LITERATURE CITED

(1) Bianchi, G., *Electrochem. Soc.* **112**, 233 (1965).
(2) Bianchi, G., Barosi, A., Faita, G., Mussini, T., *Ibid.*, **112**, 921 (1965).
(3) Biermann, W. E., Yamasaki, R.S., *J. Am. Chem. Soc.* **77**, 241 (1955).
(4) Erber, W., *Z. Anorg. Allgem. Chem.* **248**, 32 (1941).
(5) Gupta, S.R., Hills, G.J., Ives, D.J.G., *Trans. Faraday Soc.* **59**, 1886 (1963).
(6) Harned, H.S., Donelson, J.G., *J. Am. Chem. Soc.* **59**, 1280 (1937).
(7) Harned, H.S., Keston, A.S., Donelson, J.G., *Ibid.*, **58**, 989 (1936).
(8) Hetzer, H.R., Robinson, R.A., Bates, R.G., *J. Phys. Chem.* **66**, 1423 (1962).
(9) Ives, D.J.G., Janz, G.J., "Reference Electrodes," p. 207, Academic Press, New York, 1961.
(10) Livingston, R.S., *J. Am. Chem. Soc.* **48**, 45 (1926).
(11) *Natl. Bur. Std. (U. S.), Circ.* **500**, "Selected Values of Chemical Thermodynamic Properties," p. 1, Washington, D. C., 1952.
(12) *Ibid.*, pp. 9, 222, 225.
(13) *Ibid.*, pp. 28, 29.
(14) Owen, B.B., Foering, L., *J. Am. Chem. Soc.* **58**, 1575 (1936).

RECEIVED for review July 5, 1965. Accepted December 23, 1965.

Phase Equilibria in the System Hydrazine Perchlorate–Water

L. T. CARLETON[1] and R. E. LEWIS
Aerojet-General Corporation, Azusa, Calif.

Phase equilibria between hydrazine monoperchlorate and water were determined experimentally. The relation of solubility to temperature was completely defined. Important features include the limiting melting temperature of the salt (142.4° C.), the occurrence of a solid hydrate decomposing at 64° C., and of a eutectic point at −4.1° C. and 80% water. A further determination was made of pressures of water vapor in equilibrium with the condensed phases from 5.0 to 75.6° C. These experiments identified the hydrate as $N_2H_5ClO_4 \cdot \frac{1}{2} H_2O$, and fixed the quadruple point at 64° C., and 88 mm. of Hg.

THE PRACTICAL USE of anhydrous hydrazine monoperchlorate requires that it be isolated as free-flowing, void-free crystals of regulated size, and stored without change. Decrepitation, agglomeration, and surface caking, which are produced by traces of moisture, must be scrupulously avoided.

Thus it is necessary to define the conditions under which the salt absorbs or loses water. The equilibria among phases of the binary system, which control these tendencies, must be completely determined.

The principal experimental difficulty is the nature of the salt, which is an extremely sensitive high explosive. Quantities of more than a few milligrams must be handled with tongs and kept removed from the body.

Some of the requisite data have already been published. Christensen and Gilbert (*4*) determined the vapor pressure of water over a mixture of hydrazine perchlorate and hydrazine perchlorate hydrate in the range 24° to 59° C. They stated the hydrate contained one-half molecule of water, and decomposed into anhydrous salt and water at 60.5° C. ± 0.5° C. The same composition of the hydrate was indicated by other workers (*3, 6*). However, the existence of higher hydrates had been suggested in earlier papers, and has never been positively confirmed or disproved. Moreover, reported values of the melting point of the anhydrous salt, (*1, 3, 7, 8*) and of the solubilities in water, (*1, 3, 7*) were rather discrepant.

