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Received for review April 19, 1976. Resubmitted January 21, 1977. Accepted June 14, 1977.

Extraction of Acetonitrile from Aqueous Solutions. 1. Ternary Liquid Equilibria

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Ternary liquid equilibrium data at 31 °C for the system water–acetonitrile–chlorobenzene, water–acetonitrile–xylene, and water–acetonitrile–*n*-butyl acetate are presented. The tie-line data are well correlated by the methods of Othmer–Tobias and Hand. The selectivity increases in the order xylene, chlorobenzene, and *n*-butyl acetate. The system water–acetonitrile–chlorobenzene exhibits solutropy.

The importance of phase equilibrium data for ternary liquid systems in the design of any liquid–liquid extraction process need not be over emphasized. The experimental phase equilibrium data are preferred to that from theoretical predictions as the theoretical data do not always represent actual behavior and the basic thermodynamic data for the predictions are not available for several systems.

The separation of acetonitrile from aqueous solutions is of particular interest in wake of the development of significant demand for acetonitrile as a solvent and starting material for syntheses. Hence, in an attempt to find suitable solvents by liquid–liquid extraction in preference to costlier distillation, the phase equilibrium relationships for the ternary systems acetonitrile–water with chlorobenzene, xylene, and *n*-butyl acetate are studied at 31 °C. Xylene (mixed) is reported (4) to have been used as a solvent for extracting acetonitrile from aqueous solutions.

Chemicals

Acetonitrile supplied by Sarabhai M. Chemicals is further purified by fractionation and the fraction boiling at 81.7 °C is collected and used. All the solvents are of reagent grade and are used directly without any further purification. Distilled water free from carbon dioxide is used throughout the work. The physical properties of the chemicals are given in Table I.

Experimental Procedure

The mutual solubility line (binodal curve) is determined at 31 °C by the method as described by Othmer et al. (3); i.e., the solubility line is determined by titration of one binary, solute and water or solute and solvent with solvent or water, respectively, until the appearance of turbidity which indicates the presence of a second liquid phase. In the titrations the amount of the third component required could be reproduced to within 0.2% of the total volume (30 mL).

Table I. Physical Properties of the Chemicals

Chemical	Density at 20 °C, g/mL	Refractive index	Bp at 760 mmHg, °C
Acetonitrile	0.781	1.3420 at 25 °C	81.6
Xylene	0.864	1.4930	137–142
Chlorobenzene	1.1065	1.5220 at 25 °C	131.6
<i>n</i> -Butyl acetate	0.881	1.3898 at 30 °C	126.0

Table II. Mutual Solubility and Tie-Line Data for Acetonitrile–Water–Xylene at 31 °C (values expressed in weight percent)

Xylene	Mutual Solubility Data				
	Acetonitrile	Water	Xylene	Acetonitrile	Water
0.7	10.5	88.8	19.4	69.1	11.5
0.8	21.6	77.6	33.6	60.4	6.0
1.0	33.8	65.2	36.1	58.5	5.4
2.3	45.7	52.0	46.9	49.5	3.6
4.4	58.1	37.5	60.8	36.0	3.2
5.2	62.1	32.7	73.1	23.9	3.0
9.4	68.5	22.1	85.5	11.8	2.7

Tie-Line Data					
Water layer			Organic layer		
Xylene	Acetonitrile	Water	Xylene	Acetonitrile	Water
0.4	4.0	95.6	95.4	2.1	2.5
0.7	8.8	90.5	93.7	3.6	2.7
1.0	13.8	85.2	92.5	4.8	2.7
1.0	18.0	81.0	87.6	9.4	3.0
1.2	24.0	74.8	84.8	12.2	3.0
1.2	27.4	71.4	77.3	19.6	3.1
1.5	33.8	64.7	68.4	28.4	3.2

For the determination of the tie-line data, the specific gravities corresponding to the points on the binodal curve are determined and a standard plot is prepared by plotting weight percent acetonitrile vs. specific gravity. Different mixtures of the three components within the heterogenous system are shaken thoroughly in separating funnels and then allowed to settle overnight. The two layers are then separated and weighed. The percent of acetonitrile in each layer is determined from the standard plot described above. The complete compositions of the conjugate layers are estimated with the help of the binodal curve. The precision in the composition measurement of the each phase is estimated to be within ± 0.005 weight fraction.

