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LITERATURE CITED

(1) Air Conditioning and Refrigeration Institute, Washington, D. C., "Properties of Commonly Used Refrigerants," 1957.
(2) American Society of Refrigerating Engineers, New York, "ASRE Refrigerating Data Book," Table 34, p. 194, 1951.
(3) Felsing, W. A., Jessen, F. W., *J. Am. Chem. Soc.* **55**, 4418-22 (1933).
(4) Felsing, W. A., Thomas, A. R., *Ind. Eng. Chem.* **21**, 1269 (1929).
(5) Keenan, J. H., Keyes, F. G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
(6) Macriss, R. A., Eakin, B. E., Ellington, R. T., Huebler, J., "Physical and Thermodynamic Properties of Ammonia-Water Mixture," *Inst. Gas Technol. Research Bull. No.* **34**, September 1964.
(7) Storvick, T. S., Ph.D. dissertation, Purdue University, Lafayette, Ind., 1959.

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Ternary Systems: Water-Acetonitrile-Salts

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Salting-out characteristics have been determined for the fluoride, chloride, iodide, bromide, acetate, carbonate, sulfate, and nitrate salts of lithium. Binodal curves and tie-line data have been obtained at 25° C. for ternary systems of water-acetonitrile and potassium acetate, lithium acetate, lithium chloride, and lithium sulfate. Various tie-line correlations and methods of determining plait points have been applied to these systems. A novel method is proposed for plait point determination.

IN TWO preceding papers (*8*, *9*) the authors have presented the salting-out characteristics of acetonitrile-water with the following salts: potassium carbonate, potassium fluoride, potassium bromide, sodium sulfate, sodium thiosulfate, sodium carbonate, sodium citrate, and ammonium sulfate. Acetonitrile having becoming an extremely versatile material, the authors decided to continue their investigation on phase equilibria of ternary acetonitrile–water–salts systems.

EXPERIMENTAL

A new series of qualitative tests on the salting-out power of other salts is presented in Table I. The ternary diagrams for water-acetonitrile–K acetate, water-aceonitrile–Li chloride, water-acetonitrile–Li acetate, and water-acetonitrile–Li sulfate 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° ± 0.05° C. As described previously (*8*, *9*), the binodal curves were determined by the well known cloud point method utilizing closed vials for the weighed components. Tie lines were constructed by preparing mixtures of known composition within the limits of the two-phase region, shaking mechanically for 20 minutes, and allowing the two layers to separate while immersed in the 25° C. bath. The two layers were analyzed for salt content by evaporation to dryness to constant weight. The plait point was determined by the method of Coolidge (*4*), and checked by the method of Othmer and Tobias (*7*), as well as by a novel method proposed below. The hydrated salts of Li acetate$\cdot 2H_2O$ and Li sulfate$\cdot H_2O$ were used. Because of some discrepancies in the quantities of moles of water of hydration, the water content was checked by thermal balance and the calculations were corrected to the basis of anhydrous salts. Weighings were made to 0.1 mg. (Mettler balance) and compositions were expressed to the nearest 0.1% by weight. Data for the systems are given in Tables II and III and binodal curves in Figures 1 and 2.

MATERIALS

The salts used (99.7+% purity) were potassium acetate (crystals), analytical reagent Mallinckrodt; lithium sulfate, Baker analyzed reagent; lithium acetate and lithium chloride, Fisher certified reagents. The acetonitrile was high-purity spectro grade (Matheson, Coleman and Bell) with a refractive index at 20° C. of 1.3440 [literature value = 1.3441 (*11*)]. Distilled water was used in all of the experimental work.

RESULTS

The data for the four systems show that K acetate has the greater salting-out power, followed successively by Li chloride, Li acetate, and Li sulfate. The solubility in the salt solutions increases from K acetate, Li sulfate, Li acetate, to Li chloride. Table I shows that of all the halogens of lithium, only Li chloride has salting-out properties.

