

Melting Point Measurements for the Tetramethylammonium Nitrate–Nitric Acid System

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SOLID-LIQUID equilibria between nitrate salts and anhydrous nitric acid have been studied recently for the solutes potassium nitrate and ammonium nitrate (7, 8). This report presents melting point data for a chemically similar salt, tetramethylammonium nitrate. Measurements have been made over a temperature range from -74° to $+52^{\circ}$ C. covering a range of salt concentrations up to about 50% by weight.

EXPERIMENTAL

Materials. Anhydrous nitric acid was prepared and stored as previously described (5). Tetramethylammonium nitrate (Dow Chemical Co., Pittsburg, Calif.) was stored over P_2O_5 . The purity of the sample was determined by precipitation of the tetramethylammonium ion with Reinecke's salt (1). The proportion of tetramethyl was 98% of theoretical. The major impurity was found to be 1.8% of ammonium nitrate.

Apparatus and Procedure. Data points on the equilibrium curve were obtained by visual determination of the melting point, the temperature at which the last trace of solid dissolved on heating a sample. For all determinations below room temperature an alcohol bath externally cooled by dry ice, was used. To obtain temperatures below about -60° C., additional carbon dioxide snow was dropped directly into the bath. For determinations above room temperature a water bath was used. Sample sizes were about 10 to 20 cc. The samples were made up by weight in a capped glass tube about 10 inches in length and $\frac{3}{4}$ inch in diameter. The tube was mounted externally so that it extended down into the bath liquid to a depth of about 6 inches; the mounting was connected to an arm which rocked the tube and its contents through an arc of about $\pm 10^{\circ}$ at 120 c.p.m. The bath temperature was determined by a platinum resistance thermometer, and the experiments were performed so that, within stated limits, the sample temperature could be assumed equal to the bath temperature.

Equilibrium mixtures of solid and liquid were prepared and heated at a rate of 0.01° to 0.02° C. per minute. The melting point was defined as the lowest temperature for which no solid was observed.

For salt concentrations sufficiently high that the solid phase was not pure nitric acid, the melting point determinations were relatively simple and precise, since at these compositions the density of the solid was only slightly greater than that of the liquid. Thus, an even dispersion of solid throughout the liquid was provided by the rocking motion supplemented, occasionally, by manual shaking. The reproducibility of the melting points for a single sample was usually better than 0.05° C. and the scatter among different samples of very similar concentration was about 0.1° C. Where the solid was pure nitric acid, more frequent shaking was necessary because of the large density difference between the two phases. However, except for the lowest salt concentration, two-phase equilibrium seems to have been maintained up to the melting point. For the lowest salt concentration, 1.7%, equilibrium was probably not maintained. Apparently, the lowest rate at which the small

proportion of liquid could be heated exceeded the rate at which the relatively large mass of solid could melt. Thus, solid would persist when the liquid was at a temperature higher than the thermodynamic melting point. By comparing the melting point at 1.7% salt with the known melting point of the pure acid and also with previously reported melting points for NH_4NO_3 - HNO_3 system at low concentration (2, 8), the melting point at present reported for 1.7% salt is estimated high by about 0.2° C.

RESULTS AND DISCUSSION

Description of Results. The experimental data are summarized in Table I, and the melting point diagram is shown in Figure 1. Several broad features of the curve were noted. First, the data for low salt concentration extrapolate smoothly to the generally accepted freezing point of nitric acid, -41.6° C., indicating that the acid used was reasonably pure. Second, the eutectic involving the pure solid HNO_3 occurs at a temperature lower than the lowest temperature obtained with alcohol and dry ice, about -74° C. By simple extrapolation, the eutectic is estimated to occur near 79° C. and 23% salt by weight. The eutectic was not defined more precisely because accurate data could not be obtained below -65° C. by the procedure used. Because it was necessary to add large quantities of dry ice directly into the bath a slow, controlled heating rate could not be maintained. Furthermore, the visibility of the sample became poor. Third, flat maxima are found near 27 and 42% salt, at temperatures near -60° and -23° C. Beyond the second maximum the curve rises very steeply, indicating that, at ordinary temperatures, the solubility of the salt is not very dependent on temperature. Fourth, there appears to be a slight break

