Extraction of Acetonitrile from Aqueous Mixtures. 2. Ternary Liquid Equilibria

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Ternary liquid equilibrium data at 30 ± 0.1 °C for the systems water–acetonitrile–toluene, water–acetonitrile–methyl isobutyl ketone, water–acetonitrile–isoamyl acetate, water–acetonitrile–isoamyl alcohol, and water–acetonitrile–methyl ethyl ketone are obtained. The tie-line data for the first three systems are well correlated by the methods of Othmer–Tobais and Hand. For the other two systems the area of heterogeneity is found to be small. The selectivity increases in the order methyl isobutyl ketone, isoamyl acetate, and toluene.

Previous work[4] on the mutual solubility and equilibrium distribution data for the ternary systems water–acetonitrile–xylene, water–acetonitrile–chlorobenzene, and water–acetonitrile–*n*-butyl acetate has shown that *n*-butyl acetate is the best solvent of the three for extraction of acetonitrile from aqueous mixtures. In continuation of the above work, five more solvents have been studied for their suitability for the extraction of acetonitrile and to obtain the fundamental data required for extraction, namely, the mutual solubility data for the five ternary systems and distribution data for three systems.

Chemicals

Acetonitrile supplied by Veblaborchemie Apolda, GDR, was further purified by fractionation in a laboratory column operating at 760 ± 1 mmHg pressure and the fraction boiling at 81.6 °C was collected and used. All the solvents were of reagent grade and were used directly without any further purification. Distilled water free from carbon dioxide was used throughout the work. The physical properties of the chemicals are given in Table I.

Experimental Procedure

Determination of phase equilibrium (mutual solubility) data was carried out by the titration method of Othmer et al.[3] and tie-line data were determined by the specific gravity method.

Mutual Solubility Data

For the determination of the mutual solubility data, an accurately weighed amount of a homogeneous mixture of two components was placed in a conical flask and one of the nonconsolute components was titrated into the flask from a buret until the solution became turbid, and the amount titrated was recorded. The conical flask was kept in a constant-temperature bath. The temperature of the bath was maintained at 30 ± 0.1 °C. The end point had been confirmed by adding the consolute component till the turbidity disappears. The procedure is repeated to get the phase boundary curve. In the titrations it was found that the amount of the third component required could be reproduced to within 0.2% of the total volume (30 mL).

Tie-Line Data

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

Table I. Physical Properties of Chemicals

chemical	bp (760 mmHg), °C	density at 30 °C
acetonitrile	81.6	0.7719
toluene	110.6	0.8620
isoamyl acetate	142.0	0.8720
methyl isobutyl ketone	116.0	0.7990
isoamyl alcohol	129.5	0.8110
methyl ethyl ketone	80.0	0.8030

Results and Discussion

The experimental data of the mutual solubility for the systems water–acetonitrile–toluene, water–acetonitrile–methyl isobutyl ketone, water–acetonitrile–isoamyl acetate, water–acetonitrile–isoamyl alcohol, and water–acetonitrile–methyl ethyl ketone are presented in Tables II–VI and shown in Figure 1. The equilibrium distribution of acetonitrile between solvent and aqueous layers was obtained experimentally for the first three systems and the data are presented in Tables II, III, and IV along with mutual solubility data. These are shown in Figure 2. The area of heterogeneity for the last two systems was found to be small as is evident from Figure 1 and hence the distribution data for these two systems have not been obtained.

The selectivity diagram is plotted in Figure 3, to ascertain which of the solvents is better. The tie-line data for all three systems are satisfactorily correlated by the methods of Othmer–Tobias[2] and Hand[1]. The Othmer–Tobias correlation equation is

$$\frac{1 - X_{SS}}{X_{SS}} = K\left(\frac{1 - X_{WW}}{X_{WW}}\right)^{n}$$

The Hand correlation equation is

$$\frac{X_{CS}}{X_{SS}} = K'\left(\frac{X_{CW}}{X_{WW}}\right)^{n'}$$

Both of the correlations are shown in Figures 4 and 5. The constants of the correlations are given in Table VII and as is seen from the figures they vary with the concentration of acetonitrile. Two straight lines are obtained for the system water–acetonitrile–methyl isobutyl ketone whereas a single straight line is obtained for each of the other two systems.

The plait point data as determined by the method of Treybal et al.[5] are summarized in Table VIII and shown in Figure 5.