CORRELATIONS

Correlations of tie-line data serve the dual purpose of assisting in interpolation of the tie-line data and extrapolation of the data to the plait point. The correlations involve graphs of the binodal curve, such as the diagrams in Figures 1 and 2, similar plots on rectangular coordinates, or plots of composition variables

Table I. Effectiveness of Salts with Acetonitrile

Effective	Ineffective	Precipitated
LiCl	LiBr	LiF
$LiC_2H_3O_2$	LiI	Li_2CO_3
Li_2SO_4	$LiNO_3$	

Table II. Binodal Data at 25° C.

(Weight per cent)

System

CH_3CN	$KC_2H_3O_2$	H_2O
4.9	66.7	28.4
5.4	63.1	31.5
6.0	58.0	36.0
6.8	51.4	41.8
8.0	42.1	49.9
10.0	32.2	57.8
12.5	24.9	62.6
14.0	21.7	64.3
15.3	19.4	65.3
17.2	16.2	66.6
19.4	13.6	67.0
20.8	12.1	67.1
22.7	10.5	66.8
24.9	9.0	66.1
29.8	6.5	63.7
39.0	4.1	56.9
49.0	2.5	48.5
56.4	1.8	41.8
58.9	1.5	39.6
70.0	0.8	29.2
87.0	0.2	12.8
94.0	0.2	5.8
96.0	0.2	3.8
97.5	0.2	2.3
98.7	0.1	1.2

System

CH_3CN	$LiC_2H_3O_2$	H_2O
6.7	29.5	63.8
7.1	28.1	64.8
8.0	26.2	65.8
9.2	23.5	67.3
11.1	19.5	69.4
13.4	16.0	70.6
15.7	13.2	71.1
18.3	10.7	71.0
21.4	8.5	70.1
24.7	6.8	68.5
28.8	5.3	65.9
35.0	3.8	61.2
44.2	2.3	53.5
54.4	1.5	44.1
62.5	0.9	36.6
70.0	0.8	29.2
79.8	0.3	19.9
88.8	0.1	11.1
91.0	0.1	8.9
92.0	0.0	8.0

System

CH_3CN	LiCl	H_2O
14.0	27.8	58.2
13.8	26.7	59.5
13.9	25.1	61.0
14.1	20.9	65.0
14.5	19.0	66.5
15.1	17.5	67.4
15.7	16.3	68.0
16.3	15.2	68.5
17.6	13.4	69.0
18.8	11.8	69.4
20.3	10.2	69.5
21.7	9.0	69.3
23.1	8.0	68.9
25.6	6.7	67.7
29.4	5.1	65.5
33.3	4.2	62.5
38.9	3.0	58.1
45.4	2.0	52.6
53.5	1.7	44.8
61.9	1.1	37.0
67.7	0.8	31.5
70.4	0.7	28.9
81.0	0.4	18.6
86.6	0.3	13.1
93.1	0.2	6.7
94.2	0.1	5.7

System

CH_3CN	Li_2SO_4	H_2O
3.9	20.9	75.2
4.7	19.6	75.7
5.3	18.6	76.1
6.4	17.3	76.3
7.2	16.2	76.6
8.0	15.2	76.8
8.7	14.5	76.8
9.5	13.7	76.8
10.7	12.4	76.9
13.6	10.2	76.2
16.6	8.4	75.0
16.7	8.3	75.0
22.0	5.9	72.1
31.7	3.3	65.0
37.7	2.2	60.1
43.1	1.8	55.1
52.7	1.0	46.3
64.2	0.5	35.3
70.4	0.3	29.3
70.9	0.3	28.8
78.7	0.1	21.2

Table III. Tie-Line Data at 25° C.