Table I. Melting Points for Tetramethylammonium Nitrate–Nitric Acid System

M.P. t , $^{\circ}$ C.	Solute, Wt. %	M.P. t , $^{\circ}$ C.	Solute, Wt. %
-41.7	1.72	-42.5	32.8
-42.7	2.45	-33.7	35.3
-42.5	3.81	-27.3	37.7
-42.8	5.00	-26.0	38.5
-44.1	6.72	-23.9	40.4
-46.7	9.45	-23.3	41.3
-49.7	12.1	-23.5	41.5
-53.9	14.3	-23.6	42.3
-57.1	15.8	-23.8	43.5
-60.3	17.2	-22.9	44.3
-63.5	25.2	-19.1	45.1
-59.9	26.5	-5.5	45.8
-59.9	27.4	+8.0	46.4
-59.6	28.5	15.8	46.9
-59.3	29.1	23.2	47.5
-57.9	29.8	38.1	48.6
-57.7	29.9	46.5	49.7
-55.1	30.6	51.6	49.7
-54.0	31.0		
-45.5	32.5		

in the solubility curve between 25° and 30° C., at about 48% salt. This break, if real, indicates an incongruent melting transition.

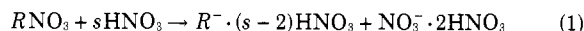
The compositions at the two maxima correspond closely to acid-salt mole ratios of 6:1 and 3:1. Such 6:1 and 3:1 complexes represent a much higher degree of solvation than the 2:1 complexes reported for N_2O_4 , KNO_3 , and NH_4NO_3 with nitric acid (4, 7, 8). The maximum near the 6:1 composition is not particularly well defined. However, no interpretation other than the existence of a 6:1 solid compound seems reasonable. For salt concentrations higher than about 45%, the composition of the equilibrium solid could be found only by direct analysis. Samples of solid were obtained by crystallization from solutions of 48 to 50% salt prepared at hot water temperature. The crystals were obtained by filtration in a dry box and dried in a stream of nitrogen. Samples were then analyzed, independently, for both tetramethylammonium nitrate and nitric acid. Results for six samples prepared independently but under nearly identical conditions were variable, acid-salt mole ratios ranging from slightly over 2:1 to slightly less than 1:1. Attempts were made to determine the melting point of the crystals. However, in all attempts neither melting nor decomposition had occurred by 250° C. The fact that the solid in equilibrium with solution was a complex and not a pure salt was shown by the fact that the solid was always heavier than the liquid, whereas the pure salt, whose partial molar volume in nitric acid (5) indicates a density near 1.0, is much lighter than any of its solutions in nitric acid (density ~ 1.5). Thus, material which precipitated out of a concentrated solution on cooling sank to the bottom, whereas salt added to such a solution floated. However, because the composition of the solid could not be determined reproducibly, the nature of

the transition could not be defined. The two most reasonable possibilities are a chemical transformation of the solid phase from a 2:1 to a 1:1 complex or a physical transformation of a 2:1 or 1:1 complex without chemical change.

Sharp eutectics are not found for the solid transformations near 28 and 43% salt; instead, shallow rounded minima occur. This effect is probably caused by the presence of the ammonium nitrate impurity, particularly, since in the course of all melting determinations near the minima, liquid was present for a few degrees below the final melting point.

