Acid	$A/1000$	B
Glycine	7.12 ± 0.02^a	14.47 ± 0.05
l-Alanine	7.22 ± 0.05	14.81 ± 0.10
l-α-Amino-n-butyric acid	8.49 ± 0.04	17.86 ± 0.09
dl-Norvaline	6.27 ± 0.01	12.89 ± 0.05
dl-Norleucine	5.98 ± 0.03	12.05 ± 0.06
Isoleucine	6.27 ± 0.05	13.05 ± 0.23
Cycloleucine	6.44 ± 0.02	13.36 ± 0.06
α-Amino-isobutyric acid	6.57 ± 0.03	13.90 ± 0.03
l-Valine	8.49 ± 0.04	17.99 ± 0.08
l-Leucine	7.86 ± 0.04	16.28 ± 0.09
l-Methionine	6.53 ± 0.05	12.67 ± 0.10
l-Phenylalanine	8.04 ± 0.04	16.22 ± 0.08
l-Proline	5.04 ± 0.04	10.32 ± 0.09

^{a}Standard deviations obtained from a least squares calculation, in which the weighting factor, $1/\sigma^2_P$, was applied.

Table III. Standard Thermodynamic Quantities
for the Sublimation of Some α-Amino Acids at 455° K.

Acid	ΔS, Cal./Deg-Mole	ΔH, Kcal./Mole	ΔG, Kcal./Mole
Glycine	53.0 ± 0.2	32.6 ± 0.1	8.48 ± 0.1
l-Alanine	54.6 ± 0.5	33.0 ± 0.2	8.17 ± 0.3
l-α-Amino-n-butyric acid	68.6 ± 0.4	38.9 ± 0.2	7.73 ± 0.3
dl-Norvaline	45.8 ± 0.2	28.7 ± 0.1	7.87 ± 0.1
dl-Norleucine	42.0 ± 0.3	27.4 ± 0.1	8.32 ± 0.2
Isoleucine	46.5 ± 1.0	28.7 ± 0.2	7.54 ± 0.5
Cycloleucine	48.0 ± 0.3	29.5 ± 0.1	7.69 ± 0.2
α-Amino-isobutyric acid	50.4 ± 0.1	30.1 ± 0.1	7.17 ± 0.2
l-Valine	69.1 ± 0.4	38.9 ± 0.2	7.46 ± 0.3
l-Leucine	61.3 ± 0.4	36.0 ± 0.2	8.11 ± 0.3
l-Methionine	44.8 ± 0.5	29.9 ± 0.2	9.49 ± 0.3
l-Phenylalanine	61.0 ± 0.4	36.8 ± 0.2	9.04 ± 0.3
l-Proline	34.0 ± 0.4	23.1 ± 0.2	7.62 ± 0.3

Table IV. Relative Mass Spectrometer Sensitivities
for Some α-Amino Acids

Acid	Calcd. From This Work	Empirically Determined (2)
Glycine	0.88	0.88
Alanine	0.88	0.87
l-α-Amino-n-butyric acid	0.84	0.89
Valine	0.96	0.96
Isoleucine	1.00	1.00

total fragment ion currents represented by the $(P\text{-}COOH)^+$ peak for each amino acid. These sensitivities are obtained from

$$S = \%(P\text{-}COOH)^- \ (I. \ C.) \ (v.p.)^{1/2}$$

where $I. \ C.$ is the ionization cross section. A comparison of the calculated values and those determined empirically are listed in Table IV. The good agreement between the calculated values and the only available empirical values indicates the utility of vapor pressure measurements in the determination of mass spectrometer sensitivities for substances of low vapor pressure.

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Ternary Systems: Water–Acetonitrile–Salts

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Phase equilibria data—binodal curves, tie lines, conjugation lines, and plait point—for the systems H_2O–CH_3CN–K_2CO_3, H_2O–CH_3CN–KF, and H_2O–CH_3CN–KBr are presented. The characteristics of these systems are correlated with the vapor pressure and solubility data.

