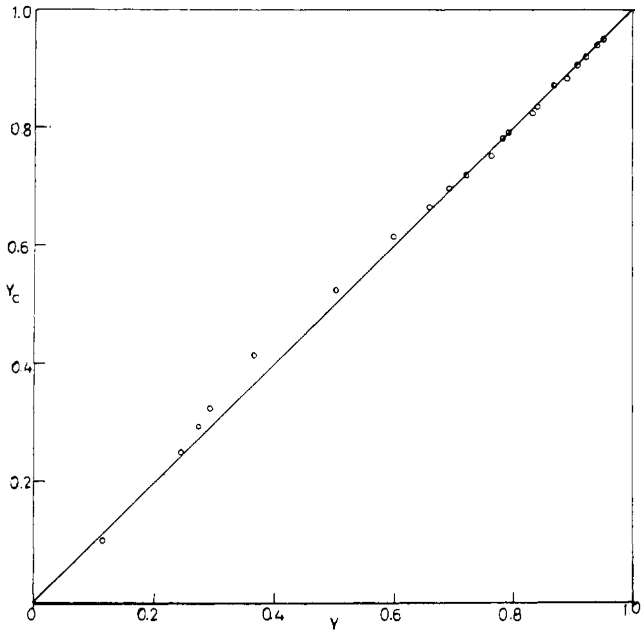

Figure 6. Experimental and calculated vapor compositions for the 2-butanol–*m*-xylene system.

both systems exhibit positive deviations from Raoult's law.

Glossary

B_{11}, B_{22}	gas-phase second virial coefficient for components 1 and 2, respectively
P	total pressure, mmHg
P_1°	vapor pressure of component 1, mmHg
R	universal gas constant, 82.054 cm^3 atm K^{-1} mol^{-1}
T	absolute temperature, K
V_1^L	liquid molar volume of component 1, cm^3/mol
x_1, x_2	mole fraction of components 1 and 2, respectively, in liquid phase
y_1	mole fraction of component 1 in vapor phase
γ_1,	activity coefficient of component 1
δ_{12}	$B_{12} - B_{11} - B_{22}$ where B_{12} is the second virial cross coefficient
λ_{12}, λ_{21}	constants in Wilson's equation
1	low boiling component
2	high boiling component

Literature Cited

(1) API Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds", Texas A&M University, College Station, Texas.
(2) Brown, I., Ewald, A. H., *Aust. J. Sci. Res., Ser. A*, **3**, 306 (1950).
(3) Brown, I., *Aust. J. Sci. Res., Ser. A*, **5**, 530 (1952).
(4) O'Connell, J. P., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Develop.*, **6**, 245 (1967).
(5) Deshpande, D. D., Pandya, M. V., *Trans. Faraday Soc.*, **63**, 2149 (1967).
(6) Dreisbach, R. R., *Adv. Chem. Ser.*, **No. 15** (1955).
(7) Herington, E. F. G., *J. Inst. Pet., London*, **37**, 457 (1951).
(8) Pitzer, K. S., Curl, R. F., Jr., *J. Am. Chem. Soc.*, **79**, 2369 (1957).
(9) Riddick, J. A., Bunger, W. S., *Tech. Chem. (N.Y.)*, **2** (1970).
(10) Timmermans, J., "Physico Chemical Constants of Pure Organic Compounds", Vol. 2, Elsevier, New York, 1965.
(11) Van Ness, H. C., "Classical Thermodynamics of Nonelectrolyte Solutions", Pergamon Press, Oxford, England, 1964, p 122.
(12) Vogel, A. I., "A Text Book of Practical Organic Chemistry", 3rd ed, E. L. B. S. and Longmans, Green, New York, 1968.
(13) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).

Received for review March 21, 1979. Accepted November 30, 1979.

