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)

Table II. (*Continued*)

System

| $CH_3CN$ | $Na_2S_2O_3$ | $H_2O$ |
|---|---|---|
| 3.9 | 31.1 | 65.0 |
| 5.0 | 28.2 | 66.8 |
| 6.4 | 24.8 | 68.8 |
| 8.4 | 20.6 | 71.0 |
| 10.0 | 18.7 | 71.3 |
| 12.4 | 15.3 | 72.3 |
| 14.3 | 13.3 | 72.4 |
| 16.4 | 11.4 | 72.2 |
| 19.8 | 9.0 | 71.2 |
| 23.0 | 7.5 | 69.5 |
| 27.5 | 5.5 | 67.0 |
| 34.0 | 3.7 | 62.3 |
| 38.5 | 2.6 | 58.9 |
| 42.8 | 2.3 | 54.9 |
| 47.0 | 1.9 | 51.1 |
| 51.7 | 1.6 | 46.7 |
| 56.7 | 1.0 | 42.3 |
| 64.6 | 0.5 | 34.9 |
| 84.3 | ... | 15.7 |

System

| $CH_3CN$ | $Na_3C_6H_5O_7$ | $H_2O$ |
|---|---|---|
| 3.1 | 35.8 | 61.1 |
| 3.8 | 33.7 | 62.5 |
| 4.6 | 31.5 | 63.9 |
| 5.9 | 27.8 | 66.2 |
| 9.0 | 21.8 | 69.2 |
| 11.3 | 18.2 | 70.5 |
| 14.0 | 14.7 | 71.3 |
| 14.8 | 13.8 | 71.4 |
| 17.9 | 11.1 | 71.0 |
| 18.4 | 10.9 | 70.7 |
| 21.0 | 9.1 | 69.9 |
| 23.7 | 7.7 | 68.6 |
| 28.3 | 5.9 | 65.8 |
| 31.5 | 4.6 | 63.9 |
| 36.7 | 3.5 | 59.8 |
| 40.2 | 3.0 | 56.8 |
| 41.1 | 2.8 | 56.1 |
| 43.7 | 2.3 | 54.0 |
| 46.0 | 2.0 | 52.0 |
| 52.0 | 1.2 | 46.8 |
| 56.3 | 0.9 | 42.8 |
| 62.7 | 0.4 | 36.9 |
| 63.5 | 0.4 | 36.1 |
| 66.2 | 0.3 | 33.5 |
| 73.2 | 0.3 | 26.5 |
| 80.8 | 0.2 | 19.0 |
| 82.7 | 0.1 | 17.2 |