ACETONITRILE and water form a binary azeotrope having 83.7 wt. % acetonitrile and boiling at 76.5° C. (760 mm. of Hg). During dehydration of acetonitrile, this mixture is usually formed. If the last trace of water must be removed, suitable entrainers which form a ternary azeotrope with the nitrile and water are used. Pratt (12) has shown the composition of the ternary azeotrope utilizing benzene and trichlorethylene. The same author mentioned the separation of water from acetonitrile by salting out but no reference is given. No data on dehydration of acetonitrile by liquid-liquid extraction is found in the literature; therefore, the authors decided to investigate the possibilities of salting out acetonitrile with different salts.

EXPERIMENTAL

A series of qualitative tests showed that some salts are effective while others are ineffective in salting out or are themselves precipitated from the aqueous solutions by the addition of acetonitrile. Table I summarized the effectiveness of the salt survey.

The ternary diagrams were determined in a laboratory air conditioned to 25° C. In addition, the experiments were conducted in a water bath thermostatically controlled at 25° C. ± 0.05° C.; the well known cloud point method was used for determining the boundary of the two-layer region. Tie lines were obtained by preparing mixtures of known over-all composition within the limits of the two-phase region, shaking thoroughly until equilibrium was attained, and allowing the two layers to separate. The two layers were analyzed for salt content by evaporation to dryness to constant weight. The system of graphical representations of the binodal and conjugation curves and interpolation to the plait point was that of Coolidge (2). Weighings were made to 0.1 mg. (Mettler balance) and final weight per cents expressed to nearest tenth. Data for the systems are given in Tables II and III, and in Figures 1, 2, and 3.

MATERIALS

The salts used were Baker analyzed reagents (99.4+% purity) and were used without further purification. Highly purified spectro grade acetonitrile (Eastman Organic Chemicals) was used without further purification. The refractive index, n_D^{20}, was 1.3440 [literature value = 1.3441 (13)]. Distilled water was used in all of the experimental work.

DISCUSSION OF THE TERNARY DATA

The data for the three systems show that potassium carbonate is highly efficient in dehydrating acetonitrile followed closely by potassium fluoride. Potassium bromide is a very poor third as it retains 21% acetonitrile, and in addition dehydrates only to 83.5%. Other salts are currently being studied.

