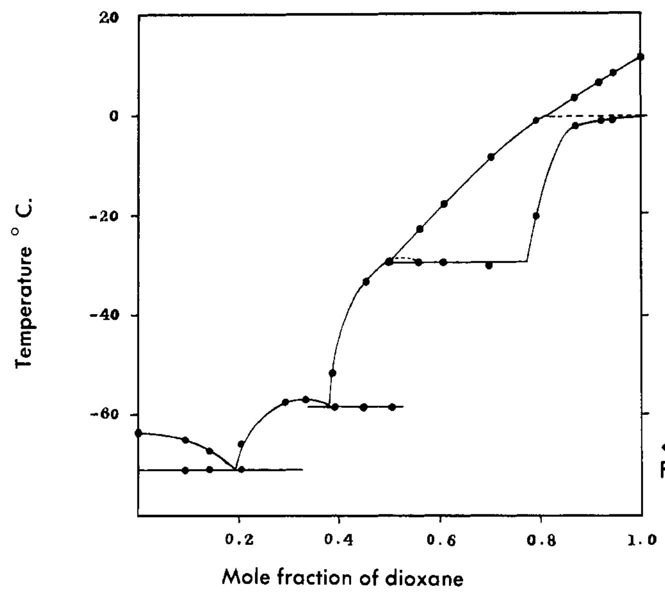

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Figure 2. Phase diagram of dioxane (A)-chloroform (B)

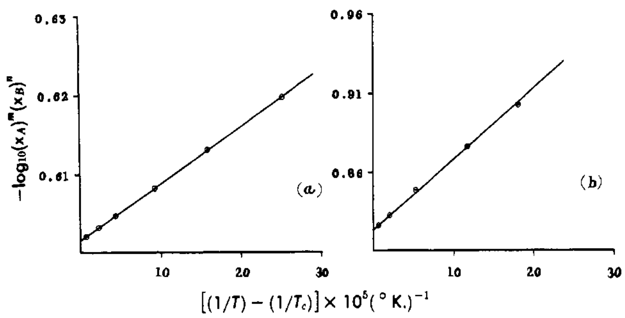

Figure 3. Estimation of heats of fusion
a. AB complex
b. AB_2 complex

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Density of Nitric Acid–Water Mixtures at Very Low Concentrations of Added Water

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THE DENSITY of nitric acid–water mixtures has been studied extensively and the results have been summarized in various places—for instance, in the International Critical Tables (*3*). However, detailed measurements have not been made at very low water concentrations in the region below 1% by weight.

Recently, the densities of solutions of ammonium nitrate and tetramethylammonium nitrate in nitric acid were measured (*2*). For both solutes, the density-composition curves at constant temperature showed features near 0.2 molal which were attributed to the onset of self-dissociation of the nitric acid in the generally accepted fashion (*3*):

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \qquad (1)$$

It was of some interest, then, to determine whether the addition of water to nitric acid gave similar effects.

EXPERIMENTAL

The nitric acid used was prepared as described previously (*1*). The water used was freshly boiled and cooled laboratory distilled water.

Density was determined from the loss in weight of a Vycor sinker suspended from one arm of a balance by a platinum wire 0.003 inch in diameter. Sinkers were used which had volumes of about 5 and 14 cc. The sample cell, containing about 50 to 100 ml. of liquid, was immersed in a water bath whose temperature was constant to ±0.01° C. The cell was fitted with a ground-glass cap having a hole about 2.5 mm. in diameter in its top, through which the suspension wire passed.

In the course of a run, the density of the pure acid was measured; then water was added through the hole in the cap in small increments. After each increment, the cell was shaken manually with the sinker suspended in place, and the change in weight was recorded.

RESULTS AND DISCUSSION

Figure 1 shows results for the addition of water to nitric acid at 16.61° ± 0.01° C., data being taken at intervals of a few tenths weight percent up to about 3% water. Figure 2 shows results in much greater detail obtained at 17.83° and 32.29° ± 0.01° C., and up to a maximum water concentration of about 0.5% by weight. The data are plotted as specific volume, in milliliters per gram against weight fraction. The results for the density of pure nitric acid at the three temperatures, combined with results from four additional independent determinations, fit the equation (5)

$$\rho = 1.54918 - 0.001809\,t \qquad (2)$$

where ρ is density in grams per milliliter and t is temperature in degrees centigrade, with a standard deviation in the density of 2.8×10^{-4} gram per ml. This result agrees very well with the data of Stern and Kay (5).

The equilibrium mixture of nitric acid with its dissociation products can be expected to have a higher specific volume than undissociated HNO_3, since the course of self-dissociation given by Equation 1 leads to an increase in the number of molecules per unit mass. As the limit of zero-added water is approached, the slope of the specific volume–composition should smoothly decrease (since the solute is less dense than the solvent)—that is, the curves should tend to flatten as all products of self-dissociation begin to appear.