Table III. Mutual Solubility and Tie-Line Data for Acetonitrile–Water–Chlorobenzene (values expressed in weight percent)

		Mutual Solubility Data			
Chlorobenzene	Acetonitrile	Water	Chlorobenzene	Acetonitrile	Water
1.0	10.4	88.6	23.5	65.6	10.9
1.1	21.3	77.6	39.2	55.0	5.8
1.3	33.7	65.0	41.0	54.1	4.9
2.6	45.8	51.6	52.6	43.9	3.5
5.8	57.4	36.8	66.4	31.3	2.3
6.1	60.5	33.4	78.0	19.8	2.2
11.4	66.8	21.8	88.3	9.6	2.1

Tie-Line Data					
Water layer			Organic layer		
Chlorobenzene	Acetonitrile	Water	Chlorobenzene	Acetonitrile	Water
0.7	4.6	94.7	95.0	2.8	2.3
0.9	9.6	89.5	90.8	6.9	2.3
0.9	14.5	84.6	87.0	10.4	2.6
1.0	16.4	82.6	82.9	14.5	2.6
1.1	17.6	81.3	77.8	19.4	2.8
1.1	20.8	78.1	72.5	24.6	2.9
1.2	21.6	77.2	68.1	28.7	3.2

Table IV. Mutual Solubility and Tie-Line Data for Acetonitrile–Water–*n*-Butyl Acetate (values expressed in weight percent)

		Mutual Solubility Data			
<i>n</i> -Butyl acetate	Acetonitrile	Water	<i>n</i> -Butyl acetate	Acetonitrile	Water
1.5	10.5	88.0	21.1	59.6	19.3
1.8	21.5	76.7	31.3	55.8	12.9
2.8	32.7	64.5	45.4	46.3	8.3
5.9	45.3	48.8	59.0	34.9	6.3
10.9	54.2	34.9	71.9	23.2	4.9
			85.2	11.8	3.0

Tie-Line Data					
Water layer			Organic layer		
<i>n</i> -Butyl acetate	Acetonitrile	Water	<i>n</i> -Butyl acetate	Acetonitrile	Water
1.0	1.0	98.0	95.4	2.8	1.8
1.0	1.8	97.2	94.0	4.0	2.0
1.0	4.0	95.0	90.5	7.2	2.3
1.1	6.1	92.8	83.5	13.3	3.2
1.1	9.9	89.0	78.7	17.8	3.5
1.2	12.0	86.8	74.8	21.7	3.5
1.2	14.6	84.2	67.5	27.6	4.9

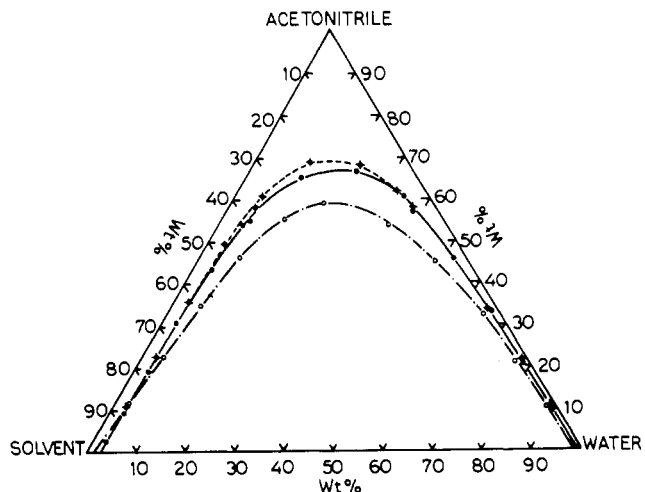


Figure 1. Comparison of mutual solubility curves for acetonitrile–water and the three solvents at 31 °C. Solvent: ●, xylene; ●, chlorobenzene; ○, *n*-butyl acetate.

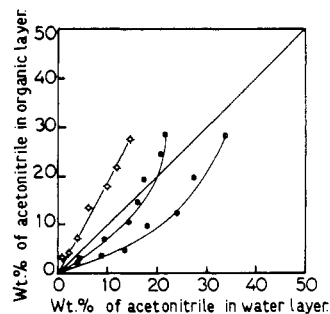


Figure 2. Equilibrium distribution diagram. Solvent: ○, xylene; ●, chlorobenzene; ◊, *n*-butyl acetate.

Results and Correlations

The experimental data for the mutual solubility and distribution for the systems acetonitrile–water–xylene, acetonitrile–water–chlorobenzene, and acetonitrile–water–*n*-butyl acetate

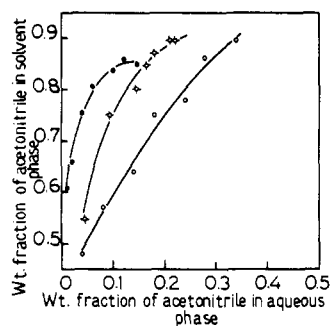


Figure 3. Selectivity diagram (all values on solvent-free basis). Solvent: O, xylene; \diamond , chlorobenzene; \bullet , *n*-butyl acetate.