The Heat of Solution of Ammonium Nitrate in Nitric Acid

Robert T. Rewick* and **B. J. Gikis**

Physical Chemistry Group and Chemical Engineering Laboratory, SRI International, Menlo Park, California 94025

The heat of solution of ammonium nitrate in nitric acid has been measured as a function of solute concentration and the degree of dilution of the acid with water. The results show a strong solute/solvent interaction, with a heat release that increases with the concentration of the salt. In anhydrous nitric acid, the strength of the hydrogen bonds between the nitrate ion and molecular nitric acid approaches 7.8 kcal/mol. In the presence of water, the concentration of molecular nitric acid is lowered and the reaction is less exothermic; in a sufficiently dilute solution, the reaction is endothermic. In NMR studies, the magnitude of the observed proton resonance shifts provides additional evidence for the supposition that strong hydrogen bonds surround the solvated nitrate ion and supports the conclusion that the ammonium ion is not directly involved in the bonding of the interaction complex.

Introduction

Ammonium nitrate, which is extensively used in explosives and fertilizers, is often subject to severe caking problems during storage because of the hydroscopic nature of the salt. For this reason, ammonium nitrate is often handled in solution form because it is readily soluble in a variety of aqueous and nonaqueous solvents. For example, ammonium nitrate is reported to be appreciably soluble in aqueous and concentrated nitric acid (*15*, *17*); solutions of 50 wt % ammonium nitrate in anhydrous nitric acid are commonly used in the manufacture of explosives.

Interesting solvent effects involving ammonium nitrate have been reported (*2*, *7*). For example, dissolution of ammonium nitrate in water (*21*) and in concentrated phosphoric acid (*22*) is accompanied by the absorption of heat; in anhydrous liquid ammonia the process is exothermic (*12*), suggesting that addition complexes are formed.

During our studies on the physical properties of ammonium nitrate/nitric acid solutions, we realized the importance of evaluating the heat effect for the dissolution of ammonium nitrate in nitric acid. Previous results have shown that the dissolution of potassium nitrate in nitric acid is accompanied by the evolution of heat (*10*), but these measurements were conducted at ice temperature over a narrow concentration range. Extrapolation of these data to higher temperatures and concentrations was difficult because reliable heat capacity data are lacking. For ammonium nitrate/nitric acid, we speculated that the dissolution process would also be exothermic, presumably because of the formation of an interaction complex involving hydrogen bonding between the nitrate ion and molecular nitric acid, $(HNO_3)_2\ NO_3^-$ (*1*, *9*).

In the present study, we conducted calorimetric measurements of the heat of dissolution of ammonium nitrate in nitric acid as a function of solute concentration and the degree of

0021-9568/80/1725-0127$01.00/0

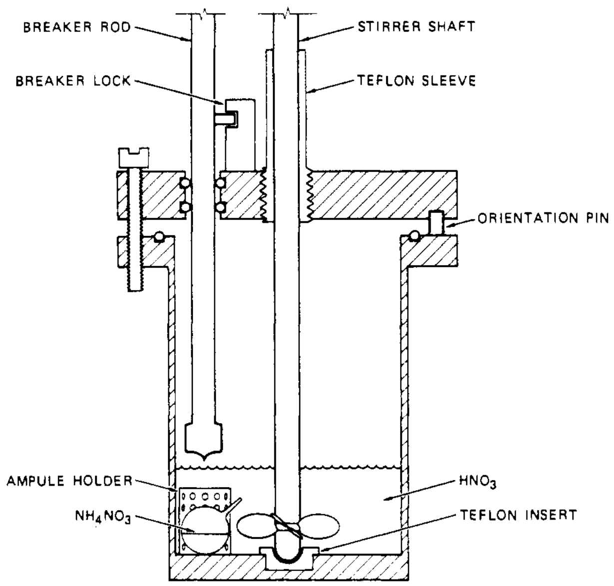

Figure 1. Schematic view of the calorimeter.

dilution of the acid with water. In addition, we observed the proton NMR spectra of ammonium nitrate/nitric acid solutions and correlated the observed proton chemical shifts with the measured heat of dissolution.

Experimental Details

Calorimeter. Figure 1 shows the calorimeter used to measure the heat of dissolution of ammonium nitrate in nitric acid. The 230-cm^3 reaction vessel is constructed from Durimet 20, a stainless steel alloy enriched in copper and nickel. This alloy is highly resistant to corrosion by 100% nitric acid (*16*).

