Liquid–Liquid Equilibria for Ternary Systems Formed by Acetonitrile, Water, and Aromatic Hydrocarbons

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Liquid–liquid equilibria were measured at 25 and 45 °C for the ternary systems formed by acetonitrile + water + an aromatic hydrocarbon (benzene, toluene, *m*-xylene, *p*-xylene, ethylbenzene). Type I isotherms were observed for the five systems both at 25 and at 45 °C. The binodal curves and tie lines may be predicted by using the NRTL model on the basis of parameters found from binary data.

Introduction

The presence of an azeotrope renders difficult the recovery of acetonitrile from aqueous solutions by distillation. Liquid extraction with an aromatic hydrocarbon as solvent has been suggested as an alternative way to perform this separation (*1*).

The extraction of acetonitrile from aqueous mixtures has been studied for a number of organic solvents (*2*-*5*).

In the present work, ternary liquid–liquid equilibria (LLE) were measured at 25 and 45 °C for the five ternary systems containing acetonitrile (1) + water (2) + benzene (3), + toluene (3), + *m*-xylene (3), + *p*-xylene (3), or + ethylbenzene (3). The information reported in the literature concerning these system appears to be limited. In particular, Hartwig et al. (*2*) reported three tie lines for the system acetontrile–water–benzene at 25 °C. Francis (*3*) reported in small triangular graphs the binodal curves for the systems acetonitrile–water–benzene and acetonitrile–water–toluene at 25 °C. Rao et al. (*4*) reported complete LLE data for the system acetonitrile–water–toluene at 30 °C, and Rao et al. (*5*) reported similar data for the system acetonitrile–water–mixture of xylenes at 31 °C.

Experimental Section

Materials. All chemicals used in this work had a minimum stated purity from the manufacturer (Farmitalia Carlo Erba) as follows: bidistilled water; acetonitrile, 99.8%; benzene, toluene, and ethylbenzene, 99.5%; *m*-xylene and *p*-xylene, 99%. No further purification was done. The actual refractive indexes of the chemicals are given in Table I.

Apparatus and Procedure. The measurements were carried out in a glass equilibrium cell, 250 mL in capacity, where the temperature was maintained constant to within ±0.1 °C. First of all, the limits of the immiscibility region were determined. To this end, binary mixtures were prepared from known amounts of two miscible components and fixed volumes (0.05 mL each time) of the third one were added until a second liquid phase appeared. After each addition the solution was vigorously stirred and then allowed to settle for about 10 min. The accuracy of the method was ±0.001 mass fraction. The measurements proved to be reproducible to within ±0.001 mass fraction.

The tie lines were then determined by preparing a ternary mixture from weighed amounts of the three components, equilibrating the system by agitation with a magnetic stirrer for at least 2 h, and allowing it to settle for 20 h. The relative amounts of the two phases were measured, on a volumetric basis, by using the graduation on the wall of the cell; samples of the light and of the heavy liquids were withdrawn, and their densities were measured by means of a pycnometer to allow the conversion of the results from a volume to a mass basis.

Table I. Refractive Indexes *n* of the Chemicals

chemical	*n*(D, 20 °C) this work	*n*(D, 20 °C) lit.[a]
acetonitrile	1.3430	1.344 11
benzene	1.5011	1.501 12
toluene	1.4961	1.496 93
m-xylene	1.4973	1.497 22
p-xylene	1.4958	1.495 82
ethylbenzene	1.4959	1.495 88

[a] Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; Techniques of Chemistry, Vol. II; John Wiley & Sons: New York, 1986.