The solvents studied, i.e., toluene, methyl isobutyl ketone, and isoamyl acetate, have good solvent properties. They are fairly nonvolatile and the density difference between water and these solvents is considerable. The mutual solubility and distribution

0021-9568/79/1724-0241$01.00/0

Table II. Liquid–Liquid Equilibrium Data at 30 °C in the Acetonitrile–Water–Toluene System[a]

toluene	acetonitrile	water
0.09	0.00	99.91
0.11	8.35	91.54
0.26	16.17	83.57
0.38	24.45	75.17
0.83	33.99	65.18
1.46	42.98	55.55
2.81	52.30	44.89
4.98	60.98	34.04
8.91	68.64	22.45
9.10	69.52	21.38
19.97	69.26	10.77
30.43	62.83	6.74
41.00	54.93	4.07
51.81	45.67	2.52
61.15	37.30	1.55
71.39	27.82	0.79
80.89	18.63	0.48
89.76	9.95	0.29
99.74	0.00	0.26

water layer			organic layer		
toluene	acetonitrile	water	toluene	acetonitrile	water
0.50	10.50	89.00	88.60	10.83	0.57
0.65	12.25	87.10	85.10	14.30	0.60
0.75	17.25	82.00	70.80	27.80	1.40
0.80	17.50	81.70	68.40	30.10	1.50
0.85	19.65	79.50	62.00	36.10	1.90
0.80	21.80	77.40	54.00	43.30	2.70
0.85	23.15	76.00	43.70	52.30	4.00
0.90	25.30	73.80	37.50	57.40	5.10
0.95	26.65	72.40	35.50	59.00	5.50
1.00	27.30	71.70	34.80	59.50	5.70
1.05	28.75	70.20	30.40	62.60	7.00

[a] Composition on weight percent basis.

Table III. Liquid–Liquid Equilibrium Data at 30 °C for the Acetonitrile–Water–Isobutyl Methyl Ketone System[a]

isobutyl methyl ketone	acetonitrile	water
0.40	0.00	99.60
0.80	8.5	90.70
1.65	16.94	81.41
2.61	24.62	72.77
3.84	32.72	63.44
5.65	41.33	53.02
9.50	49.50	42.00
12.66	56.25	31.19
14.59	57.02	28.39
17.50	58.50	24.00
25.88	57.00	17.12
35.58	51.84	12.58
45.25	44.59	10.16
56.01	37.02	6.97
66.50	28.21	5.29
77.40	18.76	3.78
87.97	9.76	2.27
99.25	0.00	0.75

water layer			organic layer		
isobutyl methyl ketone	aceto-nitrile	water	isobutyl methyl ketone	aceto-nitrile	water
1.00	8.50	90.50	79.60	17.50	2.90
1.10	11.00	87.90	79.00	18.00	3.00
1.70	15.20	83.10	72.50	23.50	4.00
2.00	17.70	80.30	54.50	38.00	7.50
2.20	20.50	77.30	42.00	47.50	10.50
2.40	22.60	75.00	35.00	52.00	13.00
2.70	25.10	72.20	25.20	57.30	17.50

[a] Composition on weight percent basis.

Table IV. Liquid–Liquid Equilibrium Data at 30 °C in the Acetonitrile–Water–Isoamyl Acetate System[a]

isoamyl acetate	acetonitrile	water
0.19	0.00	99.81
0.34	7.89	91.77
0.96	15.91	83.14
1.00	24.45	74.55
1.96	33.29	64.75
3.60	41.87	54.53
6.47	50.16	43.38
10.30	57.63	32.07
17.37	62.15	20.48
18.52	61.21	20.27
28.34	58.18	13.48
38.64	51.75	9.61
50.71	42.80	6.49
59.53	35.47	5.00
69.80	26.32	3.88
79.51	17.89	2.59
89.78	8.79	1.43
99.85	0.00	0.15

water layer			organic layer		
isoamyl acetate	aceto-nitrile	water	isoamyl acetate	aceto-nitrile	water
0.65	8.30	91.05	86.00	12.00	2.00
0.70	11.00	88.30	83.10	14.50	2.40
0.75	12.40	86.85	78.70	18.30	3.00
0.80	13.70	85.50	76.60	20.30	3.10
0.85	14.50	84.65	71.80	24.40	3.80
0.90	15.50	83.60	69.70	26.30	4.00
0.95	17.50	81.55	64.40	31.00	4.60
1.00	18.30	80.70	61.80	33.50	4.70
1.00	19.00	80.00	59.70	35.30	5.00
1.05	20.00	78.95	58.50	36.00	5.50
1.10	23.70	75.20	51.00	42.30	6.70

[a] Composition on weight percent basis.