EXPERIMENTAL

Materials. Because a single large batch of high-purity salt was not available at the beginning of the phase equilibrium studies, it was necessary to use several different specimens. (All preparations were originally small, because of the hazards of handling.) These were prepared by neutralization in either water or isopropanol, followed by isolation of the solid salt and vacuum drying at elevated temperatures. The conditions used were known, on the basis of much previous experience with elemental analyses, titrations, melting determenations, and other tests, to give salts of high purity. An additional, final purification step was applied to all samples used in compositions of low-water content. After charging the tubes used for observation of melting points, the last trace of volatiles was removed by melting under vacuum. In this step, a slight degassing of the water-white melt was first observed, after which the evolution of gas ceased. No decomposition was observable.

The melting point of pure hydrazine perchlorate was determined in a separate experiment. Two additional specimens were used, prepared by neutralization in water, with the final product vacuum-dried as the melt, and by neutralization in isopropanol, with the solid product vacuum-dried at 60° C. The impurity of these products was estimated incidentally in determining the melting point, as described in the following section.

The hydrazine perchlorate used for determining vapor pressures was prepared by titrating pure hydrazine with pure aqueous perchloric acid to the neutral end point. A solid, presumed to be the hydrate, crystallized out, and this was vacuum-dried for 2 days. (After charging to the apparatus, this sample was also melted under vacuum, so that removal of the last vestiges of volatiles was assured.)

Descriptions and analyses of all preparations used in the various measurements are given in Table I.

Phase Equilibria. The various regions of the phase diagram were mapped by different experimental techniques, as follows:

The high-temperature region, directly below the melting point of pure salt, was defined by observing melting temperatures (temperatures of disappearance of solid phase)

---

[1] Present address: Space-General Corporation, El Monte, Calif.

Table I. Summary of Hydrazine Perchlorate Specimens Used

		Analyses, %					Theory, %	
Application	Preparation	N_2H_4	$HClO_4$	C	Cl	H_2O	N_2H_4	$HClO_4$
Solubilities in water	Aqueous neutralization, product (1) crystallized from water, or recrystallizated from (2) ethanol or (3) isopropanol. Vacuum-dried 6–18 hr. at 65° C. (4) neutralized in isopropanol, crystallized, vacuum-dried.	(2) 23.35	74.5	...	0.00	0.04	24.18	75.82
Melting temperature curves	(1) Aqueous neutralization; product vacuum-dried as melt. (2) Neutralization in isopropanol; product recrystallized from isopropanol and vacuum-dried.							
Vapor pressures	Aqueous neutralization; product vacuum-dried.	24.19	74.56	0.02	...	0.36[a]		

[a] The small analytical specimens had to be handled extensively. Their water contents are probably much higher than those of fresh preparations used in the actual measurements.

of samples of known composition, sealed in glass tubes. From 0.1 to 0.3 gram of dry powder was weighed on an analytical balance and transferred quantitatively to the open tube, prepared from 6-mm. O.D. glass tubing. The tube was attached to a vacuum rack, and the salt was melted by heating to 150° C. and degassed under vacuum. Next the tube was opened, chilled in dry ice, and distilled water was added from a graduated 100-μl. syringe provided with a long needle, while the opening was blanketed with a steady flow of dry nitrogen. The injected water froze immediately and the chilled tube was closed, evacuated, and sealed off under vacuum.

Samples of higher water content (above 35%) and correspondingly lower melting temperatures were prepared similarly but without melting or sealing under vacuum. After filling, the tubes were tightly stoppered with glass ball joints clamped into place. This simplification was possible because these samples are less subject to contamination, and less influenced by trace contaminants.

The temperature of disappearance of the solid phase (melting temperature) was determined by carefully heating each sample in a stirred oil bath. Temperatures were read on a calibrated mercury thermometer with graduations of 0.1° C. Lags due to delayed solution or supercooling were minimized by bracketing each final temperature within 0.5°, and often within 0.2°.

Samples for the ice curve were chilled in a Beckmann cryoscopic molecular-weight apparatus and the temperatures of appearance of ice were determined in the usual way. A series of points were determined by adding weighed increments of solute to an original charge of water, until the eutectic composition was reached.