Table I. Effectiveness of Salts

Effective	Ineffective	Precipitated
K_2CO_3	KI	KCl
KF		K_2SO_4
KBr		
$KC_2H_3O_2$		
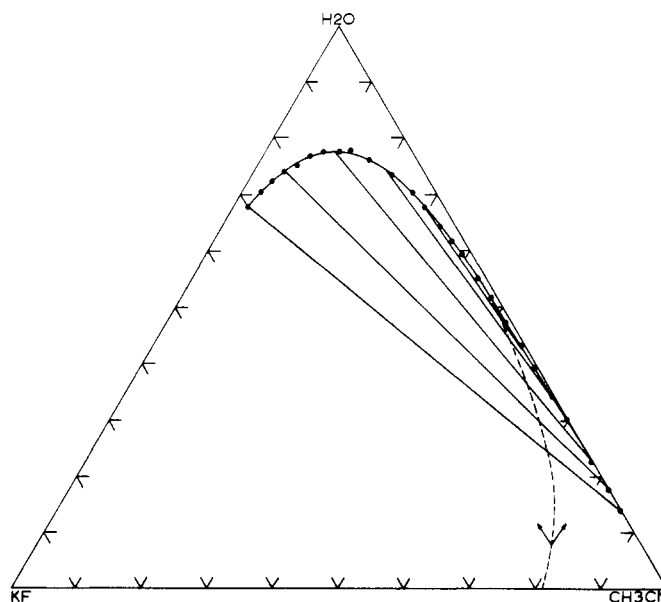
Figure 2. Ternary diagram: H_2O–CH_3CN–KF
——————————————— Tie lines
-------------------------------- Conjugation line
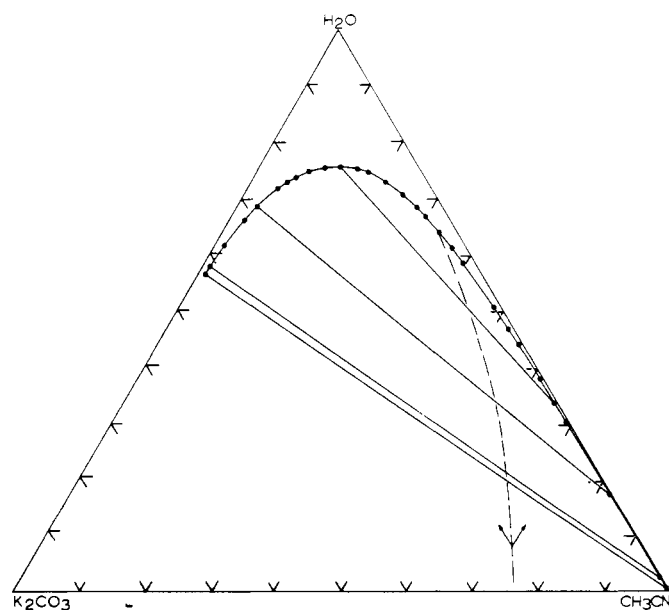
Figure 1. Ternary diagram: H_2O–CH_3CN–K_2CO_3
——————————————— Tie lines
-------------------------------- Conjugation line