(Weight per cent)

Salt-Rich Phase				Acetonitrile-Rich Phase		
$KC_2H_3O_2$	H_2O	CH_3CN		CH_3CN	H_2O	$KC_2H_3O_2$
66.7	28.4	4.9		98.7	1.2	0.1
60.9	33.6	5.5		97.5	2.3	0.2
49.8	43.3	6.9		96.0	3.8	0.2
35.6	55.1	9.3		92.5	7.3	0.2
25.0	62.5	12.5		88.9	10.8	0.3
10.6	66.9	22.5		78.5	21.1	0.4
			P.P.[a]	50.4	47.1	2.5
$LiC_2H_3O_2$	H_2O	CH_3CN		CH_3CN	H_2O	$LiC_2H_3O_2$
29.5	63.8	6.7		92.0	8.0	0.0
19.8	69.2	11.0		88.8	11.1	0.1
6.8	68.7	24.5		73.2	26.0	0.8
			P.P.	49.0	49.0	2.0
LiCl	H_2O	CH_3CN		CH_3CN	H_2O	LiCl
27.8	58.2	14.0		94.2	5.7	0.1
19.3	66.0	14.7		86.6	13.1	0.3
6.9	67.4	25.7		70.7	28.8	0.5
			P.P	47.3	50.9	1.8
Li_2SO_4	H_2O	CH_3CN		CH_3CN	H_2O	Li_2SO_4
20.9	75.2	3.9		85.3	14.7	0.0
19.6	75.7	4.7		84.5	15.5	0.0
14.5	76.8	8.7		78.3	21.6	0.1
8.4	75.0	16.6		70.4	29.3	0.3
5.6	72.2	22.2		64.2	35.3	0.5
			P.P.	43.4	54.9	1.7

[a] Plait point.

other than weight or mole fractions. In addition to the solubility curves, plots are made of some composition variable in one phase *vs.* either the same variable or some other variable in the other phase.

Nernst (*6*) proposed that the ratio of X_{31}/X_{11} to X_{32}/X_{22} is constant, where X_{ij} is the weight fraction of component *i* in phase *j*. Components 1, 2, and 3 are acetonitrile, salt, and water, respectively; phases 1 and 2 are the acetonitrile-rich and salt-rich phases, respectively. Hand (*5*) proposed two correlations, the first of which said that the quantity $(X_{11}/X_{31}\text{-}X_{12}/X_{32})/(X_{21}/X_{31}\text{-}X_{22}/X_{32})$ is constant. The constants of these two correlations for the systems of this study are given in Table IV. Brancker, Hunter, and Nash (*2*) proposed a correlation based on a reference coordinate system. Bachman (*1*) applied their correlation to ordinary rectangular coordinates, obtaining a linear relation between X_{11} and X_{11}/X_{22}. Hand's second correlation predicted a linear relationship between log (X_{31}/X_{11}) and log (X_{32}/X_{22}). Othmer and Tobias (*7*) found a linear relationship between log $[(1 - X_{11})/X_{11}]$ and log $[(1 - X_{22})/X_{22}]$. Application of these methods to the systems of this study showed rather poor correlations, as shown in Figures 3 and 4 for potassium acetate. The other salts gave no better plots.