Table II. Ternary Liquid–Liquid Equilibrium Data (x_{wi}, Mass Fraction) and Percentage Standard Deviations ($100\sigma(x_w)$), Equation 6) for the Acetonitrile (1)–Water (2)–Benzene (3) System

binodal curve		tie lines			
		aqueous phase		organic phase	
x_{w2}	x_{w3}	x_{w2}	x_{w3}	x_{w2}	x_{w3}
		At 25 °C			
0.006	0.773	0.875	0.002	0.006	0.728
0.006	0.719	0.855	0.003	0.013	0.656
0.012	0.657	0.827	0.003	0.019	0.578
0.022	0.529	0.809	0.004	0.029	0.492
0.038	0.445	0.800	0.004	0.034	0.465
0.048	0.376	0.783	0.005	0.041	0.400
0.063	0.305	0.754	0.005	0.059	0.316
0.070	0.281	0.746	0.005	0.069	0.282
0.088	0.230	0.735	0.006	0.105	0.195
0.117	0.177	0.720	0.006	0.137	0.151
0.139	0.143				
0.167	0.117				
0.211	0.086				
0.251	0.068				
0.339	0.045				
0.451	0.027				
0.544	0.015				
0.641	0.009				
		At 45 °C			
0.001	0.950	0.960	0.0005	0.001	0.946
0.002	0.862	0.910	0.002	0.003	0.847
0.010	0.750	0.850	0.004	0.009	0.752
0.019	0.637	0.833	0.005	0.018	0.650
0.030	0.536	0.809	0.006	0.027	0.555
0.048	0.444	0.794	0.006	0.041	0.466
0.080	0.328	0.748	0.009	0.065	0.369
0.110	0.258	0.735	0.010	0.084	0.306
0.139	0.207	0.690	0.015	0.113	0.247
0.168	0.175				
0.205	0.143				
0.248	0.114				
0.268	0.104				
0.377	0.066				
0.470	0.042				
0.578	0.026				
0.681	0.016				

$100\sigma(x_w) = 2.5$

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Table III. Ternary Liquid-Liquid Equilibrium Data (x_{wi}, Mass Fraction) and Percentage Standard Deviations ($100\sigma(x_w)$, Equation 6) for the Acetonitrile (1)-Water (2)-Toluene (3) System

binodal curve		tie lines			
		aqueous phase		organic phase	
x_{w2}	x_{w3}	x_{w2}	x_{w3}	x_{w2}	x_{w3}
At 25 °C					
0.006	0.797	0.923	0.001	0.005	0.872
0.015	0.609	0.882	0.002	0.007	0.812
0.023	0.489	0.847	0.003	0.010	0.698
0.041	0.400	0.836	0.003	0.012	0.660
0.062	0.293	0.827	0.003	0.013	0.645
0.085	0.240	0.820	0.004	0.015	0.611
0.114	0.178	0.796	0.004	0.023	0.527
0.137	0.153	0.790	0.004	0.028	0.500
0.139	0.144	0.771	0.005	0.040	0.400
0.161	0.121	0.754	0.005	0.049	0.336
0.192	0.107	0.744	0.006	0.054	0.311
0.222	0.072	0.742	0.006	0.059	0.293
0.249	0.069	0.738	0.006	0.075	0.246
0.280	0.065				
0.295	0.049				
0.378	0.037				
0.400	0.030				
0.474	0.021				
0.581	0.013				
0.691	0.007				
At 45 °C					
0.001	0.904	0.917	0.001	0.001	0.910
0.007	0.795	0.890	0.002	0.006	0.833
0.013	0.685	0.835	0.003	0.009	0.721
0.026	0.588	0.803	0.004	0.018	0.642
0.039	0.479	0.782	0.005	0.027	0.563
0.050	0.406	0.758	0.006	0.036	0.485
0.079	0.331	0.733	0.007	0.053	0.398
0.111	0.252	0.712	0.008	0.075	0.331
0.141	0.202	0.662	0.010	0.113	0.239
0.168	0.167	0.640	0.010	0.140	0.200
0.207	0.136				
0.241	0.113				
0.310	0.080				
0.374	0.060				
0.477	0.034				
0.582	0.018				
0.691	0.010				