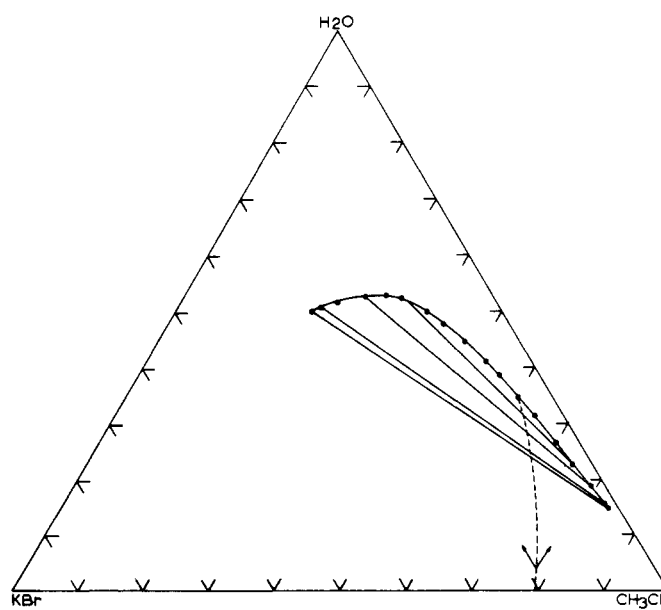
Figure 3. Ternary diagram: H_2O–CH_3CN–KBr
——————————————— Tie lines
-------------------------------- Conjugation line
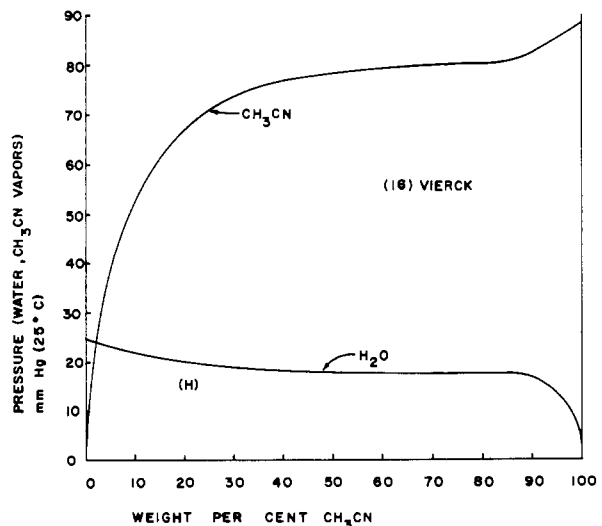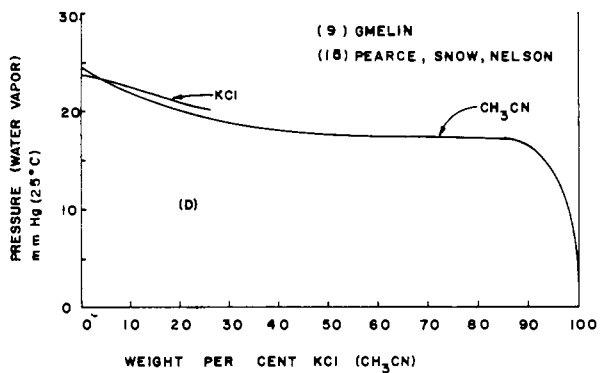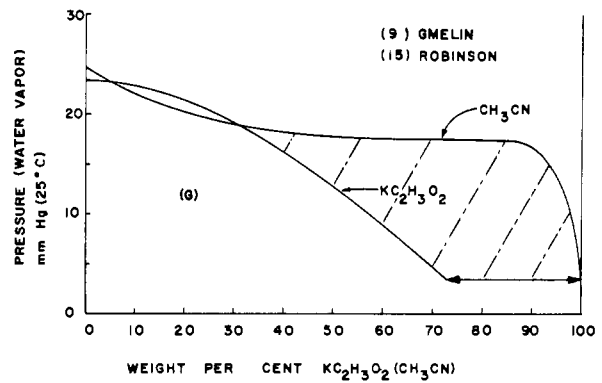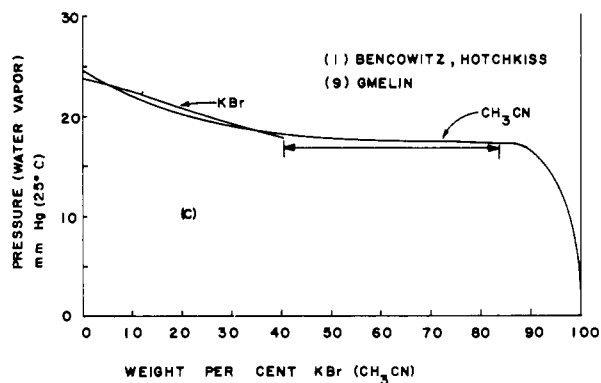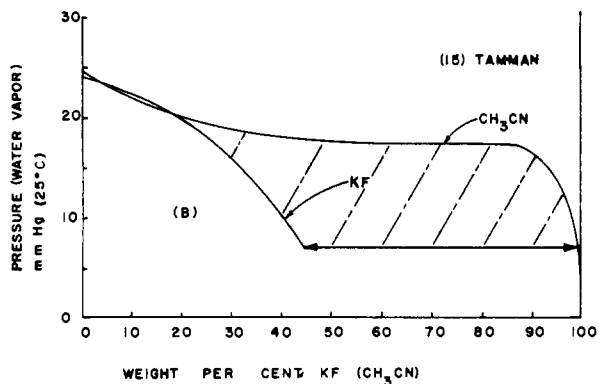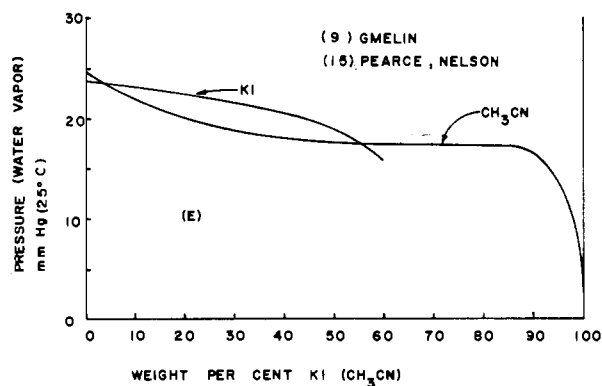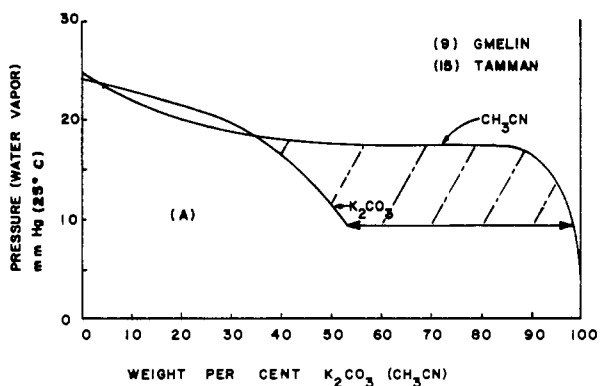
Figure 4. Vapor pressure curves