As shown in Figure 1, a glass ampule containing ammonium nitrate is held in place at the bottom of the reactor. The holder is perforated to allow rapid contact with stirred nitric acid when the ampule is broken. The Durimet 20 stirrer is mounted on a Teflon shaft that is supported by a Teflon insert at the bottom of the reactor. The head of the reaction vessel contains the breaker rod and the stirrer shaft.

For proper orientation of the ampule breaker rod with the holder, the reactor head can be attached in only one position by the use of the orientation pins near the Teflon "O" ring. A locking mechanism for the breaker rod avoids accidental breakage of the ampule before the desired reaction time. The stirrer shaft extends through a Teflon sleeve to avoid leakage of water from the outside bath into the reactor.

The sealed reactor is immersed in a 4-L Dewar flask containing about 2700 cm^3 of distilled water; the flask is insulated with a 1-in. Styrofoam jacket and cover. In addition to the ampule breaker and stirrer connections, a Teflon stirring paddle, a quartz-encased calibration heater, and a NBS-calibrated Leeds and Northrup platinum resistance thermometer (Model No. 8164) extend through the cover.

The heat capacity of the calorimetric system was evaluated by supplying a known quantity of electrical energy to the system during a measured time period through a calibrated 57-Ω quartz-encased heater and then by measuring the temperature rise with the platinum resistance thermometer. Temperature readings were recorded in terms of resistance (measured with a Leeds and Northrup Mueller bridge, Model No. 8067) of the calibrated Pt thermometer.

Materials. Ammonium nitrate (99.5% assay) was obtained from the Mallinckrodt Chemical Co. The samples were dried for several hours at 130 °C and transferred to a drybox (Vacuum Atmospheres Corp., No. HE-43-6) through an antechamber evacuated to <50 μmHg. A Karl-Fischer titration of an ammonium nitrate sample stored in the drybox showed the presence of <0.1 wt % H_2O, and X-ray analysis showed a diffraction pattern identical with the literature spectrum for the dry salt.

Anydrous nitric acid was prepared by a procedure similar to that described by Liang (*8*), except that 90% nitric acid (Fisher Scientific Co.) was vacuum-distilled from oleum rather than from concentrated sulfuric acid and oxides of nitrogen were removed before distillation by treatment with urea. Potentiometric titration of nitric acid aliquots (stored in the dark at -80 °C to prevent photodecomposition) with standard 1 N NaOH gave an average nitric acid content of 99.6 ± 0.2 wt %. Aqueous nitric acid samples were prepared by dilution of more concentrated material and were analyzed in a similar manner.

Because of the corrosive nature of the chemicals used in the calorimetric system, we were concerned that wall attack and water pickup might lead to spurious results. To evaluate these possibilities, we stored samples of nitric acid in the sealed reaction vessel for a time equivalent to a calorimetric measurement (about 30 min) and then withdrew aliquots for analysis. Titration results indicated that sample purity had not changed by more than ± 0.5% and only background levels (0.3 ppm) of iron and nickel were detected by atomic absorption analysis.

Procedure. Ammonium nitrate samples were transferred in the drybox into weighed 7-cm^3 glass ampules that were then flame-sealed, reweighed, and mounted in the sample holder of the reaction vessel. A measured volume of nitric acid was then quickly added to the reactor under a stream of flowing dry nitrogen. After the reactor was sealed and immersed in water in the insulated Dewar flask, the Styrofoam cover (containing the stirring rod, the calibration heater, and the platinum resistance thermometer) was carefully positioned on top of the flask. The temperature of the water bath was then adjusted to 298 ± 0.05 K by using the calibration heater or adding ice, and the temperature was read with the platinum resistance thermometer and Mueller bridge. The nitric acid sample inside the reactor and the heat sink fluid were stirred at a predetermined rate that minimized the time lag between the heat release period and the initial and final drift rate equilibria of the calorimetric determination.

After establishing the slope of the initial drift rate period, we broke the glass ampule containing ammonium nitrate by depressing the breaker rod. The resulting temperature change of the calorimeter was recorded as often as possible during the reaction period. Measurements were continued after the reaction period to establish the slope of the final drift rate period, which also served as the initial slope of the subsequent heat capacity determination.