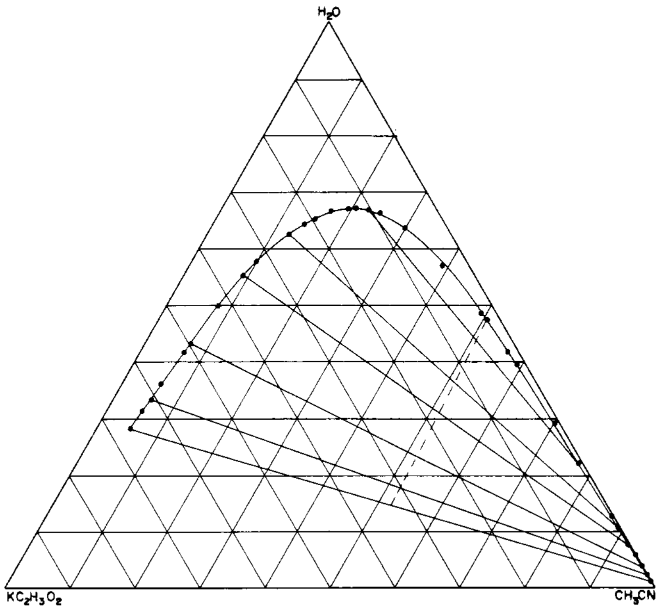

Figure 1. Ternary diagram for H_2O-CH_3CN-$KC_2H_3O_2$

——————— Tie lines

– – – – – – – – – Locus of midpoints

Coolidge (*4*) proposed a plot of X_{22} *vs.* X_{11} on a triangular diagram as a tie-line correlation (conjugate curve). Sherwood (*10*) proposed a similar plot of X_{31} *vs.* X_{12}. Determination of the plait point by these methods requires extrapolation of nonlinear curves over a considerable distance. The uncertainty in-

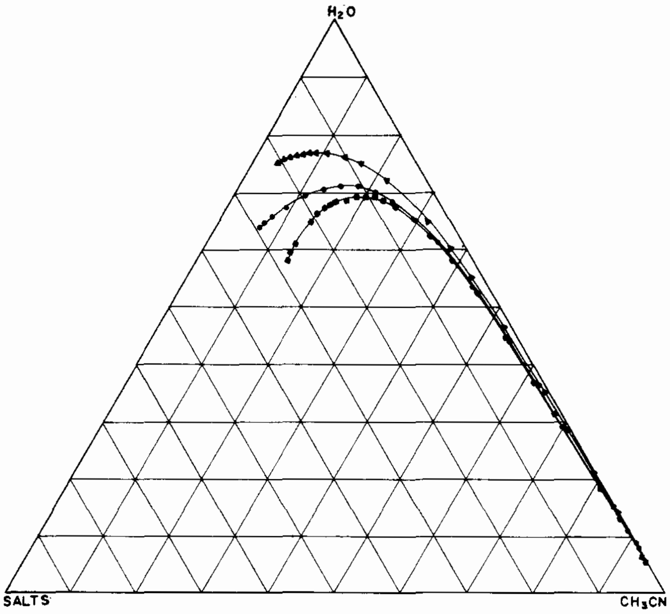

Figure 2. Ternary diagrams for H_2O-CH_3CN-salts

▲ Li_2SO_4
● $LiC_2H_3O_2$
■ LiCl

Table IV. Nernst and Hand Constants

Salt	Nernst Constant		Hand Constant	
	Range	Av.	Range	Av.
$KC_2H_3O_2$	0.0286–0.0509	0.0437	20.23–36.20	24.91
$LiC_2H_3O_2$	0.0356–0.0408	0.0381	24.65–35.25	29.39
LiCl	0.0289–0.0442	0.0382	23.72–35.45	27.93
Li_2SO_4	0.0392–0.0521	0.0453	19.07–23.84	21.22

