tapered pores, "bottle"-shaped pores, and others. Indeed, in using diffusion measurements to study porous structure, useful information may be obtained (*3*) by distinguishing between steady-state and transient measurements.

On the other hand, comparison (especially within a series of chemically similar materials) of pore size distributions as calculated by some consistent scheme will in many cases lead to fruitful distinctions between catalyst materials. Such might arise, for example, in studies on catalyst development, where it is desirable to distinguish among a series of catalyst preparations in order to follow the effect of variations in preparation technique. Alternatively, such considerations might be useful in assisting catalyst users (such as refiners) in selecting the most suitable catalyst grade from a line of available catalysts.

In this report, we describe, in summary form, an examination of the pore size distributions of a series of catalyst materials either actually or potentially usable in oil refining processes. In all cases shown, the distributions can be approximated by a single relatively simple model; moreover, the distributions can be reproduced by simple measurements which are normally made on most catalyst samples—namely, the total pore volume and the B.E.T. surface area.

EXPERIMENTAL

Samples. Preparations studied were mainly samples of commercial or commercial-type cracking, reforming, or hydrodesulfurization catalysts. Some of the samples were pilot plant preparations; one group (4 to 8) was provided by Koninklijke Zwavelzuurfabrieken v/h Ketjen n.v. of

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