The measured resistance change was corrected for thermal leakage and heat of stirring during the nonequilibrium portion of the calorimetric experiment by using Jessup's (*6*) method, which involves the slopes of the initial and final drift rate periods. This procedure empirically gives correct results within about 0.01% of the total resistance change and provides simpler calculations than the more accurate but tedious procedures based on Newton's law of cooling (*18*).

Proton NMR spectra of ammonium nitrate/nitric acid solutions were observed at 28 °C by using a Varian Model EM-360, 60 MHz spectrometer. Weighed NMR tubes were loaded in a drybox with ammonium nitrate. The tubes were then reweighed and flame-sealed after the addition, under nitrogen, of 0.5 cm^3 of nitric acid and a sealed capillary containing tetramethylsilane (Me_4Si) reference standard.

Results and Discussion

Table I summarizes the calorimetric data obtained for the dissolution of ammonium nitrate in nitric acid. A plot of the results from a typical experiments is shown in Figure 2.

Table I. Summary of Calorimetric Data

run no.	system	mol of reactant	reactant	molality of NH_4NO_3	run temp, K	C_p,[a] kcal/Ω	ΔT,[b] Ω	no. kcal	kcal/mol of NH_4NO_3
1	NH_4NO_3/HNO_3	0.0301 1.198	NH_4NO_3 HNO_3	0.40	298.04	32.423	0.0061	0.1978	-6.58
2	NH_4NO_3/HNO_3	0.0441 1.196	NH_4NO_3 HNO_3	0.58	298.05	31.154	0.0084	0.2617	-5.93
3	NH_4NO_3/HNO_3	0.0378 1.196	NH_4NO_3 HNO_3	0.50	298.02	30.710	0.0073	0.2242	-5.93
4	NH_4NO_3/HNO_3	0.0469 0.0478	NH_4NO_3 HNO_3	1.55	298.02	28.994	0.0088	0.2551	-5.44
5	NH_4NO_3/HNO_3	0.0748 0.239	NH_4NO_3 HNO_3	4.95	298.02	31.982	0.0074	0.2367	-3.16
6	NH_4NO_3/HNO_3	0.04998 0.239	NH_4NO_3 HNO_3	3.31	298.01	30.522	0.0070	0.2137	-4.28
7	NH_4NO_3/HNO_3	0.1427 0.239	NH_4NO_3 HNO_3	9.44	298.00	30.908	0.0077	0.2380	-1.67
8	$NH_4NO_3/H_2O/HNO_3$	0.0199 0.0555 0.478	NH_4NO_3 H_2O HNO_3	0.64	298.04	30.756	0.0039	0.1199	-6.01
9	$NH_4NO_3/H_2O/HNO_3$	0.0378 1.176 0.785	NH_4NO_3 H_2O HNO_3	0.54	297.99	31.472	0.0019	0.0598	+1.58
10	$NH_4NO_3/H_2O/HNO_3$	0.0375 1.983 0.441	NH_4NO_3 H_2O HNO_3	0.59	297.97	30.682	0.0039	0.1197	+3.19
11	$NH_4NO_3/H_2O/HNO_3$	0.0378 0.330 1.087	NH_4NO_3 H_2O HNO_3	0.51	298.01	31.497	0.0058	0.1827	-4.83
12	$NH_4NO_3/H_2O/HNO_3$	0.0374 0.753 0.941	NH_4NO_3 H_2O HNO_3	0.51	297.99	30.280	0.0020	0.0606	-1.62
13	$NH_4NO_3/H_2O/HNO_3$	0.0765 1.176 0.785	NH_4NO_3 H_2O HNO_3	1.07	297.98	30.762	0.0028	0.0861	+1.14

[a] NBS-calibrated Leeds and Northrup platinum resistance thermometer Model No. 8164. [b] 1 Ω = 9.917 °C.

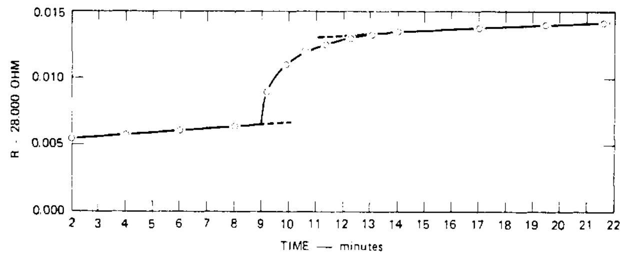

Figure 2. Typical calorimetric curve (run no. 1).