The melting point of pure hydrazine perchlorate was determined separately from melting temperature curves obtained in a semimicro apparatus. The experiment is described by Carleton (*2*). A small specimen is melted in an apparatus of low heat capacity, under conditions which so approach equilibrium that a pure sample gives a long, flat isothermal plot of temperature against time. An impure sample melts with a sloping curve on which the temperature at each point is lower by an amount ΔT than the impure sample's final melting temperature, T_0. Analysis of the curve yields a straight-line plot of ΔT against reciprocal of fraction melted (the slope of which is proportional to the mole fraction of impurity). The melting point of pure salt is calculable from T_0 by adding the value of ΔT for the sample one-half melted.

Calibrated thermometers graduated in intervals of 0.1° C. and a calibrated Beckmann thermometer were used for the measurements described above.

Vapor Pressures. Equilibrium pressures of water vapor over different solid and liquid phases were measured with an isoteniscope connected to a mercury manometer. The isoteniscope is essentially a closed-end, U-tube manometer, in which the U is sealed by a small amount of liquid sample. Vapor pressure of the sample in the closed end is measured by balancing it against an adjustable inert gas pressure on the open end. The isoteniscope and manometer were immersed in a constant-temperature bath whose temperature was measured with a calibrated thermometer graduated in 0.1° C. intervals. To permit changing the amount of water in the condensed phase, a connection was provided for removing increments of water vapor through the manometer by lowering the mercury level. These increments were collected for measurement (by their vapor pressure) in a calibrated bulb of 3167-ml. capacity.

In operation, the salt, weighing 1.026 grams, was charged to the sample container and melted under vacuum. The sample container was chilled in dry ice and 100 mg. of water was weighed in. (This amount would give a condensed sample consisting of the expected hemihydrate and saturated solution.) With the sample kept chilled, the entire isoteniscope was evacuated, and the charging tube was sealed off. The mercury level in the manometer was then adjusted to permit a slow efflux of gas, and the sample was warmed. Water vapor was removed into the calibrated bulb in sufficient amount to renew the vapor in the isoteniscope approximately 50 times, and to carry off any remaining traces of air and volatile impurities. Enough water (7.1%) was retained in the sample to maintain an excess of solution in contact with the solid hydrate. Then the equilibrium vapor pressures of water over these phases were determined from 5.0° to 49.5° C., to yield the pressure-temperature relation of Curve I, Figure 1.

The composition corresponding to transition from solution + hydrate to hydrate + anhydrous salt was determined next. With the sample maintained at 19.9° C., measured increments of water were withdrawn and the vapor pressures corresponding to each new composition were noted. When a plot of vapor pressure *vs.* water content of sample showed that the transitional composition has been passed, a second series of vapor pressures were measured.

Curve II, representing the pressure of water vapor over salt and hemihydrate, was determined from 19.9° to 61.7° C. Water contents from 4.6 to 3.9% were used, as a small amount was expended in occasional purges of the vapor space. The attainment of equilibrium was assured by working up and down the curve.

Above 61.7° and below 65.8° C., the slope of Curve II changed abruptly. A new pressure-temperature curve (III)