$100\sigma(x_w) = 2.4$

Table IV. Ternary Liquid-Liquid Equilibrium Data (x_{wi}, Mass Fraction) and Percentage Standard Deviations ($100\sigma(x_w)$, Equation 6) for the Acetonitrile (1)-Water (2)-*m*-Xylene (3) System

binodal curve		tie lines			
		aqueous phase		organic phase	
x_{w2}	x_{w3}	x_{w2}	x_{w3}	x_{w2}	x_{w3}
At 25 °C					
0.005	0.716	0.880	0.0005	0.0005	0.971
0.015	0.613	0.848	0.001	0.002	0.894
0.026	0.510	0.800	0.002	0.006	0.750
0.033	0.456	0.757	0.003	0.017	0.598
0.041	0.405	0.726	0.004	0.030	0.485
0.051	0.354	0.677	0.005	0.056	0.330
0.055	0.351	0.622	0.008	0.104	0.188
0.076	0.262				
0.113	0.196				
0.151	0.130				
0.206	0.088				
0.275	0.059				
0.292	0.050				
0.340	0.042				
0.341	0.039				
0.358	0.039				
0.374	0.036				
0.450	0.021				
0.555	0.010				
At 45 °C					
0.004	0.889	0.891	0.003	0.005	0.902
0.007	0.828	0.844	0.003	0.008	0.817
0.011	0.745	0.802	0.005	0.009	0.749
0.021	0.623	0.748	0.007	0.019	0.619
0.038	0.500	0.713	0.009	0.033	0.510
0.066	0.376	0.688	0.010	0.050	0.440
0.074	0.343	0.658	0.010	0.078	0.330
0.086	0.311	0.629	0.011	0.110	0.252
0.114	0.247	0.596	0.012	0.140	0.202
0.148	0.191				
0.179	0.159				
0.221	0.126				
0.248	0.109				
0.309	0.080				
0.443	0.037				
0.489	0.026				
0.599	0.014				
0.676	0.012				

$100\sigma(x_w) = 2.5$

The tie lines were then determined by applying the lever rule, the limits of the immiscibility region being known. The accuracy of the method was ±0.002 mass fraction. The observed reproducibility of the reported LLE data has been estimated to be within ±0.002 mass fraction.

Results and Discussion

The experimental data are reported in Tables II-VI. Type I isotherms were observed in all cases, acetonitrile being completely miscible with water and with all the aromatic hydrocarbons. The immiscibility region decreases by increasing the temperature from 25 to 45 °C.

The comparison with literature data is restricted to the systems containing benzene and toluene and, only qualitatively, to those containing *m*-xylene and *p*-xylene. Our data compare reasonably with the data measured by Hartwig et al. (*2*) at 25 °C for the system acetonitrile-water-benzene and by Rao et al. (*4*) at 30 °C for the system acetonitrile-water-toluene and with the graphs reported by Francis (*3*) for both of these systems at 25 °C. With regard to the systems containing xylenes, our binodal curves are fairly close to that reported by Rao et al. (*5*) for the system acetonitrile-water-mixed xylenes at 31 °C, while some discrepancies appear in the slopes of the tie lines.

To provide a fit for the ternary LLE, the thermodynamic relationship

$$(\gamma_i x_i)_{j=1} = (\gamma_i x_i)_{j=2} \qquad i = 1, 2, 3 \tag{1}$$

was applied. The activity coefficients γ_i in the liquid aqueous (j = 1) and organic (j = 2) phases were calculated by means of the NRTL equation (*6*)

$$\ln \gamma_i = \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{p=1}^{3} G_{pi} x_p} + \sum_{j=1}^{3} \left[\frac{x_j G_{ij}}{\sum_{p=1}^{3} G_{pj} x_p} \left[\tau_{ij} - \frac{(\sum_{r=1}^{3} x_r \tau_{rj} G_{rj})}{\sum_{p=1}^{3} G_{pj} x_p} \right] \right] \tag{2}$$

where $\tau_{ji} = (g_{ji} - g_{ii})/RT$, $G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$, $g_{ij} = g_{ji}$, and $\alpha_{ij} = \alpha_{ji}$. The parameters $g_{ij} - g_{jj}$ and $g_{ji} - g_{ii}$ were assumed to be linearly dependent on the temperature T, according to the following relationships (*7*):

$$g_{ij} - g_{jj} = a_{ij} + b_{ij}((T/\mathrm{K}) - 273.15) \tag{3}$$

$$g_{ji} - g_{ii} = a_{ji} + b_{ji}((T/\mathrm{K}) - 273.15) \tag{4}$$

The NRTL model presents the advantage that predictions of ternary phase equilibria can be carried out on the basis of