Table V. Liquid–Liquid Equilibrium Data at 30 °C for the Acetonitrile–Water–Isoamyl Alcohol System[a]

isoamyl alcohol	acetonitrile	water
0.27	0.00	99.73
1.59	7.52	90.89
4.40	15.39	80.21
8.48	21.16	70.36
19.07	27.49	53.44
29.27	30.78	39.95
32.17	31.11	36.72
43.79	28.17	28.04
55.49	22.81	16.70
66.94	16.16	16.90
79.78	8.70	11.52
92.90	0.00	7.10

[a] Composition on weight percent basis.

Table VI. Liquid–Liquid Equilibrium Data at 30 °C for the Acetonitrile–Water–Methyl Ethyl Ketone System[a]

methyl ethyl ketone	acetonitrile	water
13.58	0.00	86.42
13.72	6.60	79.68
17.84	13.47	68.69
34.95	16.30	48.75
41.45	17.42	41.13
62.05	15.50	22.45
76.18	8.36	15.46
90.62	0.00	9.38

[a] Composition on weight percent basis.

data indicate that the 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 systems studied in the order methyl isobutyl ketone, isoamyl acetate, and toluene.

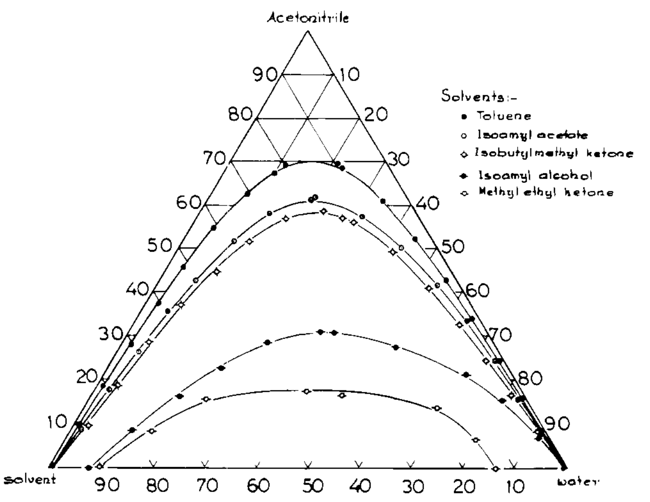

Figure 1. Phase equilibrium diagram.

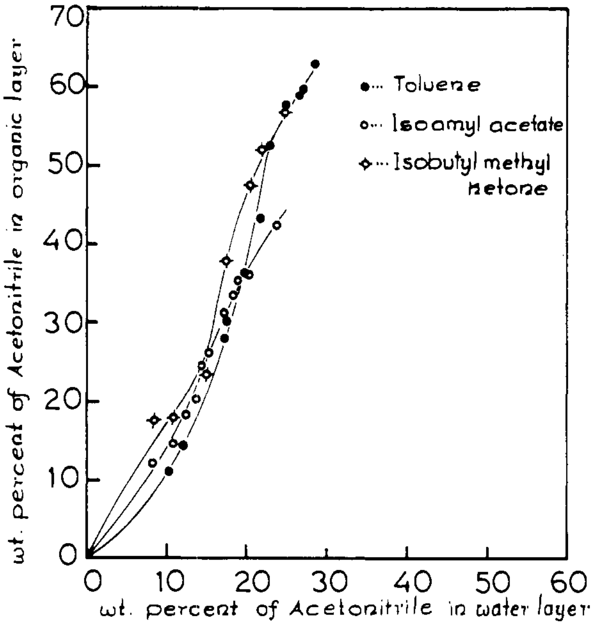

Figure 2. Equilibrium distribution diagram for acetonitrile between water and solvents.