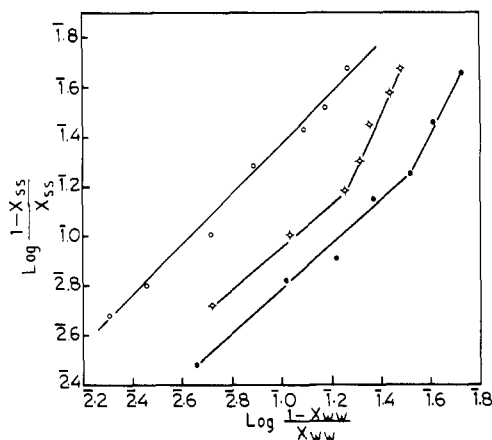


Figure 4. Othmer-Tobias plot of tie-line data. Solvent: \bullet , xylene; \diamond , chlorobenzene; O, *n*-butyl acetate.

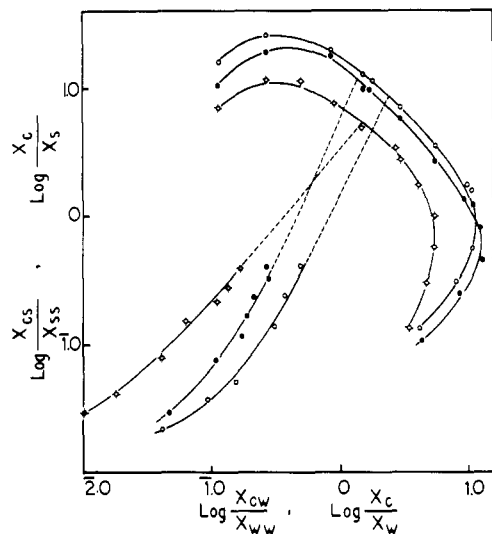


Figure 5. Hand plot of tie-line data and Plait point determination. Solvent: O, xylene; \bullet , chlorobenzene; \diamond , *n*-butyl acetate.

Table V. Plait Point Data

System	Water	Acetonitrile	Solvent
Acetonitrile-water-xylene	26.9	65.7	7.4
Acetonitrile-water-chlorobenzene	40.6	55.5	3.9
Acetonitrile-water- <i>n</i> -butyl acetate	35.7	54.0	10.3

are given in Tables II, III, and IV, respectively. The binodal curves for the three systems are shown in Figure 1. The equilibrium distribution of acetonitrile between solvent and aqueous layers for the three systems is represented in Figure 2. The calculations of plait points for the three systems are illustrated in Figure 5 by use of Treybal's method (5) on Hand's coordinates.

A selectivity diagram is plotted (Figure 3) to ascertain which of the solvents is better. The tie-line data for all the systems are satisfactorily correlated by the method of Othmer and Tobias (2) and Hand (1). Both the correlations are shown in Figures 4 and 5.

Discussion

The solvents studied, i.e., xylene, chlorobenzene, and *n*-butyl acetate have good solvent properties. They are fairly nonvolatile and the density difference between water and these solvents except for chlorobenzene is considerable. The tie-line data and the mutual solubility data indicate that these solvents can be used in the liquid-liquid extraction of acetonitrile.

It is evident from Figure 1 that the area of heterogeneity increases for the solvents studied in the order *n*-butyl acetate, chlorobenzene, and xylene. This is because of higher mutual solubilities of water and *n*-butyl acetate when compared with that for water-xylene and water-chlorobenzene.

As seen from the distribution diagram, acetonitrile prefers solvent phase in the acetonitrile-water-*n*-butyl acetate system and aqueous phase in the other two systems.

In the Othmer-Tobias and Hand correlations two straight lines are obtained for each system for the tie-line data. However, smooth curves are found to fit the data better in the latter correlation. With regard to the distribution and selectivity the order of solvents is *n*-butyl acetate, chlorobenzene, and xylene. The system chlorobenzene-acetonitrile-water exhibits the phenomenon of solutropy, i.e., in the lower concentrations the solute prefers the water phase whereas at higher concentrations it shows affinity toward the solvent phase.

Glossary

C	solute
W	water
X_{cs}	weight fraction of solute in solvent layer
S	solvent
X_{cw}	weight fraction of solute in water layer
X_{ww}	weight fraction of water layer
X_{ss}	weight fraction of solvent in solvent layer

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Received for review June 14, 1976. Accepted July 13, 1977.