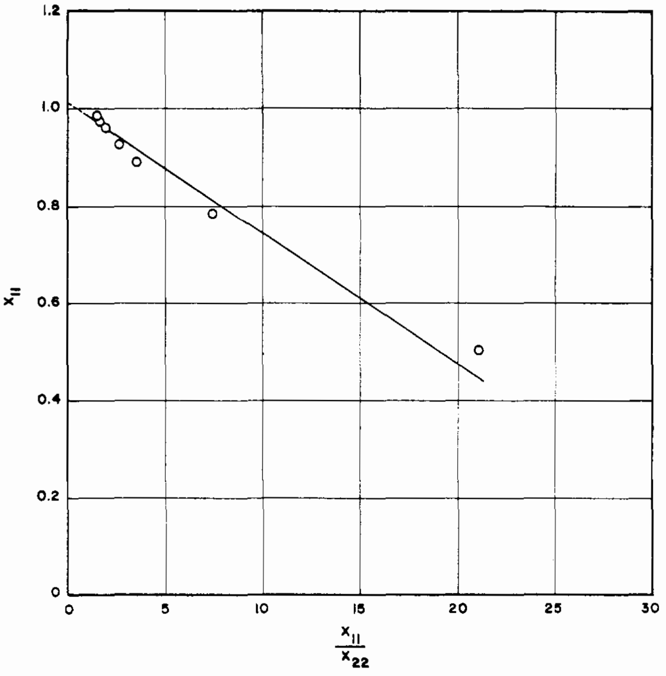

Figure 3. Bachman plot for H_2O-CH_3CN-$KC_2H_3O_2$

troduced by this extrapolation can be reduced significantly by employing the law of rectilinear diameters, which has been used to advantage in determining critical densities of fluids (*3*) and critical solution compositions of binary solutions (*12*). The locus of the midpoints of the tie lines exhibits almost no curvature, and requires very little extrapolation to the plait point, as shown by the dashed line in Figure 1. Plait points determined by the methods of Coolidge and of Othmer and Tobias, and by rectilinear diameters, are presented in Table V.

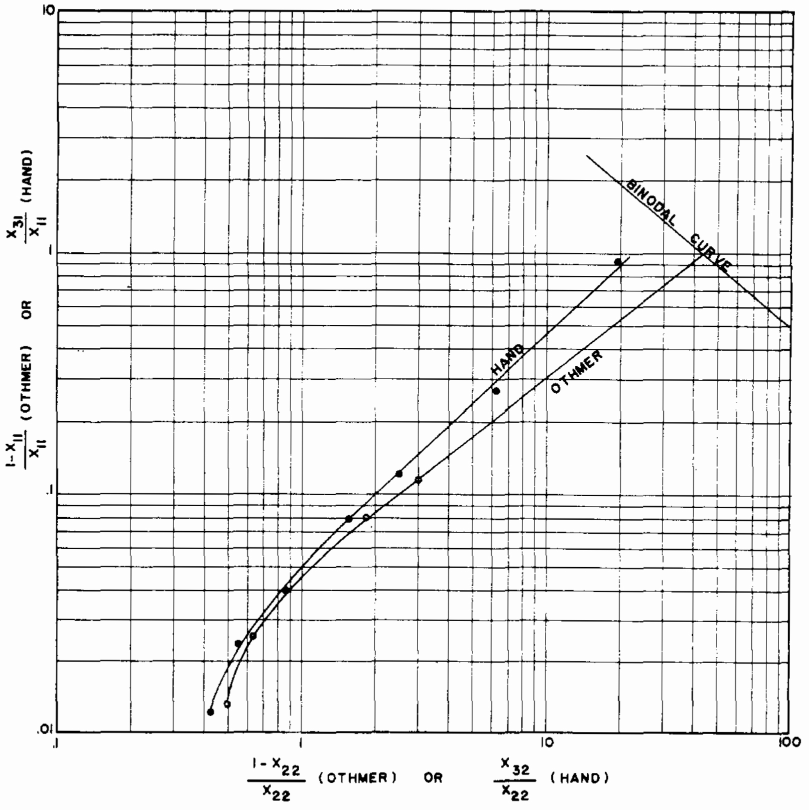

Figure 4. Hand (*11*) and Othmer-Tobias plots for H_2O-CH_3CN-$KC_2H_3O_2$

Table V. Plait Points

Salt	Coolidge			Othmer and Tobias			Rectilinear Diameters		
	X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
$KC_2H_3O_2$	0.515	0.022	0.463	0.501	0.024	0.475	0.504	0.025	0.471
$LiC_2H_3O_2$	0.492	0.020	0.488	0.483	0.018	0.499	0.490	0.020	0.490
LiCl	0.480	0.020	0.500	0.488	0.019	0.493	0.473	0.018	0.509
Li_2SO_4	0.435	0.017	0.548	0.427	0.017	0.556	0.434	0.017	0.549

The authors conclude that the tie lines for the present systems are most conveniently correlated by the conjugate curve of Coolidge, or of Sherwood, with the plait point estimated by rectilinear diameters.