Table V. Ternary Liquid-Liquid Equilibrium Data (x_{wi}, Mass Fraction) and Percentage Standard Deviations ($100\sigma(x_w)$), Equation 6) for the Acetonitrile (1)-Water (2)-*p*-Xylene (3) System

binodal curve		tie lines			
		aqueous phase		organic phase	
x_{w2}	x_{w3}	x_{w2}	x_{w3}	x_{w2}	x_{w3}
At 25 °C					
0.002	0.906	0.852	0.002	0.004	0.862
0.006	0.778	0.819	0.003	0.006	0.772
0.011	0.687	0.796	0.004	0.008	0.704
0.018	0.587	0.751	0.005	0.023	0.553
0.031	0.472	0.735	0.005	0.031	0.465
0.045	0.382	0.725	0.005	0.040	0.410
0.071	0.281	0.710	0.005	0.058	0.319
0.091	0.227	0.703	0.006	0.066	0.289
0.114	0.180	0.681	0.007	0.090	0.222
0.139	0.144	0.664	0.008	0.100	0.210
0.165	0.117	0.642	0.009	0.110	0.190
0.206	0.088				
0.233	0.074				
0.261	0.062				
0.316	0.046				
0.399	0.031				
0.483	0.017				
0.586	0.009				
0.696	0.005				
At 45 °C					
0.002	0.903	0.948	0.002	0.003	0.965
0.009	0.793	0.909	0.003	0.003	0.927
0.013	0.683	0.850	0.004	0.006	0.843
0.020	0.595	0.806	0.005	0.011	0.741
0.035	0.503	0.753	0.008	0.019	0.625
0.051	0.421	0.713	0.008	0.034	0.508
0.078	0.330	0.688	0.008	0.047	0.433
0.109	0.254	0.645	0.008	0.076	0.335
0.134	0.212	0.610	0.010	0.106	0.262
0.163	0.174	0.600	0.010	0.134	0.213
0.206	0.136				
0.258	0.105				
0.332	0.070				
0.499	0.023				
0.599	0.011				
0.695	0.009				

$100\sigma(x_w) = 1.6$

parameters determined from the constituting binary systems. For each binary system a proper value of α_{ij} was assumed (*6*) (Table VIII). The values of the parameters a_{ij}, a_{ji}, b_{ij}, and b_{ji} were determined as follows.

For the systems water-aromatic hydrocarbons, they were directly obtained by applying eqs 1 and 2 to recommended LLE data (*8*) at two different temperatures; for the system water-*p*-xylene, the data were found only at one, temperature and, consequently, the parameters b_{ij} and b_{ji} were assumed equal to zero.

For the systems acetonitrile-aromatic hydrocarbons and water-acetonitrile, the values of the parameters were obtained by submitting to regression vapor-liquid equilibrium (VLE) data of each examined binary system: in particular, two sets of isobaric VLE data at 28.0 and 101.3 kPa (*9*), for the system acetonitrile-aromatic hydrocarbons, and two sets of VLE data, one isobaric at 101.3 kPa (*10*) and the other isothermal at 60 °C (*11*), for the system acetronitrile-water. The calculation procedure, described in detail elsewhere (*9*), was based on the minimization of the objective function, S:

$$S = \sum_{m=1}^{N} \{[F_{y_1}(y_{1m,\text{exp}} - y_{1m,\text{calc}})]^2 + [F_P(P_{m,\text{exp}} - P_{m,\text{calc}})]^2 + [F_T(T_{m,\text{exp}} - T_{m,\text{calc}})]^2\} \quad (5)$$

The weighting factors F_P, F_T, and F_{y_1} used for each binary system are given in Table VII.