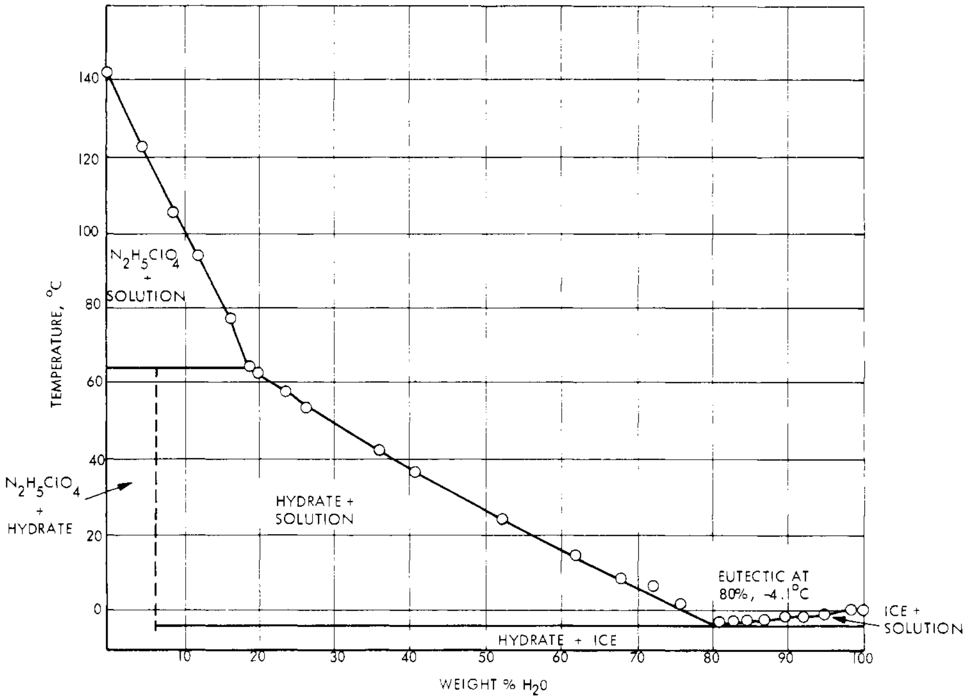

Figure 1. Vapor pressure of water over wet hydrazine perchlorate

was determined for temperatures above 65.8° C. without removing further water. Measurements were discontinued at 75.6° C. because of the onset of a slow increase of pressure with time. Although hydrazine perchlorate alone is thermally stable at even higher temperatures, possible reactions with mercury vapor from the manometer were feared. At the conclusion of these measurements, most of the remaining water was pumped from the sample tube into the vapor bulb for measurement, and the solid residue was weighed. The material balance was very close, as shown:

	Solid, grams	H_2O, gram
In:	1.026 (salt)	0.100
Out:	1.030	0.095

RESULTS AND DISCUSSION

Equilibria Among Condensed Phases. The complete solubility diagram is given in Figure 2. The curve is discontinuous at 19% H_2O, 64° C., indicating the occurrence of a hydrate of lower water content which decomposes at this temperature. At temperatures ranging from the melting temperature to 64° C., the saturated liquid is in equilibrium with pure salt, while between 64° C. and the eutectic temperature, it is in equilibrium with the hydrate. The continuous uninflected line extending below 64° C., precludes the occurrence of the higher hydrates suggested by some workers (*3 8*). The eutectic point occurs at 80% H_2O and −4.1° C. Because the proper compositions could not be preselected, the eutectic point was not directly determined by measurement but had to be located indirectly. First the temperature was fixed at the value at which both water and salt first crystallized simultaneously from chilled mixtures of slightly different compositions. The eutectic composition was next determined by extending the straight-line plot of temperature *vs.* % H_2O to intersect this temperature. A single point of higher salt concentration was also determined at 75.9% H_2O, + 1.2° C. by careful warming of this partly frozen composition in the Beckmann apparatus.