Effect of Ammonium Nitrate Concentration. As shown in Figure 3, heat is evolved when ammonium nitrate is disolved in 99.6 wt % nitric acid. This observation is consistent with the reported strong interaction between the nitrate ion and molecular nitric acid (*1*, *9*). The initial step in the dissolution of ammonium nitrate in nitric acid requires the absorption of heat to breakup the crystal lattice; thus the observed results suggest that the strength of the solute/solvent bonds exceeds 1.3 kcal/mol, the heat of fusion of ammonium nitrate (*19*).

As shown in Figure 3, curve a, the partial molal heat of solution of ammonium nitrate in nitric acid is calculated from the initial slope to be -6.5 kcal/mol. This heat of solution represents the heat evolved when a mole of the salt is dissolved in an infinitely large amount of the acid to form an infinitely dilute solution. The same value can be estimated from the limiting heat of solution approached in Figure 3, curve b.

At low concentrations of ammonium nitrate in nitric acid, the heat of solution is nearly proportional to the salt concentration (Figure 3, curve a). At higher concentrations, the solution is less ideal; the decreasing evolution of heat suggests that effects such as solute-solute interactions or disturbance of the polymeric lattice of the acid may compete thermally with the heat of formation of the complex species.

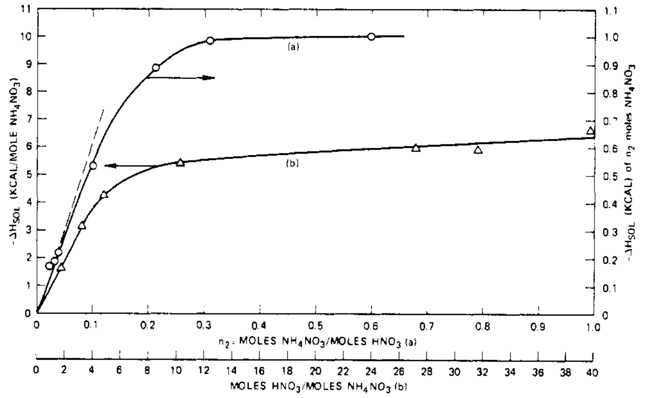

Figure 3. Heat of solution of NH_4NO_3(s) in 99.6 wt % HNO_3(l).

The difference between any two integral heats of solution represents a value for the integral heat of dilution or concentration; hence, Figure 3, curve b, provides a convenient method for calculating the heat effect resulting from the addition of HNO_3 or NH_4NO_3 to ammonium nitrate/nitric acid solutions. For example, we calculate that the dilution with HNO_3 of a 20 mol % NH_4NO_3 solution to a 10 mol % solution will evolve about a 1.5 kcal/mol of heat.

Similar studies conducted on thermal effects in the potassium nitrate/nitric acid system (*10*) reported heats of solution at 273 K over a narrow concentration range. To compare these data with the results for NH_4NO_3, measured at 298 ± 0.05 0.05 K, it is necessary to have information on the dependence of heat capacity and heat of reaction with temperature. Assuming that these effects are small, we suggest that the reaction may be more exothermic for the potassium salt (Table II). As described in a later section, proton NMR spectra provide additional evidence to support this conclusion.

Table II. Heats of Solution of Nitrates in Anhydrous Nitric Acid

	$-\Delta H$, kcal/mol	
molality	NH_4NO_3 (298 K)[a]	KNO_3 (273 K)[b]
0.2	6.65	6.83
1.0	5.72	6.33
1.5	5.30	6.20
2.3	4.70	5.24

[a] Present work. [b] Reference 9.