Table VII. Constants in Othmer–Tobias and Hand Correlation

	Othmer–Tobias		Hand	
system	*K*	*n*	*K'*	*n'*
isoamyl acetate–acetonitrile–water	0.774	1.63	0.748	1.61
	(0–23.7%)		(0–23.7%)	
toluene–acetonitrile–water	1.242	2.44	1.144	2.23
	(0–28.75%)		(0–28.75%)	
isobutyl methyl ketone–acetonitrile–water	−0.379	0.22	−0.305	0.35
	(0–12.5%)		(0–13.1%)	
	16.69	3.13	1.627	2.81
	(12.5–25.1%)		(13.1–25.1%)	

Table VIII. Plait Point Data[a]

system	water	acetonitrile	solvent
acetonitrile–water–isoamyl acetate	44.74	49.30	5.96
acetonitrile–water–isobutyl methyl ketone	63.44	32.72	3.84
acetonitrile–water–toluene	45.89	51.49	2.62

[a] Composition on weight percent basis.

This is because of higher mutual solubilities of water and methyl isobutyl ketone when compared with those for water and isoamyl acetate and water and toluene.

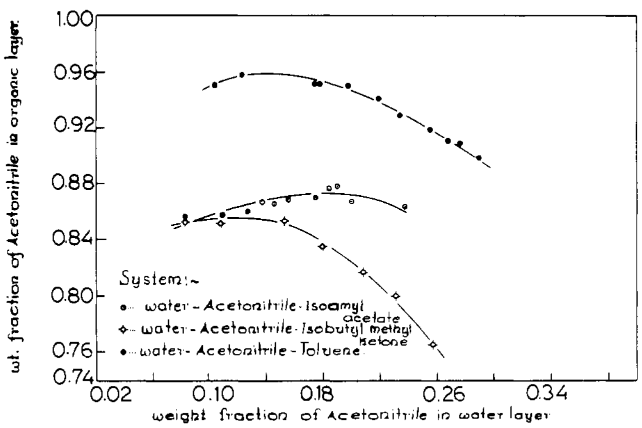

Figure 3. Selectivity diagram (weight fraction, solvent free basis).

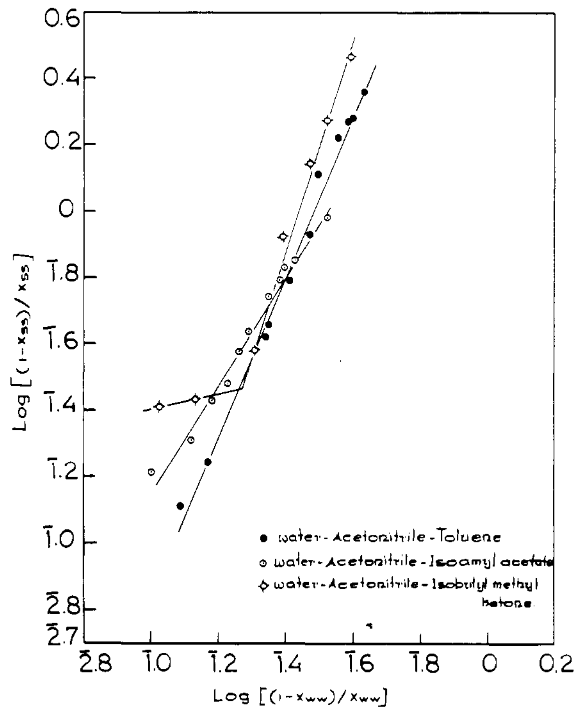

Figure 4. Othmer–Tobias correlation.

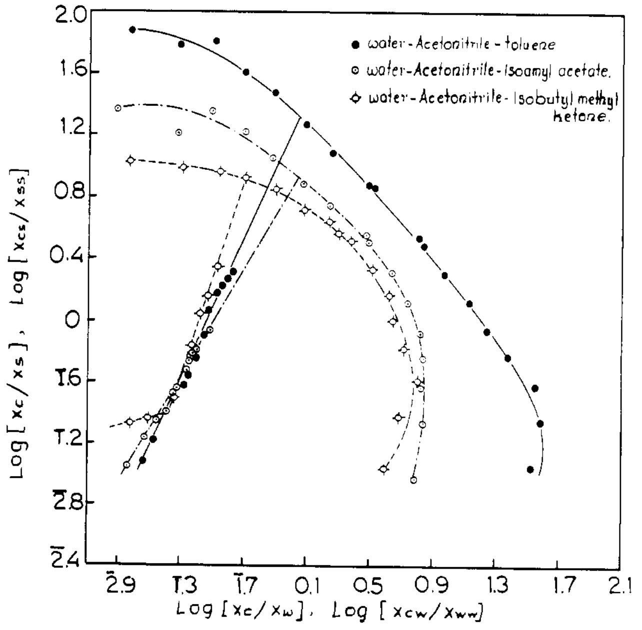

Figure 5. Plait point determination on Hand's coordinates.

