(3) I. Prigogine and R. Defay, "Chemical Thermodynamics", Longmans Green, London, 1967.
(4) L. O. Sundelöf, *Ark. Kemi*, **20**, 369 (1963).
(5) J. S. Kirkaldy and G. R. Purdy, *Can. J. Phys.*, **47**, 865 (1969).
(6) R. L. Scott, *Ber. Bunsenges. Phys. Chem.*, **76**, 296 (1972).
(7) V. Vitagliano, R. Sartorio, S. Scala, and D. Spaduzzi, *J. Solution Chem.*, **7**, 605 (1978).
(8) L. D. Roberts and J. E. Mayer, *J. Chem. Phys.*, **9**, 852 (1941).
(9) F. Kohler, *Monatsh. Chem.*, **82**, 913 (1951).
(10) F. Kohler and O. K. Rice, *J. Chem. Phys.*, **26**, 1614 (1957).
(11) F. Kohler, H. Arnold, and R. J. Munn, *Monatsh. Chem.*, **92**, 878 (1961).
(12) R. Haase and M. Siry, *Z. Phys. Chem.* (*Frankfurt am Main*), **57**, 56 (1968).
(13) R. Haase, *Ber. Bunsenges. Phys. Chem.*, **76**, 256 (1972).
(14) G. J. Dudley and H. J. Tyrrell, *J. Chem. Soc., Faraday Trans.*, **69**, 2188, 2200 (1973).
(15) A. N. Campbell and S. Y. Lamm, *Can. J. Chem.*, **51**, 4005 (1973).
(16) L. J. Gosting, E. H. Hanson, G. Kegeles, and M. Morris, *Rev. Sci. Instrum.*, **20**, 209 (1949).
(17) A. Weissberger, "Physical Methods of Chemistry", Vol. 1, Part IV, Wiley, New York, 1972.
(18) M. Fixman, *J. Chem. Phys.*, **36**, 310 (1962).
(19) J. Timmermans, "The Physico-Chemical Constants of Binary Systems", Vol. 4, Interscience, New York, 1960, p 81.
(20) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed., Butterworths, London, 1959, p 328.
(21) V. Vitagliano and P. A. Lyons, *J. Am. Chem. Soc.*, **78**, 4538 (1956).

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Vapor–Liquid Equilibria: Systems 2-Butanol–*p*-Xylene and 2-Butanol–*m*-Xylene

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Vapor–liquid equilibrium data have been measured for the binary systems 2-butanol–*p*-xylene and 2-butanol–*m*-xylene, at 685 mmHg pressure. The activity coefficients have been evaluated by taking into consideration the vapor phase nonideality. The t–x–y data have been subjected to a thermodynamic consistency test, and the activity coefficients have been correlated by Wilson's equation.

Introduction

The separation of the C_8 hydrocarbons, particularly *p*-xylene and *m*-xylene, is difficult. An attempt has been made here to separate the above mixtures by employing azeotropic distillation techniques. We have chosen 2-butanol as the entrainer. The vapor–liquid equilibria have been evaluated for the systems 2-butanol–*p*-xylene and 2-butanol–*m*-xylene.

Experimental Section

Materials. *p*-Xylene "Lab Chem" grade, obtained from E. Merck, West Germany, and *m*-xylene, "Lab Chem" grade, obtained from M/s. Pfizer, India, Ltd., were purified by the methods given by Riddick and Bunger (*9*). The 2-butanol supplied by Riedel-De-Haen AG, West Germany, was purified by the method suggested by Vogel (*12*). The *p*-xylene and *m*-xylene were dried over dry sodium, and 2-butanol was dried over anhydrous calcium chloride.

The liquids were distilled in a 30-mm glass column packed with 10-mm Raschig rings to a height of 1 m. The column was operated at total reflux for 30 min. The low boiling impurities were drawn off at a very low rate as rejects. When the desired boiling temperature was reached and remained constant for 15 min, the fraction was collected, while the column was operated at nearly total reflux. The physical properties of the materials used are listed in Table I.

Apparatus and Analytical Procedure. A vapor recirculation type equilibrium still described by Brown (*2*, *3*) was used to study the vapor–liquid equilibrium. The apparatus is shown in Figure 1.