Analysis of Data at Low Salt Concentration. Figure 2 shows present results in the region where the solid is pure nitric acid plotted together with the data of Potier and Potier (8) and Dunning and Nutt (2) for NH_4NO_3 (data for KNO_3 virtually coincide with those for NH_4NO_3). Results for all solutes approach the composition of pure solvent with the same slope and, in fact, coincide out to a mole fraction of about 0.025. At higher concentrations, the tetramethylammonium nitrate gives a progressively larger depression of the freezing point. Finally near the eutectic the effect is about three times as large. This large difference in behavior between ammonium and tetramethylammonium nitrate contrasts with the fact that the behavior of the partial molar volumes of both salts with change of concentration is strikingly similar (5).

Following a procedure often used, one may examine the difference on the basis that all deviations from ideality are caused by ion solvation. Thus, the process of dissolution and dissociation of any nitrate salt RNO_3 in nitric acid can be described by the equation



in which it is assumed that the solvation number of NO_3^- is 2 (6). One can then apply Gillespie, Hughes, and Ingold's equation (6) for nitric acid solutions

$$\frac{d\theta}{dm} = 2.682 \left[1 - 0.0045\theta + \frac{(2s-v)m}{15.87} \right] \quad (2)$$

where θ is the freezing point depression, m the molality and v

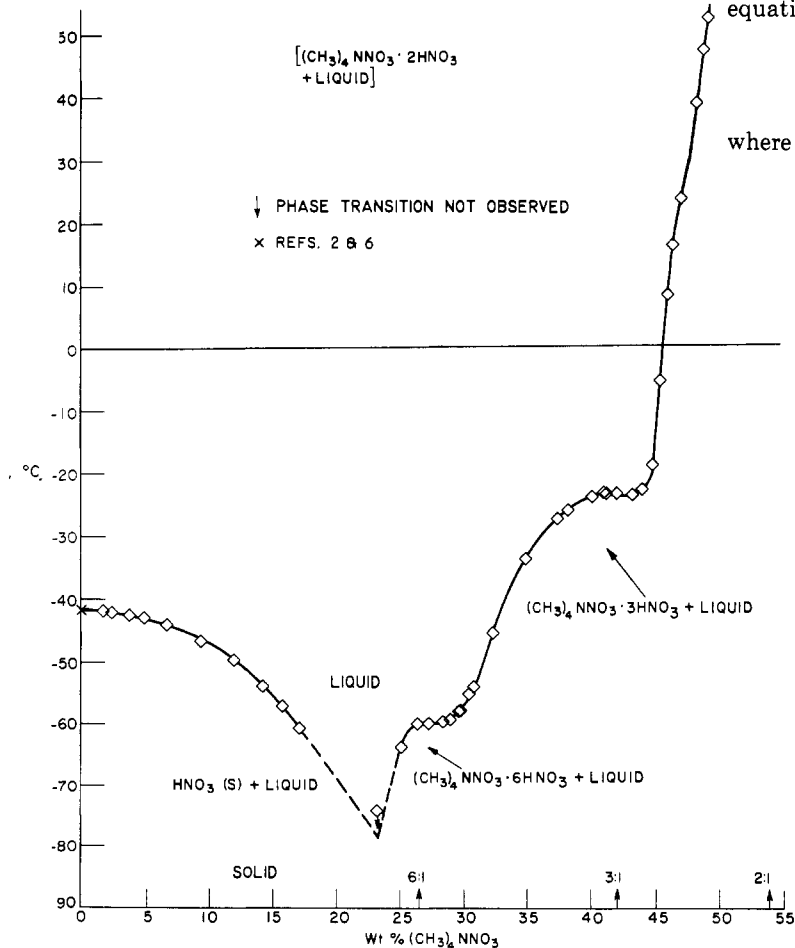


Figure 1. Melting points of the tetramethylammonium nitrate-nitric acid system

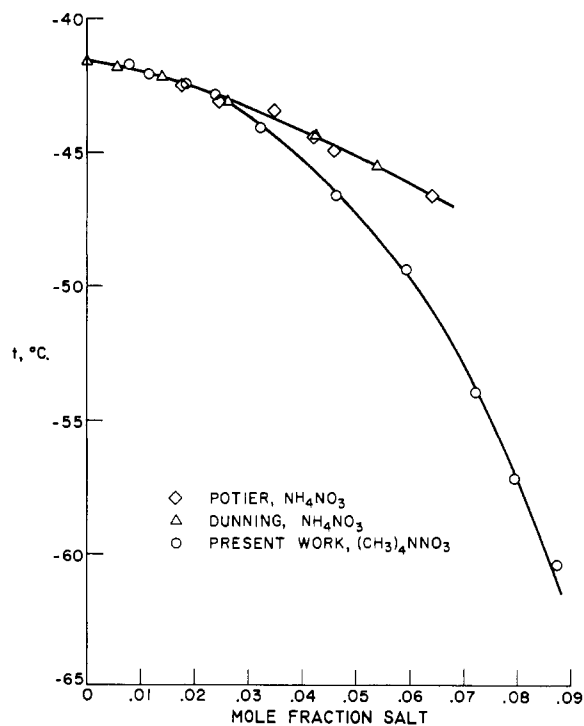


Figure 2. Effect of NH_4NO_3 and $(CH_3)_4NNO_3$ on freezing point of HNO_3

the total number of molecules on the right side of Equation 1. For a mole fraction of 0.05, the measured value of $d\theta/dm$ for NH_4NO_3 is most closely reproduced by $s = 2$, which indicates no interaction of cation and solvent. For tetramethylammonium nitrate, in the range from about 0.04 to 0.07 mole fraction, Equation 2 is satisfied by s values from 12 to 15, which would indicate a cation solvation number of 10 to 13. The salt concentrations considered were sufficiently high that the value of $d\theta/dm$ was not significantly affected by self-dissociation. Such a degree of solvation is unexpectedly high since the relatively large tetramethylammonium ion should have a small surface charge density. The presence