As seen from the distribution diagram acetonitrile prefers solvent phase in all three systems. With regard to the distribution, the order of solvents studied is toluene, methyl isobutyl ketone, and isoamyl acetate.

In this study the order of solvents for selectivity is toluene > isoamyl acetate > methyl isobutyl ketone.

Because toluene is more available and at a cheaper rate when compared to the other solvents, toluene can be used for the extraction of acetonitrile. However, this should be ascertained by experimentation in conventional extraction equipment.

Glossary

C	solute
K, K'	constants in Othmer-Tobias and Hand correlations
n, n'	constants in Othmer-Tobias and Hand correlations
S	solvent
W	water
X_{CS}	weight fraction of solute in solvent layer
X_{CW}	weight fraction of solute in water layer
X_{SS}	weight fraction of solvent in solvent layer
X_{WW}	weight fraction of water in water layer

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Received for review June 23, 1978. Accepted February 5, 1979.

Thermal Conductivity of Liquids

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A new equation is presented which correlates thermal conductivity data as a function of both temperature and chemical structure. This enables values to be estimated for other liquids with a similar chemical structure.

1 Introduction

When process equipment is designed, accurate thermal conductivity data are required over a wide range of temperatures. Thermal conductivity is however a difficult property to measure and since there are many thousands of possible liquids it is not possible to supply industries' needs over the entire range experimentally. The necessary data may be obtained in various ways and the following broadly divides these methods in order of preference: (a) careful assessment of extensive experimental data, (b) a combination of limited experimental data and theoretical or empirical procedures, (c) derivation from experimental data for structurally similar chemicals, (d) prediction methods. Prediction methods are important and in some instances essential, but in this paper only the first three methods are considered with the emphasis being on (b) and (c).

2 Correlation of Data as a Function of Temperature

The initial task was to collect all the available literature data and make an assessment of accuracy. This has been completed[1] and, while there are much data, compared with all the possible liquids and temperature ranges there are relatively few available. In addition relatively few authors provide enough information for an objective assessment to be made of their work. Most claim accuracies of a few percent or better but these are seen to be grossly optimistic when the data for a common liquid are plotted as in Figure 1. Detailed references to the individual authors are in ref 1. It might be thought that the scatter is due to the age of some of the work but Figure 2 shows that while this may be partially true it is by no means the entire explanation.

When the assessed accuracies are also considered it is, however, often possible to sketch a line showing how thermal conductivity varies with temperature. The next task was therefore to develop an equation which fitted the experimental data adequately. Relatively simple equations were found suitable for certain liquids over limited temperature ranges but it was found that close to the critical temperature, thermal conductivity increased very rapidly, possibly approaching infinity at the critical point. It was therefore apparent that an equation with a small number of constants could only be found if the critical region is ignored and if a "pseudocritical thermal conductivity" value is used. The latter is obtained by extrapolating data from lower temperatures to the critical temperature and the difference between the pseudovalue and the real value being dealt with as a "critical enhancement".

The simplest equation found to be suitable for all organic liquids was

$$\lambda = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau) \qquad (1)$$

where $\tau = 1 - T/T_c$, where T_c is the critical temperature, B, C, and D are constants, and A is the pseudocritical thermal conductivity.

With eq 1 it is possible to represent carefully assessed experimental data to within their estimated accuracy over the approximate temperature range from melting point to $0.9T_c$. Above $0.9T_c$ there are very few experimental values but it is believed that eq 1 will remain accurate until within a few degrees of the critical temperature at which point the "critical enhancement" becomes large.

3 Correlation of Data as a Function of T and of Chemical Structure

When the best available experimental data are collected, for a single class of liquids such as the n-alkanes, an inconsistent set of values is generally found.[2] When this was investigated it was found that, for each liquid, the experimental values were such that four or five different lines could be used to plot the variation with temperature and the difference between each line could be well within the experimental uncertainty of the data. It was therefore thought that greater reliability would be achieved if lines could be selected such that the constants in eq 1 varied smoothly as a function of the chemical structure.

For this approach eq 1 must be considered as an equation with four disposable parameters. It is however unlikely that all four of these constants can be related to structure and so an