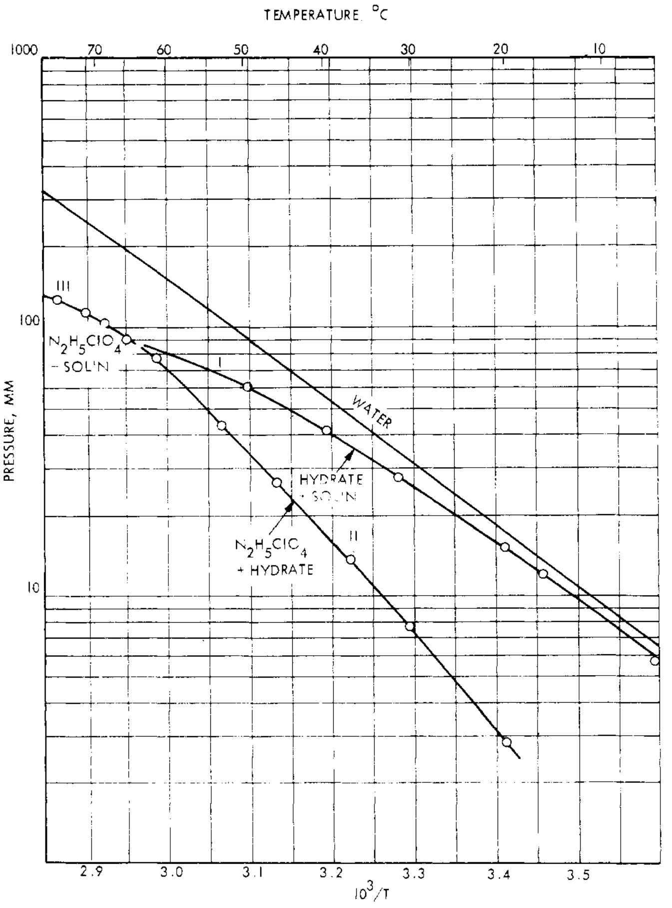

Figure 2. Complete $N_2H_5ClO_4$–H_2O equilibrium diagram

The melting temperature of pure hydrazine perchlorate was fixed at 142.4° C. by analyses of repeated melting temperature curves for two actual specimens. The results of these analyses are summarized as follows:

Preparation	Run	T_0	ΔT for 1/2 Melted, ° C.	Melting Temp. of Pure Salt, ° C.	Estimated Mole % Impurity
From aqueous neutralization,	1	142.0	0.4	142.4	0.3
vacuum-dried as melt	2	142.2	0.8	143.0	0.6
Recrystallized from refluxing	1	141.9	0.55	142.45	0.4
isopropanol and vacuum-dried	2	142.2	0.25	142.45	0.2

The changes of content of impurity in successive runs are not surprising, but indicate that prolonged melting may produce either slight decomposition or loss of volatile impurities, or perhaps both.

Vapor Pressure Curves and Composition of Hydrate. Pressures of water vapor over pairs of condensed phases in equilibrium are compiled in Table II and are plotted on Figure 1. The condensed phases are identified as

Curve I: saturated solution + hydrate (7.1% water in sample)

Curve II: hydrate + anhydrous salt (4.6 to 3.9% water)

Curve III: saturated solution + anhydrous salt (3.9%) water)

Curve III was determined immediately after Curve II by raising the temperature, with the same sample retained in the isoteniscope. The beginning of Curve III appeared as a discontinuous change in direction between points of 61.7 and 65.8° C. The solubility curve identifies this change as the locus of decomposition of hydrate to anhydrous salt and solution, occurring at 64° C. It should appear as a quadruple point on the vapor pressure plot, and is so shown in Figure 1. The vapor pressure at this point is 88 mm.

The position of Curve I relative to the line for pure water confirms the indication of the solubility diagram that no higher hydrates can exist. Strictly, although this conclusion is clearly indicated in the solubility diagram, it is only strongly suggested in the vapor pressure diagram, which does not cover the complete temperature range. A downward extension of this curve appears to approach and join the vapor pressure curve for ice, as the solubility diagram would predict.

Curve II agrees reasonably well with the similar curve determined by Christensen and Gilbert (*4*).

The hydrated phase was identified as the hemihydrate, $N_2H_5ClO_4 \cdot 1/2\ H_2O$, by observing the transition between Curves I and II. When water is removed slowly from the sample held at constant temperature, the discontinuous change in equilibrium vapor pressure occurs precisely at the hydrate composition. Figure 3 shows the effect on vapor pressure of removing small increments of water at 19.9° C. from the sample used to determine Curve I. After 6.5% H_2O remained, the rate of equilibration became very slow, and the final equilibrium pressure became uncertain. The lag in response persisted down to 5.0% H_2O. At this composition, the pressure dropped from 14.6 to 8.1 overnight. This appreciable drop indicated that the transitional composition had been passed. Without further waiting, additional water was removed and the pressure appeared stabilized at 2.8 mm. and Curve II was determined directly.