No flattening is found in Figure 1. Some effect is found in the more detailed curves of Figure 2. However, the flattening becomes noticeable at concentrations of an order of magnitude less than the equilibrium concentration of water, as estimated from other measured properties (*2, 4*), and involves changes in density near the limit of precision of the data. One must conclude, therefore, that the effect of self-dissociation on the density, even if real, is much smaller than was previously found with ammonium and tetramethylammonium nitrate.

Because both components are liquids in the pure state, one may examine the data in terms of the excess specific volume defined as

$$\Delta v = v - \sum v_i w_i \qquad (3)$$

where v is the specific volume at a given concentration, and v_i and w_i are specific volumes and weight fractions of each component. In Figures 1 and 2 Δv values are thus given by the vertical difference between data points and solid lines. Where flattening occurs, the excess volume is zero or very slightly negative. However, with increasing concentration it becomes increasingly positive, levels off at a weight fraction of about 0.006, and, as shown by Figure 1, decreases and goes negative near 0.015. The maximum value of Δv lies in the range 7 to 8 × 10^{-4} ml. per gram. The positive values of the excess volume suggest that, at low concentration, water behaves as a simple nonelectrolyte, showing neither association nor attractive interaction with the solvent. Such behavior could conceivably mask the flattening of the specific volume–composition curve which would be expected on account of self-dissociation.

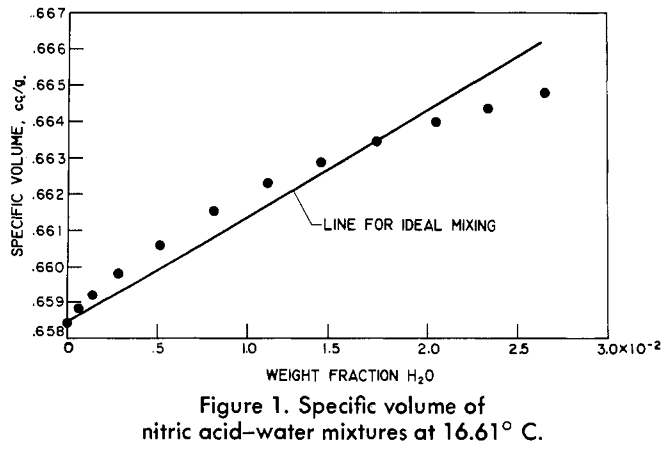

Figure 1. Specific volume of nitric acid–water mixtures at 16.61° C.

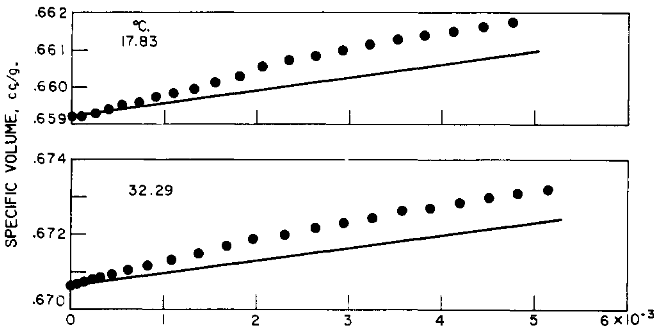

Figure 2. Specific volume of nitric acid–water mixtures

For comparison, the behavior can be examined from another viewpoint by considering $\bar{V}$, the partial molar volume of water in nitric acid. This is related to the excess volume, ΔV, in a general way, by the relation

$$\int_0^n \bar{V}\,dn = nV^\circ + \Delta V \qquad (4)$$

where n is the number of moles of water added to a given quantity of nitric acid and V° is the molar volume of pure water. The partial molar volume can be computed from specific volume–composition data by standard methods. In the concentration region where the excess specific volume is increasing, the partial molar volume assumes values of 25 to 30 ml. per mole. These values are significantly larger than the molar volume of pure water and suggest, once again, that here water acts like a simple nonelectrolyte. As the excess volume rises to its maximum value, $\bar{V}$ decreases to about 18 ml. per mole, indicating that, as the water concentration increases, association among water molecules becomes more important. On further increase in water concentration, $\bar{V}$ continues to decrease, but relatively slowly.

The partial molar volume of water in nitric acid can be compared with that previously reported for ammonium nitrate. For that solute, a maximum in $\bar{V}$ of about 48 ml. per mole was found near a weight fraction of 0.01 and a minimum of 40 ml. per mole, near 0.08. The molar volume of supercooled liquid NH_4NO_3 is not known. However, if the density of the liquid equals or is less than the density of the solid, 1.72, the molar volume should equal or exceed the maximum partial molar volume. This contrasts with the behavior found for water and is consistent with the fact that NO_3^- ions, produced in the dissociation of NH_4NO_3, are strongly solvated.

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