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

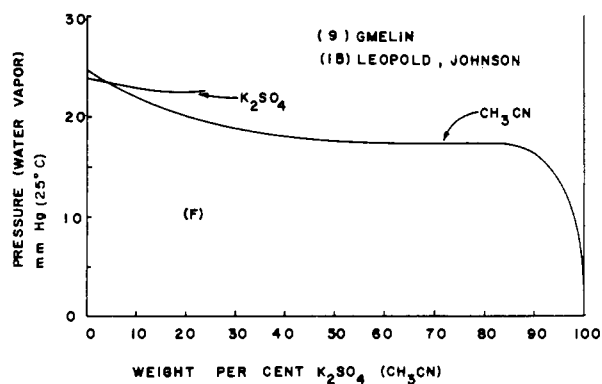| System, CH_3CN-K_2CO_3-H_2O			System, CH_3CN-KF-H_2O		
CH_3CN	K_2CO_3	H_2O	CH_3CN	KF	H_2O
1.1	42.0	56.9	2.2	30.0	67.8
1.4	39.7	58.9	2.9	26.9	70.2
2.7	31.2	66.1	3.8	24.1	72.1
4.7	23.4	71.9	4.7	21.5	73.8
5.6	21.5	72.9	6.4	19.0	74.7
6.5	19.9	73.6	7.4	16.1	76.5
6.8	19.5	73.7	8.9	13.8	77.3
8.1	17.4	74.5	11.4	11.4	77.2
8.8	16.0	75.2	13.0	9.4	77.6
9.1	15.2	75.7	16.6	7.5	75.9
10.1	14.4	75.5	21.6	5.2	73.3
10.3	13.9	75.8	26.0	3.8	70.2
10.9	13.2	75.9	29.2	3.1	67.7
13.2	11.2	75.6	33.3	2.4	64.3
13.4	11.3	75.3	36.4	1.9	61.7
15.4	9.6	75.0	39.1	1.7	59.2
17.2	8.3	74.5	43.6	1.4	55.0
17.9	7.8	74.3	51.8	1.0	47.2
20.5	6.6	72.9	60.0	0.6	39.4
21.3	6.4	72.3	65.2	0.4	34.4
24.6	5.0	70.4	69.0	0.2	30.8
27.6	4.0	68.4	77.0	0.1	22.9
29.7	3.7	66.6	82.0	...	18.0
36.7	2.3	61.0	86.1	...	14.9
38.1	2.6	59.3			
39.4	2.0	58.6			
47.9	1.4	50.7	System, CH_3CN-KBr-H_2O		
49.3	1.3	49.4	CH_3CN	KBr	H_2O
51.9	1.0	47.1	20.9	29.0	50.1
53.5	1.0	45.5	23.8	24.4	51.8
53.6	1.0	45.4	27.7	19.5	52.8
54.8	0.9	44.3	30.8	16.1	53.0
61.6	0.6	31.8	33.3	14.3	52.4
64.1	0.4	35.5	38.5	11.5	50.0
66.1	0.3	33.6	42.0	10.2	47.8
82.0	...	18.0	46.9	8.4	44.7
96.2	...	3.8	51.8	7.1	41.1
99.0	...	1.0	55.0	6.3	38.7
			59.8	5.5	34.7
			63.9	4.7	31.4
			69.6	3.7	26.7
			74.2	2.9	22.9
			79.2	2.3	18.8
			82.6	1.7	15.7
			83.5	1.5	15.0