System

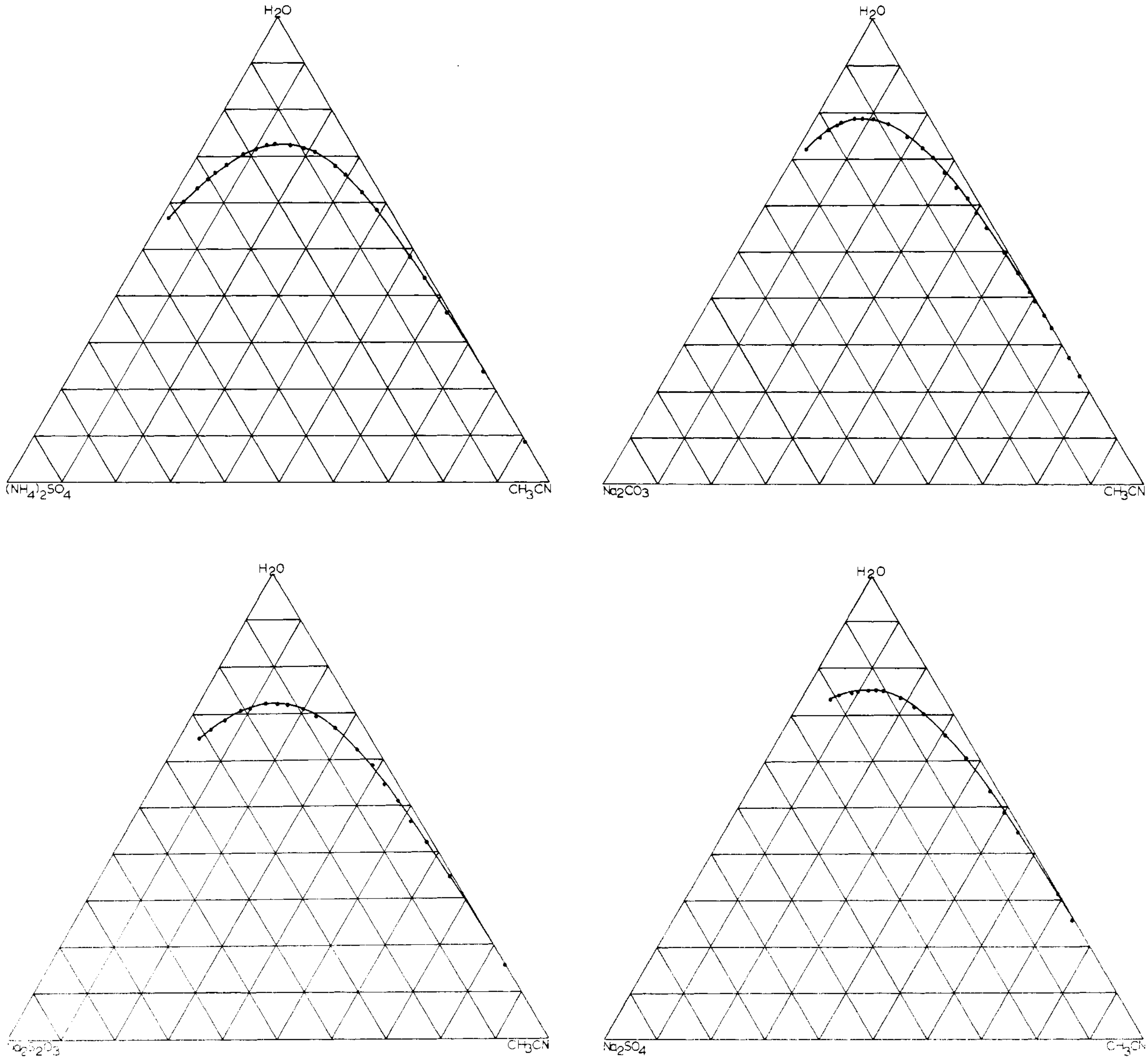
| $CH_3CN$ | $Na_2CO_3$ | $H_2O$ |
|---|---|---|
| 1.6 | 26.3 | 72.1 |
| 2.7 | 22.6 | 74.7 |
| 3.7 | 20.1 | 76.2 |
| 5.1 | 16.9 | 78.0 |
| 7.3 | 14.2 | 78.5 |
| 8.9 | 12.5 | 78.6 |
| 10.8 | 10.6 | 77.5 |
| 14.1 | 8.4 | 77.5 |
| 19.0 | 6.2 | 74.8 |
| 23.0 | 4.7 | 72.3 |
| 25.9 | 3.9 | 70.2 |
| 29.8 | 3.1 | 67.1 |
| 33.5 | 2.6 | 63.9 |
| 36.6 | 1.8 | 61.6 |
| 40.0 | 1.6 | 58.4 |
| 43.6 | 1.4 | 55.0 |
| 49.4 | 0.8 | 49.8 |
| 54.0 | 0.7 | 45.3 |
| 58.2 | 0.4 | 41.4 |
| 60.1 | 0.2 | 39.7 |
| 66.3 | 0.1 | 33.6 |
| 72.6 | 0.1 | 27.3 |
| 76.6 | ... | 23.4 |

System

| $CH_3CN$ | $Na_2SO_4$ | $H_2O$ |
|---|---|---|
| 5.6 | 21.0 | 73.4 |
| 6.3 | 19.7 | 74.0 |
| 7.0 | 18.7 | 74.3 |
| 8.1 | 17.2 | 74.7 |
| 8.9 | 16.2 | 74.9 |
| 9.7 | 15.1 | 75.2 |
| 12.0 | 12.7 | 75.3 |
| 13.4 | 11.4 | 75.2 |
| 14.9 | 10.3 | 74.8 |
| 18.9 | 7.7 | 73.7 |
| 22.1 | 6.2 | 71.7 |
| 24.7 | 5.2 | 70.1 |
| 31.0 | 3.7 | 65.3 |
| 37.0 | 2.6 | 60.4 |
| 45.3 | 1.6 | 53.1 |
| 50.8 | 1.1 | 48.1 |
| 54.6 | 0.8 | 44.6 |
| 59.8 | 0.4 | 39.8 |
| 68.6 | 0.2 | 31.2 |
| 73.2 | 0.1 | 26.7 |
| 74.2 | ... | 25.8 |