LITERATURE CITED

(1) Bachman, I., *Ind. Eng. Chem., Anal. Ed.* **12,** 38 (1940).
(2) Brancker, A. V., Hunter, T. G., Nash, A. W., *Ibid.*, **12,** 35 (1940).
(3) Cailletet, L., Mathias, *Compt. Rend.* **102,** 1202 (1886).
(4) Coolidge, A. S., "International Critical Tables," Vol. III, pp. 398–403, McGraw-Hill, New York, 1928.
(5) Hand, D. B., *J. Phys. Chem.* **34,** 1961 (1930).
(6) Nernst, W., *Z. Physik. Chem.* **8,** 110 (1891).
(7) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.* **34,** 693 (1942).
(8) Renard, J. A., J. CHEM. ENG. DATA **11,** 169 (1966).
(9) Renard, J. A., Oberg, A. G., *Ibid.*, **10,** 152 (1965).
(10) Sherwood, T. K., Pigford, R. L., "Absorption and Extraction," 2nd ed., p. 402, McGraw-Hill, New York, 1952.
(11) Sohio Chemical Co., "Technical Information Bulletin," p. 37, 1960.
(12) Weber, H. C., Meissner, H. P., "Thermodynamics for Chemical Engineers," p. 466, Wiley, New York, 1957.

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Volume Changes of Mixing: Dichloromethane with Acetone and Methyl Acetate

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Volume-change-of-mixing data are reported for the acetone-dichloromethane and methyl acetate–dichloromethane systems at 25° and 30° C. These data together with data from the literature provide a basis for comparison of both ΔV and ΔH for several related systems.

THIS paper reports the results of measurements (*4*) of volume changes of mixing for the binary liquid systems acetone-dichloromethane and methyl acetate–dichloromethane. Data were taken at 25° and 30° C. with a dilatometer that has previously been described (*6*), and are listed in Table I. The measurements were made at atmospheric pressure in a bath controlled to ±0.001° C. The data are believed to be accurate to within ± 1%.

The results at 25° C. are correlated by the following equations, where ΔV is in cubic centimeters per gram mole and x is mole fraction.

For acetone (1)-dichloromethane (2) at 25° C.:

$$\frac{\Delta V}{x_1x_2} = 0.5118 - 0.0678x_1 + 0.1964x_1^2$$

For methyl acetate (1)–dichloromethane (2) at 25° C.:

$$\frac{\Delta V}{x_1x_2} = 1.2672 - 0.0771x_1$$

The root mean-square deviations of the data points from these correlations are less than 0.5%.

A comparison of the data at 30° C. with those at 25° C. reveals that ΔV decreases with increasing temperature for acetone-dichloromethane, whereas it shows the opposite trend for methyl acetate–dichloromethane. To a first approximation $d(\Delta V/x_1x_2)/dT$ is -0.01 fo acetone-dichloromethane and $+0.005$ for methyl acetate–dichloromethane between the temperatures of 25° and 30° C.

Heats of mixing for these same systems (and from the same lots of the components) were reported by Winterhalter and Van Ness (*7*). In addition, ΔV and ΔH data are available in the literature for the acetone–carbon tetrachloride (*1, 2*) and acetone-chloroform (*3, 5*) systems. The ΔV and ΔH curves for all four systems, shown in Figure 1, allow some interesting comparisons.

Note first that the ΔV curves for acetone-CCl_4 and acetone-$CHCl_3$ are quite similar, skewed, and mostly negative. On the other hand, the ΔH curves for these systems are very different. The acetone-CCl_4 system gives relatively small positive values of ΔH (endothermic), while for acetone-$CHCl_3$, ΔH has large negative values (exothermic). For the acetone-CH_2Cl_2 system ΔV becomes entirely positive and symmetrical. ΔH is negative with values less than half those for acetone-$CHCl_3$. Comparison of the methyl acetate-CH_2Cl_2 and acetone-CH_2Cl_2 systems shows that although the ΔH curves are very close the ΔV values for methyl acetate are more than twice those for acetone.

The heats of mixing should reflect the strengths of the intermolecular forces, and no doubt the negative heats exhibited by the systems containing $CHCl_3$ and CH_2Cl_2

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