The apparatus consists of a cylindrical-shaped boiler, one end of which is tapered gradually to a Cottrell pump which in turn is connected to a separation chamber. The inside wall of the boiler is coated with pulverized glass powder to avoid superheating and bumping. The boiler is heated with an external heater made of nichrome wire. Another heater is wound round the entire length of the Cottrell pump and the separating chamber. Plaster of paris is applied over the heater windings, and above this asbestos rope is wound. The other end of the boiler is fused to a B_{19} socket. An internal heater, made of nichrome wire fused to two tungsten leads which in turn are fused to a B_{19} cone, fits into this socket.

Table I. Physical Properties of Materials

	2-butanol	*p*-xylene	*m*-xylene
mole wt	74.12	106.16	106.16
density at 30 °C, g/cm³			
exptl	0.7984	0.8524	0.8555
lit.	0.7983[a]	0.8525[b]	0.8557[b]
refractive index at 25 °C			
exptl	1.39492	1.49321	1.49462
lit.	1.39500[a]	1.49325[b]	1.49464[b]

[a] Reference 9. [b] Reference 10.

The sampling trap used is shown in Figure 2. The sample traps are provided with magnetically operated valves. Liquid and vapor samples could be withdrawn without disturbing the working of the still. At the time of sampling, the sample traps were cooled with freezing mixture and then the magnetic valves opened and the samples collected. The samples were analyzed by using a Pulfrich refractometer. All measurements were made at 30 ± 0.1 °C. A Colora ultrathermostat with a mercury to mercury thermoregulator was used to maintain the temperature during measurements to within ±0.1 °C. The samples were kept in the thermostatic bath for about 30 min, before being fed to the refractometer. The refractive index was measured with an accuracy of ±0.000 01. A mercury-in-glass thermometer calibrated against the vapor pressure measurements was used for temperature measurements. Several samples of known compositions were prepared, and their refractive index was measured. Thus a calibration chart was prepared. All the unknown compositions were obtained from this calibration chart and their refractive index.

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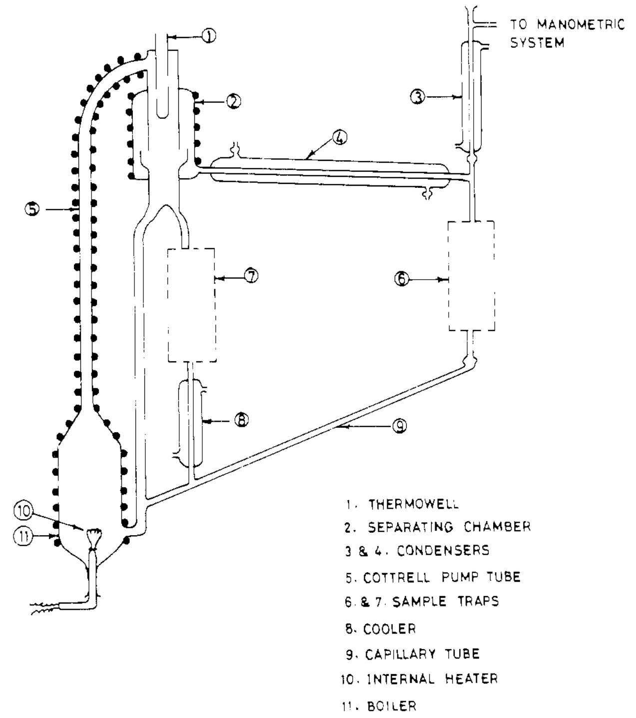

Figure 1. Schematic diagram of the vapor-liquid equilibrium still.

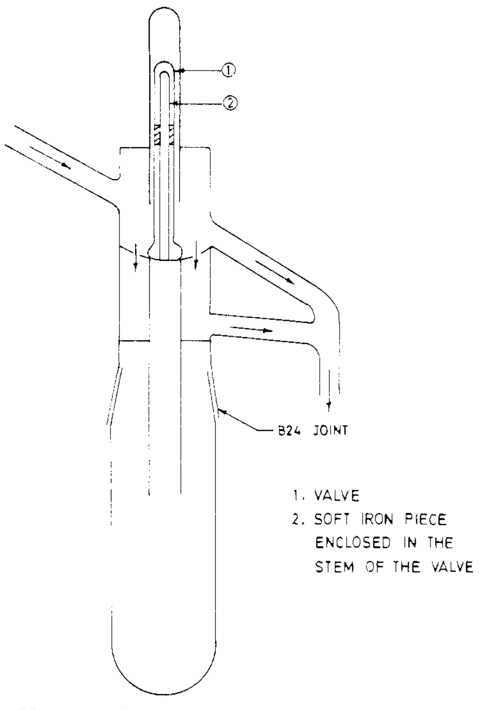

Figure 2. Diagram of the sample trap.