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

Salt Rich Phase			Organic Rich Phase		
K_2CO_3	H_2O	CH_3CN	CH_3CN	H_2O	K_2CO_3
42.0	56.9	1.1	99.0	1.0	...
40.6	58.2	1.2	96.2	3.8	...
28.0	68.8	3.2	82.0	18.0	...
11.8	75.5	12.7	66.3	33.4	0.3
		P.P.	33.2		
KF	H_2O	CH_3CN	CH_3CN	H_2O	KF
30.0	67.8	2.2	86.1	14.9	...
21.1	74.0	4.9	82.0	18.0	...
12.0	77.4	10.6	77.0	22.9	0.1
5.9	74.2	19.6	69.0	30.8	0.2
		P.P.	46.5		
KBr	H_2O	CH_3CN	CH_3CN	H_2O	KBr
29.0	50.1	20.9	83.5	15.0	1.5
27.2	50.8	22.0	82.6	15.7	1.7
19.2	52.9	27.9	78.9	18.8	2.3
13.7	52.0	34.3	74.2	23.9	2.9
		P.P.	55.4		

Table IV. Solubility Data (25°C.) (10, 13)

Graph		In Water, Wt. %	In CH_3CN, Wt. %
A.	K_2CO_3	52.85	Insoluble
B.	KF	48.00 (18° C.)	Insoluble
C.	KBr	40.44	0.02
D.	KCl	26.19	Insoluble
E.	KI	59.67	1.90
F.	K_2SO_4	23.76	Insoluble
G.	$KC_2H_3O_2$	72.95	Insoluble

lowering the vapor pressure of water. The salting-in effect of KI is due to the appreciable solubility of this salt in CH_3CN and its ineffective lowering of the vapor pressure of water. Preliminary tests indicate that $KC_2H_3O_2$ is an effective salting-out agent, and the curves of graph F suggest this conclusion. Graph G, while not needed to predict results, is included for completeness. It presents the partial pressures of water and CH_3CN over all possible mixtures of these two compounds.

CORRELATIVE DATA

Frankforter and Frary (8) first reported the salting-out power of KF and K_2CO_3 for alcohols. Early correlations have been in terms of lyotropic series (3–6). Fogg (7) established the effect of dissolved salts on the relative volatilities of mixtures of ethylene glycol and water. Stanton (14) and Meissner and Stokes (11) found it possible to predict the dehydration power of several salts from the vapor pressure of water over the stable hydrate.

Since no one has made use of complete vapor pressure and solubility data, the object of this section is to show that these data may be used readily to predict both the probability and extent of the salting out of an organic compound from its water solution. Data from the literature were used to prepare the vapor pressure curves of graphs A to H (Figure 4) and the solubility information in Table IV.

Thermodynamic considerations have shown that the solution of a salt either in water or in an organic compound lowers the vapor pressure of the water or organic compound. In the case of a one-phase binary mixture of water and organic compound, the addition of a salt soluble only in the water will lower the vapor pressure of water but raise the vapor pressure of the organic compound, and the binary liquid will separate into two liquid phases which are in equilibrium. The vapor pressure of each component will be the same in the two phases, and the extent of salting out will be determined by the resulting vapor pressures.

K_2CO_3, KF, and KBr are insoluble in CH_3CN and are effective in lowering the vapor pressure of water. KCl and K_2SO_4 are insoluble in CH_3CN but are ineffective in

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