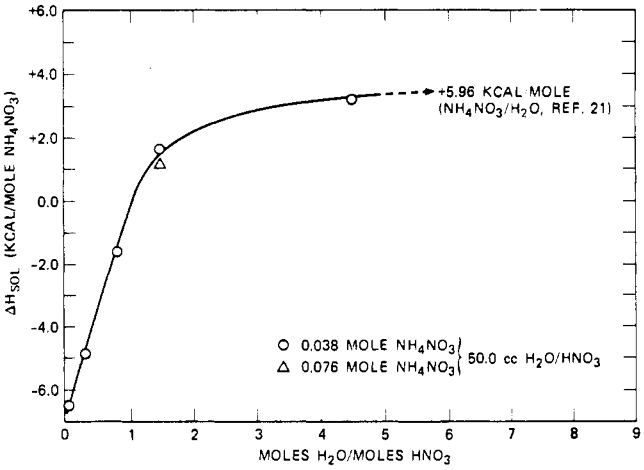

Figure 4. Integral heat of solution of $NH_4NO_3(s)$ in $H_2O/HNO_3(l)$.

Effect of Water. To study the effect of water on the dissolution of ammonium nitrate in nitric acid, we chose a fixed concentration of the salt and varied the mole ratio of water to nitric acid. The results, shown in Figure 4, demonstrate that the dissolution process can absorb or evolve heat depending on the value of this ratio. Thus, the heat effect appears to be a function of the relative concentrations of water, nitric acid, and ammonium nitrate, which can be related through a series of equilibria:

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

$$HNO_3 + H_2O \overset{(a)}{\rightleftarrows} H_3NO_4 \overset{(b)}{\rightleftarrows} H_3O^+ + NO_3^- \qquad (2)$$

$$2HNO_3 + NH_4NO_3 \rightleftarrows (HNO_3)_2NO_3^- + NH_4^+ \qquad (3)$$

A variety of evidence suggests that eq 1 represents the primary ionization equilibrium for anhydrous nitric acid. In the presence of water, however, eq 2 becomes important, but little ionization occurs to H_3O^+ and NO_3^- at a mole ratio $H_2O/HNO_3 < 1$. Rather, a substantial fraction of the liquid exists as molecular nitric acid and as the monohydrate H_3NO_4 (*3–5*), eq 2a. In the water-deficient region ($H_2O/HNO_3 < 1$), the heat released during the dissolution of ammonium nitrate appears inversely proportional to the amount of water added (Figure 4). This suggests that the formation of the monohydrate removes molecular nitric acid that is needed for complexing the nitrate ion (*1*, *9*) and evolving heat, eq 3.

Equation 2b represents the primary ionization equilibrium for the acid after the nitric acid is diluted further ($H_2O/HNO_3 > 1$). In this concentration region, the heat of dissolution of ammonium nitrate becomes endothermic because the heat of separation of the ions in the crystal lattice of the salt (heat of fusion) is greater than the heat of formation of the hydrogen bonds in the complex species. For infinitely dilute nitric acid, we estimate that the heat of solution of ammonium nitrate will asymptotically approach 5.96 kcal/mol, the literature value (*21*) for the solution process in pure water at the concentration of our experiment (molality = 0.75).

Table III. Proton Resonance Shifts (Relative to Me_4Si) for HNO_3/NO_3^- Solutions

	δ			
mol NO_3^-/mol HNO_3	$NaNO_3$ (28 °C)[a]	KNO_3 (28 °C)[a]	NH_4NO_3 (28 °C)[a]	KNO_3 (27 °C)[b]
0			11.86	12.41
0.019			12.07	12.64
0.113	12.66	13.34	12.92	13.69
0.164			13.38	14.25
0.221			13.90	14.78
0.248			14.15	15.00
0.318			14.78	15.57

[a] Present work. [b] Reference 4.

As shown in Figure 4, the heat of dissolution of ammonium nitrate in aqueous nitric acid is thermoneutral near a mole ratio $H_2O/HNO_3 = 1$. The position of the thermoneutral point, determined in our measurements for one salt concentration, is expected to vary with the composition of the solution (eq 1–3). The concentration dependence, however, does not appear to be large, since a single point measurement of the heat of solution at twice the ammonium nitrate concentration is close to the observed behavior (Figure 4).