Table II. Refractive Index-Composition Data at 30 °C

2-butanol-*p*-xylene		2-butanol-*m*-xylene	
mole fraction *p*-xylene	refractive index	mole fraction *m*-xylene	refractive index
0.0000	1.392 68	0.0000	1.392 68
0.0285	1.398 44	0.0245	1.396 38
0.0566	1.401 45	0.0885	1.404 22
0.1243	1.408 60	0.1108	1.406 09
0.1512	1.411 41	0.1893	1.414 71
0.2052	1.416 98	0.2211	1.417 77
0.2561	1.422 16	0.2563	1.421 90
0.2808	1.423 56	0.2981	1.426 31
0.3315	1.429 70	0.3584	1.432 57
0.3916	1.435 60	0.3903	1.435 83
0.4476	1.441 00	0.4229	1.439 63
0.4812	1.444 21	0.4752	1.444 34
0.5146	1.448 41	0.5204	1.448 93
0.5748	1.452 96	0.5963	1.456 06
0.6166	1.456 72	0.6508	1.461 17
0.6712	1.461 73	0.6943	1.465 18
0.7346	1.467 36	0.7223	1.467 73
0.7792	1.471 21	0.7848	1.473 32
0.8341	1.475 96	0.8104	1.475 57
0.8915	1.480 09	0.8783	1.481 44
0.9108	1.482 41	0.9101	1.483 58
0.9457	1.485 29	0.9481	1.487 30
0.9742	1.487 62	0.9730	1.489 36
1.0000	1.490 25	1.0000	1.492 25

Table III. Vapor-Liquid Equilibrium Data at 685 mmHg: 2-Butanol-*p*-Xylene System

t, °C	x_1	y_1	γ_1	γ_2
96.7	1.0000	1.0000	1.0000	0.0000
97.0	0.9629	0.9681	0.9961	2.7430
97.2	0.9050	0.9307	1.0090	2.2980
97.9	0.8264	0.8909	1.0320	1.9250
98.6	0.7581	0.8601	1.0600	1.7260
98.9	0.7054	0.8434	1.1080	1.5710
99.7	0.6606	0.8207	1.1170	1.5150
101.5	0.5210	0.7657	1.2430	1.3180
102.1	0.4665	0.7460	1.3207	1.2380
103.8	0.3857	0.7155	1.4490	1.1530
105.9	0.2947	0.6701	1.6610	1.0950
108.1	0.2353	0.6241	1.8020	1.0720
110.8	0.1766	0.5710	2.0420	1.0640
113.4	0.1362	0.5191	2.4770	1.1700
114.4	0.1312	0.5054	2.1720	1.0240
116.2	0.1057	0.4482	2.2580	1.0330
118.9	0.0743	0.3842	2.5000	1.0270
121.2	0.0566	0.3320	2.6650	1.0230
123.2	0.0466	0.2912	2.6800	1.0140
125.3	0.0345	0.2473	2.9890	1.0030
126.5	0.0291	0.2247	2.9000	1.0020
128.7	0.0181	0.1624	3.0140	0.9712
134.5	0.0000	0.0000	0.0000	1.0000

The atmospheric pressure prevailing in this laboratory is 685 mmHg. The pressure was measured with a mercury manometer. The mercury levels were read with a Kathetometer to within ±0.1 mm. A large monostat of 250-L capacity was used to maintain the pressure. We observed that with this we could maintain the pressure to within ±0.5 mmHg.

Results and Discussion

The refractive index-composition data for the mixtures are given in Table II. The vapor-liquid equilibrium data collected at 685 mmHg pressure are given in Tables III and IV. Figures 3 and 4 represent the boiling point-composition diagrams for the two binaries studied.