of impurities could account in part for the result, giving values of $d\theta/dm$ which are too large, but it seems unlikely that impurities could account for more than a small part of the difference in behavior between ammonium and tetramethylammonium nitrate. One would conclude, therefore, that the tetramethyl ion is solvated in nitric acid solution, whereas the ammonium ion is not. This conclusion is consistent with the observation that tetramethylammonium nitrate forms solid compounds with nitric acid of higher complexity than ammonium nitrate. The possibility remains, of course, that some contribution to the observed value of s arises from sources of nonideality other than simple solvation.

Another comparison can be made: comparison of the relative behavior of ammonium and tetramethylammonium nitrates as solutes in nitric acid and water as solvents. This is most conveniently done in terms of the osmotic coefficient. The freezing point depression can be expressed in terms of the molal osmotic coefficient of the solvent by the equation:

$$\frac{Rv_m M_1 \varphi}{1000} = \frac{1}{T_m^2} \left[\Delta H_1^0 \theta + \left(\frac{\Delta C_p^0}{T_m} - \frac{\Delta C_p}{2} \right) \theta^2 + \left(\frac{\Delta H_1^0}{T_m^2} - \frac{2\Delta C_p}{3T_m} \right) \theta^3 \right] \quad (3)$$

This equation is similar to that developed by Robinson and Stokes (9), but includes a term in θ^3 . Here φ is the molal osmotic coefficient, M_1 the molecular weight of solvent, ΔH_1^0 the heat of fusion of nitric acid at its melting point (2503 cal./mole), ΔC_p the difference in heat capacity of liquid and solid nitric acid (10.88 cal./mole ° K.), and T_m the melting point of pure nitric acid. Values for ΔH_1^0 and ΔC_p were taken from Elverum and Mason (4). The correction for the variation of φ with temperature was estimated to be negligible for the range of melting points considered, $\pm 9^\circ \text{C}$. The reference state for which $\varphi = 1$ was chosen as the hypothetical undissociated species HNO_3 . The heat of fusion and heat capacity difference were assumed to be the same as for the "equilibrium" acid. With this choice of reference state it was necessary to correct the observed freezing point depressions for the effects of self-dissociation. This was done by use of the equilibrium constant for self-dissociation derived by Gillespie, Hughes, and Ingold (6).