Table III. Conjugation Data at 25° C., Wt. %

| Salt-Rich Phase | | | Acetonitrile-Rich Phase | | |
|---|---|---|---|---|---|
| $(NH_4)_2SO_4$ | $H_2O$ | $CH_3CN$ | $CH_3CN$ | $H_2O$ | $(NH_4)_2SO_4$ |
| 41.8 | 57.2 | 1.0 | 90.8 | 9.2 | 0.0 |
| 41.1 | 57.8 | 1.1 | 89.8 | 10.1 | 0.1 |
| 25.1 | 68.2 | 6.7 | 75.9 | 24.0 | 0.1 |
| 11.3 | 72.8 | 15.9 | 50.0 | 48.8 | 1.2 |
| | | P.P. | 29.2 | | |
| $Na_2S_2O_3$ | $H_2O$ | $CH_3CN$ | $CH_3CN$ | $H_2O$ | $Na_2S_2O_3$ |
| 31.1 | 64.7 | 4.2 | 84.3 | 15.7 | 0.0 |
| 27.8 | 67.1 | 5.1 | 83.5 | 16.4 | 0.1 |
| 23.7 | 69.4 | 6.9 | 80.7 | 19.2 | 0.1 |
| 15.8 | 72.0 | 12.2 | 76.0 | 23.0 | 0.1 |
| 5.4 | 76.6 | 18.0 | 64.6 | 34.9 | 0.5 |
| | | P.P. | 47.0 | | |
| $Na_3C_6H_5O_7$ | $H_2O$ | $CH_3CN$ | $CH_3CN$ | $H_2O$ | $Na_3C_6H_5O_7$ |
| 35.8 | 61.1 | 3.1 | 82.7 | 17.2 | 0.1 |
| 31.7 | 63.9 | 4.4 | 80.8 | 19.0 | 0.2 |
| 21.3 | 69.4 | 9.3 | 73.2 | 26.5 | 0.3 |
| 9.8 | 70.5 | 19.7 | 62.7 | 35.9 | 0.4 |
| 6.7 | 67.1 | 26.2 | 56.0 | 43.1 | 0.9 |
| | | P.P. | 46.0 | | |
| $Na_2CO_3$ | $H_2O$ | $CH_3CN$ | $CH_3CN$ | $H_2O$ | $Na_2CO_3$ |
| 26.3 | 72.1 | 1.6 | 76.6 | 23.4 | 0.0 |
| 18.0 | 77.2 | 4.8 | 72.6 | 27.3 | 0.1 |
| 11.0 | 78.4 | 10.6 | 66.3 | 33.6 | 0.1 |
| 5.9 | 75.0 | 19.1 | 60.1 | 39.7 | 0.2 |
| | | P.P. | 43.5 | | |
| $Na_2SO_4$ | $H_2O$ | $CH_3CN$ | $CH_3CN$ | $H_2O$ | $Na_2SO_4$ |
| 21.0 | 73.4 | 5.6 | 74.2 | 25.8 | 0.0 |
| 20.2 | 73.7 | 6.1 | 73.2 | 26.7 | 0.1 |
| 18.2 | 74.4 | 7.4 | 72.5 | 27.4 | 0.1 |
| 13.0 | 75.0 | 12.0 | 68.6 | 31.2 | 0.2 |
| 6.3 | 71.7 | 22.0 | 59.8 | 39.8 | 0.4 |
| | | P.P. | 39.5 | | |



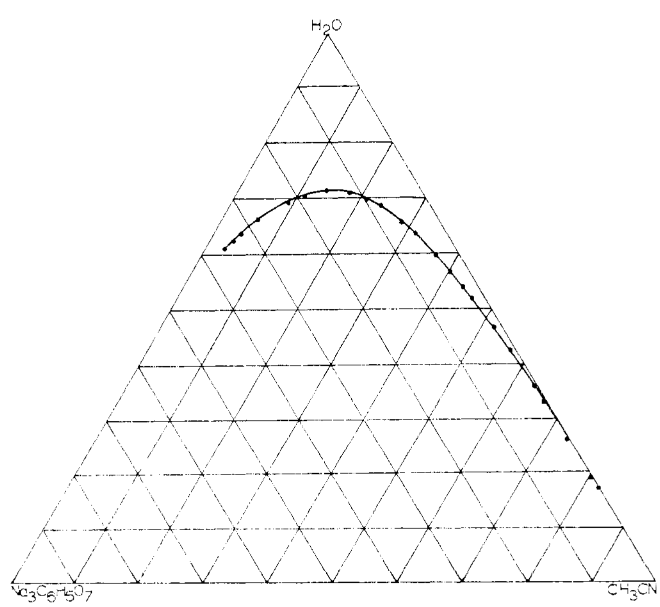




Figure 1. Ternary diagrams: water-acetonitrile-salts

## RESULTS

The data for the five systems show that $(NH_4)_2SO_4$ has the greater salting-out power followed successively by, $Na_2S_2O_3$, $Na_3C_6H_5O_7$, $Na_2CO_3$, and $Na_2SO_4$. The solubility of acetonitrile in the salt solutions increases from $(NH_4)_2SO_4$ in the following order: $Na_2CO_3$, $Na_3C_6H_5O_7$, $Na_2S_2O_3$, and $Na_2SO_4$. Other salts are being studied currently.

## LITERATURE CITED


(1) Coolidge, A.S., "International Critical Tables," Vol. III, pp. 398–403, McGraw-Hill, New York, 1928.
(2) Renard, J.A., Oberg, A.G., J. Chem. Eng. Data 10, 152 (1965).
(3) Sohio Chemical Co., "Technical Information Bulletin," p. 37, 1960.



Received for review June 14, 1965. Accepted December 31, 1965. Part of a work performed under a grant appropriated by the State of Texas.