One important implication of the thermoneutral point is that the energy required to disrupt the ammonium nitrate lattice (1.3 kcal/mol) (*19*) is exactly balanced by the heat of formation of the solvent/solute bonds. In an ideal solution (having no solvent/solute interactions), the heat of solution of a substance in a solvent must be exactly equal to the heat of fusion. Thus, the bond energy between nitric acid and the nitrate ion is 1.3 kcal/mol at the thermoneutral point and increases to about 7.8 kcal/mol for the species formed in the anhydrous acid.

Data Reliability. As a measure of the reliability of our thermochemical measurements, we evaluated the heat release for a similar reaction that could easily be calculated from literature data. For the system

$$NH_3(l) + HNO_3(l) \rightarrow NH_4NO_3(s) \qquad (4)$$

the heat of reaction at 298 K is calculated (*19*, *21*) to be −29.06 kcal/mol.

Direct measurement of reaction 4 was difficult in our calorimeter because of handling problems associated with liquid ammonia; therefore, we evaluated the reaction

$$NH_3{\cdot}H_2O(l) + (excess)HNO_3(l) \rightarrow NH_4NO_3{\cdot}H_2O{\cdot}HNO_3(l) \qquad (5)$$

Using standardized 25 wt % ammonia and 99.6 wt % nitric acid, which has a product molality of 0.65, we determined the heat of reaction 5 at 298 K to be −42.43 kcal/mol. The standard deviation for four replicate measurements was 0.56 kcal/mol.

To obtain a value for reaction 4 we used Hess' law to combine the heat of reaction 5 with the heats of reaction for a series of thermochemical steps. The heat of reaction 4 at 298 K using this procedure is −31.75 kcal/mol. Assuming that the calculated value (−29.06 kcal/mol) is accurate, we can assign an error limit to our measurements of about 9%.

Proton NMR Spectra. A number of workers have reported proton nuclear magnetic resonance data on nitric acid and nitric acid–water systems (*3–5*, *11*, *14*). In a study similar to ours, Happe and Whittaker (4) have measured proton resonance shifts for the potassium nitrate/nitric acid system (Table III). They found that the nitrate ion is very effective in unshielding the proton in nitric acid and that this unshielding results in a large chemical shift toward lower applied fields. Their data also support the previous observation (*1*, *10*) that the nitrate ion in nitric acid is solvated with two molecules of the acid. In the work of Happe and Whittaker (4), however, all chemical shifts are reported relative to water as an external standard. In our experience, this practice introduces possible errors in chemical shift measurements due to sample tube inhomogeneity.

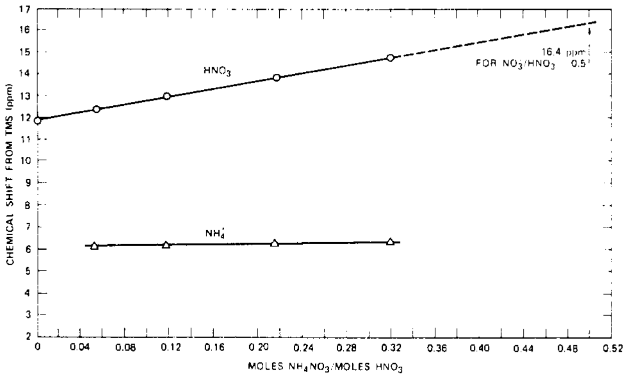

Figure 5. Proton chemical shifts for the NH_4NO_3/HNO_3 system.

In the present study, we observed the proton NMR spectra of solutions of ammonia nitrate in 99.6 wt % nitric acid. The resonance results, relative to an internal tetramethylsilane (Me_4Si) standard, provide additional information about the chemical environment of the cation because the proton spectrum of NH_4^+ is observable (*13*). Thus, information was obtained on the effect of the ammonium ion on the interaction between HNO_3 and NO_3^-.

As shown in Figure 5, the addition of ammonium nitrate to nitric acid results in a large chemical shift toward a lower applied field. Hydrogen bonding in general produces chemical shifts in this direction, and there is evidence that the strength of the hydrogen bond formed is reflected in the magnitude of the resonance shift observed (*7*). The chemical shifts observed in the present study are believed to arise from the formation of a solvated nitrate ion involving strong hydrogen bonding between the ion and the solvent molecules (*1*, *9*). A possible structure for this species has been proposed by Happe and Whittaker (*4*).