The liquid phase activity coefficients were calculated from the experimental data by using the equation (*11*)

$$\gamma_1 = (y_1/x_1p^\circ_1)\exp\left[\frac{(B_{11} - V_1^L)(P - p_1^\circ)}{RT} + Py_2^2\delta_{12}'\right] \tag{1}$$

The vapor pressures of the pure components were calculated from the Antoine equation. The Antoine constants were taken from the literature (*1*, *6*).

Table IV. Vapor-Liquid Equilibrium Data at 685 mmHg: 2-Butanol-*m*-Xylene System

t, °C	x_1	y_1	γ_1	γ_2
96.7	1.0000	1.0000	1.0000	0.0000
97.0	0.9282	0.9498	1.0140	2.2770
97.1	0.9099	0.9393	1.0170	2.1810
97.4	0.8751	0.9184	1.0250	2.0930
97.6	0.8450	0.9033	1.0350	1.9790
97.8	0.8050	0.8856	1.0570	1.8470
98.4	0.7612	0.8673	1.0720	1.7120
98.8	0.6952	0.8383	1.1190	1.6080
99.3	0.6696	0.8291	1.1131	1.5440
100.1	0.5754	0.7902	1.2190	1.4330
100.3	0.5587	0.7823	1.2350	1.4210
101.5	0.4746	0.7598	1.3540	1.2630
103.5	0.3899	0.7201	1.4550	1.1820
104.9	0.3409	0.6909	1.6250	1.1550
106.8	0.2835	0.6556	1.6310	1.1110
110.1	0.2134	0.5975	1.7790	1.0650
115.0	0.1326	0.4988	2.0460	1.0290
120.9	0.0775	0.3784	2.2210	1.0060
124.6	0.0505	0.2917	2.3650	0.9996
125.6	0.0438	0.2712	2.4680	0.9936
126.8	0.0336	0.2410	2.7650	0.9900
131.7	0.0105	0.1131	3.6430	0.9865
135.3	0.0000	0.0000	0.0000	1.0000

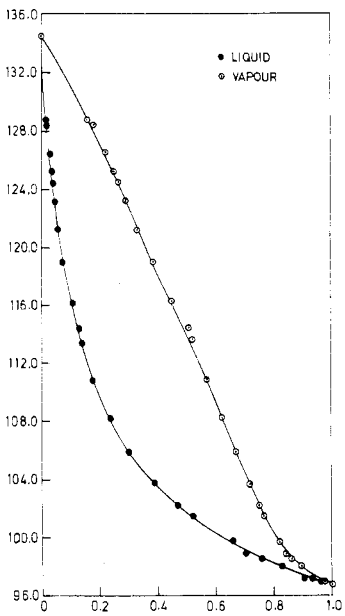

Figure 3. Boiling point-composition diagram for the 2-butanol-*p*-xylene system.

The gas-phase second virial coefficients for *p*-xylene were estimated by the Pitzer and Curl correlation (*8*) and for 2-butanol by the O'Connell correlation (*4*). The gas-phase second virial coefficients for *m*-xylene were calculated from the Berthelot equation (*5*) and were fitted to the O'Connell correlation (*4*). The virial cross coefficients were calculated according to the combination rules (*4*).

The activity coefficient data satisfied the Herington consistency criteria (*7*): $D \leq J$. The activity coefficients were fitted to the Wilson equations (*13*)

$$\ln \gamma_1 = -\ln (X_1 + \lambda_{12}X_2) + X_2\left[\frac{\lambda_{12}}{X_1 + \lambda_{12}X_2} - \frac{\lambda_{21}}{\lambda_{21}X_1 + X_2}\right] \tag{2}$$

$$\ln \gamma_2 = -\ln (X_2 + \lambda_{21}X_1) - X_1\left[\frac{\lambda_{12}}{X_1 + \lambda_{12}X_2} - \frac{\lambda_{21}}{\lambda_{21}X_1 + X_2}\right] \tag{3}$$

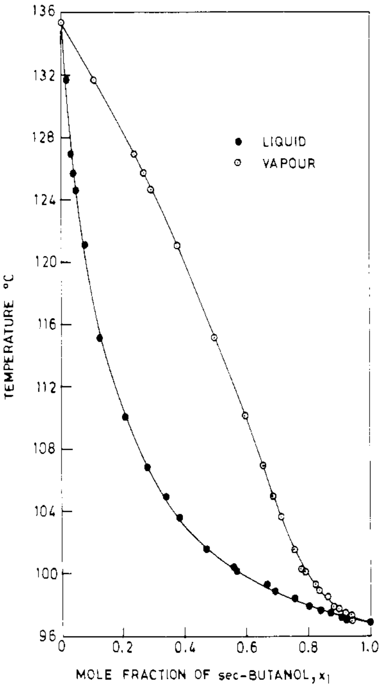

Figure 4. Boiling point-composition diagram for the 2-butanol-*m*-xylene system.