$$m_{\text{NO}_3^-} m_{\text{NO}_2^-} m_{\text{H}_2\text{O}} = 0.020 \quad (4)$$

and the approximate thermodynamic relation

$$\Delta\theta = \frac{RT_m^2}{\Delta H_1^0} \left(\frac{m^*}{m^* + 15.87} \right) \quad (5)$$

where $\Delta\theta$ is the contribution of products of self-dissociation to the freezing point depression, and m^* is the total molality of dissociation products. The quantity θ^* , the freezing point depression that would be observed in the absence of self-dissociation, is given by

$$\theta^* = (T_m^* - T_m) + (\Delta\theta - \theta) \quad (6)$$

where T_m^* is the estimated melting point of the hypothetical

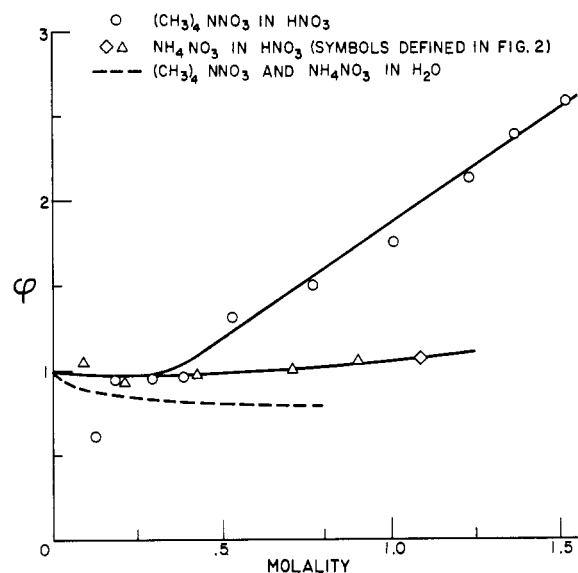


Figure 3. Comparison of molal osmotic coefficients for $(\text{CH}_3)_4\text{NNO}_3$ and NH_4NO_3 in HNO_3 and H_2O

undissociated acid (6). Values of θ^* can then be used in place of θ in Equation 3.

Results are shown plotted in Figure 3. Data for NH_4NO_3 in water were obtained from Robinson and Stokes, appendix (9) and for $(\text{CH}_3)_4\text{NNO}_3$ in water were taken from Ebert and Lange (3). The two curves virtually coincide and are shown as one. The actual values for $(\text{CH}_3)_4\text{NNO}_3$ are slightly lower. The physical correspondence between the two sets of systems is not exact. Nevertheless, a few points of comparison may be made. For both salts, the osmotic coefficients of water are less than those of nitric acid. Also, both salts give the same osmotic coefficient for water but very different osmotic coefficients for nitric acid.

The shape of the φ -molality curves for the systems with nitric acid is such that one can evaluate, at least roughly, values of γ_2 , the mean molal activity coefficient of the solute. This is done by the usual Gibbs-Duhem integration (9)

$$\ln \gamma_2 = (\varphi - 1) + \int_{m=0}^m (\varphi - 1) d \ln m \quad (7)$$

Since for any values of m less than about 0.5 the value of $\varphi - 1$ fluctuates randomly about zero, approximate values of the integral can be determined graphically. It is found that, for example, near a molality of 1.1, γ_2 for ammonium nitrate is just slightly greater than 1 whereas for tetramethylammonium nitrate the value is about 6. For both salts in water, γ_2 is less than 1. The high value of γ_2 for tetramethylammonium nitrate in nitric acid should have the same significance as the high values found for the solvation number s in Equation 2.

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