Extrapolation of the curve shown in Figure 5 to a mole ratio where ammonium nitrate/nitric acid = 0.5 for the species $(HNO_3)_2NO_3^-$ gives a chemical shift of about 16.4 ppm for the protons in the complex. A substantially higher shift of about 18.3 ppm was observed for the potassium nitrate/nitric acid system (*4*). The higher chemical shift for the potassium salt in nitric acid suggests the formation of stronger hydrogen bonds and a more exothermic heat of solution, as speculated in Table II; this indicates that the potassium ion contributes to the chemical environment of the complex. Perhaps the polymeric nature of nitric acid, which is known to exist as a dimer (*4*), is altered by the presence of the cation. Shoolery and Alder (*20*) have reported similar effects on the position of the proton resonance for water in the presence of added electrolytes. Table III summarizes the chemical shifts observed in the present work.

For the ammonium nitrate/nitric acid system, the proton chemical shift of the ammonium ion is nearly independent of concentration (Figure 5), which supports previous suggestions that it is not directly involved in the bonding of the complex. Our results further demonstrate that the heat of dissolution of ammonium nitrate in nitric acid increases with nitrate ion concentrations and a corresponding proton resonance shift toward lower applied field.

Literature Cited

(1) Chedin, J., Vandoni, R., *C. R. Hebd. Seances Acad. Sci.*, **227**, 1232 (1948).
(2) Fine, B. D., *J. Chem. Eng. Data*, **7**, 91 (1962).
(3) Gutowsky, H. S., Saika, A., *J. Chem. Phys.*, **21**, 1688 (1953).
(4) Happe, J. A., Whittaker, A. G., *J. Chem. Phys.*, **30**, 417 (1959).
(5) Hood, G. C., Redlick, O., Reilly, C. A., *J. Chem. Phys.*, **22**, 2067 (1954).
(6) Jessup, R. S., *Natl. Bur. Stand.* (*U.S.*), *Monogr.*, **No. 7** (1960).
(7) Korinek, G. J., Schneider, G. W., *Can. J. Chem.*, **35**, 1157 (1957).
(8) Liang, P., "Organic Syntheses", Collect. Vol. 3, Wiley, New York, 1955, p 804.
(9) Lloyd, L., Wyatt, P. A. H., *J. Chem. Soc.*, 4268 (1957).
(10) Lloyd, L., Wyatt, P. A. H., *J. Chem. Soc.*, 4262 (1957).
(11) Masuda, Y., Kanda, T., *J. Phys. Soc. Jpn.*, **8**, 432 (1953).
(12) Mulder, H. D., Schmidt, F. C., *J. Am. Chem. Soc.*, **73**, 5575 (1951).
(13) Ogg, R. A., *Discuss. Faraday Soc.* **17**, 215 (1954).
(14) Ogg, R. A., Day, J. D. *J. Chem. Phys.*, **25**, 1285 (1956).
(15) Perov, E. V., Kharitonov, B. I., *Tr. Novveherk. Politekh. Inst.*, **31**, 35 (1955).
(16) Perry, R. H., Chilton, C. H., Kilpatrick, S. D., "Chemical Engineers Handbook", 4th ed., McGraw-Hill, New York, 1963.
(17) Potier, J., Potier, A., Mascherpa, G., *Bull. Soc. Chim. Fr.*, 1172 (1960).
(18) Rossini, F. D., "Experimental Thermochemistry", Interscience, New York, 1956.
(19) Rossini, F. D., et al., *Natl. Bur. Stand.* (*U.S.*), *Cir.*, **No. 500** (1952).
(20) Shoolery, J. N., Alder, B. J., *J. Chem. Phys.*, **23**, 805 (1955).
(21) Wagman, D. D., et al., *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3** (1968).
(22) Zinyuk, R., Rogova, G. I., Pozin, M. E., *Zh. Prikl. Khim.*, **44**, 2318 (1971).

Received for review May 7, 1979. Accepted November 2, 1979. Partial support by the Department of the Army (ARRADCOM), Contract No. DAAA21-72-C-0230, is gratefully acknowledged.