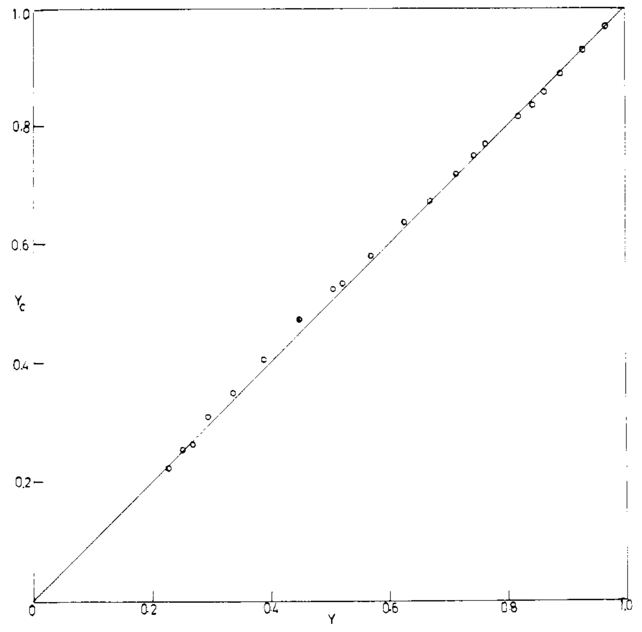

Figure 5. Experimental and calculated vapor compositions for the 2-butanol-*p*-xylene system.

The values of λ_{12} and λ_{21} were obtained by a nonlinear least-squares fitting of the activity coefficient data. All the computations were carried out in double precision arithmetic on an IBM system 360/44 digital computer.

The values of the constants λ_{12} and λ_{21} in eq 2 and 3 are the following:

	λ_{12}	λ_{21}
2-butanol-*p*-xylene	0.4880	0.5983
2-butanol-*m*-xylene	0.4549	0.6934

Tables III and IV also give the activity coefficients of the two components. Experimental and calculated vapor compositions are compared in Figures 5 and 6. From these figures, it is evident that the eq 2 and 3 fit the experimental activity coefficients very well. From the activity coefficients, it is clear that

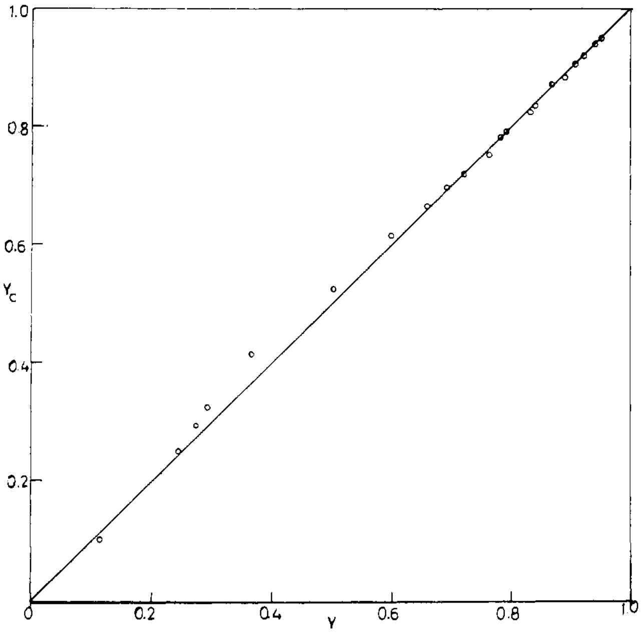

Figure 6. Experimental and calculated vapor compositions for the 2-butanol-*m*-xylene system.

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).

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The Heat of Solution of Ammonium Nitrate in Nitric Acid

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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

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