Evidently the discontinuous change between vapor pressure curves occurs at some composition close to 6.5% H_2O. However, at slightly lower water contents a new equilibrium is not immediately reached because of the slowness of the dehydration mechanism, compared with the known rapidity of hydration. Inasmuch as the crystal symmetry of hydrazine perchlorate requires a simple ratio of H_2O to salt of either 0, 1/2, 1, 1-1/2, 2, ... and does not allow intermediate values (*5*), the composition must be that of the hemihydrate, $N_2H_5ClO_4 \cdot 1/2H_2O$, which contains 6.36% H_2O.

Table II. Pressures of Water Vapor Over Hydrazine Perchlorate

Condensed Phases	Temperature, ° C.	Pressure, Mm.
Hydrate + solution	5.0	5.6
	16.0	11.8
	19.9	15.0
	31.6	27.6
	39.9	41.1
	49.5	60.3
Hydrate + salt	19.9	2.8
	30.2	7.7
	37.2	13.7
	45.9	26.4
	52.9	43.1
	61.7	78.5
Salt + solution	65.8	91.3
	68.8	104.8
	71.5	113.6
	75.6	127.4

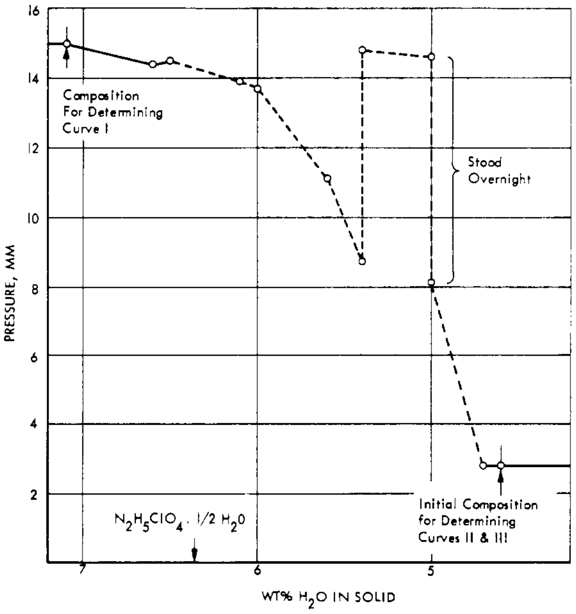

Figure 3. Variation with composition of water vapor pressure over wet hydrazine perchlorate

The heat of vaporization of water from the hemihydrate was calculated to be 17.6 kcal./mole at 20° C. from Curve II.

ACKNOWLEDGMENT

The support of the Polaris program of the U. S. Navy Special Projects Office is gratefully acknowledged.

LITERATURE CITED

(1) Barlot, J., Marsaule, S., *Compt. Rend.* **228**, 1497–1498 (1949).
(2) Carleton, L.T., *Anal. Chem.* **27**, 845–849 (1955).
(3) Carlson, B., in "Gmelins Handbuch der Anorg. Chem.", 8th ed. **23**, 556–557 (1924).
(4) Christensen, B.E., Gilbert, E.C., *J. Am. Chem. Soc.* **56**, 1897–1899 (1934).
(5) Conant, J.W., Hoogsteen, K., private communication, 1963.
(6) Panichi, U., *Z. Kryst.* **50**, 495–496 (1912).
(7) Salvadori, R., *Gazz. Chim. Ital.* **37**, 32–40 (1907).
(8) Turrentine, J.W., *J. Am. Chem. Soc.* **37**, 1105-1

RECEIVED for review May 6, 1965. Accepted December 28, 1965.

Ternary Systems: Water-Acetonitrile-Salts

JULES A. RENARD
Department of Chemical Engineering, Texas Technological College, Lubbock, Tex.

As a part of a continuing study of phase equilibrium relationship, binodal curves, tie line data, and plait point data for the systems H_2O–CH_3CN–Na_2SO_4, H_2O–CH_3CN–$Na_2S_2O_3$, H_2O–CH_3CN–Na_2CO_3, H_2O–CH_3CN–$Na_3C_6H_5O_7$, and H_2O–CH_3CN–$(NH_4)_2SO_4$ have been determined at 25° C. for the purpose of presentation of the salting-out characteristics.

THE PRESENT INVESTIGATION was undertaken as a continuing study of the phase equilibria of the ternary systems water-acetonitrile-salts (*2*). It appeared desirable to extend the knowledge of the above systems to obtain some data comparing dehydration by salting out with other methods of dehydration such as by azeotropic distillation.

EXPERIMENTAL

A preliminary series of qualitative tests have shown that some salts produce two liquid phases, some produce one liquid phase, and some precipitated from the aqueous solution by the addition of acetonitrile. Table I shows the effectiveness of the salts survey. The ternary diagrams for water-acetonitrile-Na_2CO_3, water-acetonitrile-$Na_2S_2O_3$, water-acetonitrile-Na_2SO_4, water-acetonitrile-Na citrate, and water-acetonitrile-$(NH_4)_2SO_4$ were determined in a laboratory air-conditioned to 25° C. In addition, the equilibria were reached and maintained in a water bath thermostatically controlled at 25° C. ± 0.05° C. The well known cloud point method was used throughout in the determination of the binodal curves. Owing to the great volatility of acetonitrile at room temperature, closed vials were utilized for the weighed components. Tie line data were obtained by preparing mixtures of known composition within the limits of the two-phase region, shaking mechanically to increase the rate of mass transfer and hasten the approach to equilibrium, and allowing the two layers to separate, immersed in the 25° C. bath. A centrifuge was used occasionally when one phase showed a tendency to emulsify partially with the other. The two layers were analyzed for salt content by evaporation to dryness to constant weight. The method used in this study for the graphical representations of the binodal curve and determination of the plait point was that of Coolidge (*1*). Whenever hydrates of salts were used, the calculations were corrected to the basis of anhydrous salts. Weighings were made to 0.1 mg. (Mettler balance) and final weight % expressed to nearest tenth. Data for the systems are given in Tables II and III, and binodal curves in Figure 1.

Table I. Effectiveness of Salts with Acetonitrile

Effective	Ineffective	Precipitated
Na_2CO_3	$Na_4P_2O_4 \cdot 10H_2O$	NaCl
Na_2SO_4		NH_4Cl
$Na_2S_2O_3$		
$Na_3C_6H_5O_7 \cdot 2H_2O$		
$(NH_4)_2SO_4$		

MATERIALS

The salts used were Baker analyzed reagents (99.7 + % purity) and were used without further purification. Highly purified spectro grade acetonitrile (Matheson, Coleman, and Bell) was used without further purification. The refractive index, n_D^{20} at 20° C. was 1.3440 [literature value = 1.3441 (*3*)]. Distilled water was used in all of the experimental work.

Table II. Binodal Data at 25° C., Wt. %

System		
CH_3CN	$(NH_4)_2SO_4$	H_2O
1.2	41.8	57.0
4.6	30.3	65.1
5.2	28.2	66.6
6.7	24.5	68.8
8.3	21.0	70.7
10.1	18.0	71.9
11.8	15.6	72.6
13.1	14.0	72.9
14.9	12.2	72.9
18.7	9.3	72.0
21.4	7.5	71.1
26.7	5.3	68.0
34.5	3.3	62.2
39.0	2.6	58.4
55.0	1.0	44.0
63.0	0.5	36.5
75.9	0.1	24.0
89.8	0.1	10.1
90.8	. . .	9.2

(Continued on page 170)