Table VI. Ternary Liquid-Liquid Equilibrium Data (x_{wi}, Mass Fraction) and Percentage Standard Deviations ($100\sigma(x_w)$), Equation 6) for the Acetonitrile (1)-Water (2)-Ethylbenzene (3) System

binodal curve		tie lines			
		aqueous phase		organic phase	
x_{w2}	x_{w3}	x_{w2}	x_{w3}	x_{w2}	x_{w3}
At 25 °C					
0.003	0.714	0.923	0.001	0.0005	0.920
0.006	0.629	0.897	0.002	0.001	0.906
0.012	0.572	0.877	0.002	0.001	0.868
0.023	0.474	0.833	0.003	0.001	0.802
0.027	0.461	0.798	0.003	0.002	0.743
0.041	0.377	0.771	0.004	0.004	0.667
0.055	0.319	0.742	0.004	0.011	0.559
0.063	0.292	0.723	0.005	0.029	0.433
0.107	0.203	0.708	0.006	0.040	0.376
0.119	0.168	0.693	0.006	0.069	0.278
0.141	0.139	0.643	0.006	0.136	0.154
0.147	0.138				
0.170	0.122				
0.196	0.095				
0.227	0.072				
0.253	0.068				
0.271	0.057				
0.305	0.048				
At 45 °C					
0.004	0.906	0.918	0.002	0.006	0.855
0.008	0.762	0.830	0.003	0.008	0.751
0.018	0.612	0.776	0.004	0.015	0.652
0.054	0.419	0.714	0.006	0.053	0.409
0.087	0.304	0.683	0.009	0.068	0.353
0.089	0.300	0.639	0.010	0.093	0.282
0.115	0.244	0.595	0.013	0.156	0.184
0.122	0.228	0.520	0.022	0.217	0.125
0.142	0.202				
0.160	0.179				
0.170	0.167				
0.171	0.166				
0.203	0.133				
0.249	0.107				
0.266	0.095				
0.290	0.089				
0.319	0.078				
0.334	0.072				
0.400	0.051				
0.471	0.032				
0.489	0.028				
0.505	0.026				
0.563	0.017				
0.613	0.011				

$100\sigma(x_w) = 3.2$

Table VII. Weighting Factors, F_P, F_T, F_{y_1}, Used in Deriving the Binary NRTL Parameters from VLE Data, Equation 5

component *i*-*j*	F_P	F_T	F_{y_1}
acetonitrile (1)-benzene (3)	1	1	15
acetonitrile (1)-toluene (3)	1	1	30
acetonitrile (1)-*m*-xylene (3)	1	1	60
acetonitrile (1)-*p*-xylene (3)	1	1	60
acetonitrile (1)-ethylbenzene (3)	1	1	60
acetonitrile (1)-water (2)	0.75	1	30

The values of the NRTL parameters for each binary system are summarized in Table VIII. The ternary LLE were then predicted, and the results were converted into mass fractions in order to allow a comparison with the experimental data.

Tables II-VI also report the standard devations $\sigma(x_w)$ of the fitting of the ternary equilibria, calculated as

$$\sigma(x_w) = [\sum_{k=1}^{M} \sum_{l=1}^{3} \sum_{j=1}^{2} (x_{wljk,\text{exp}} - x_{wljk,\text{calc}})^2 / 6M]^{0.5} \quad (6)$$

where M is the total number of tie lines of both isotherms. The

Table VIII. NRTL Parameters α_{ij}, a_{ij}, a_{ji}, b_{ij}, and b_{ji}, Equations 2-4, for the Binary Systems

component i–j	α_{ij}	a_{ij}/(cal mol^{-1})	a_{ji}/(cal mol^{-1})	b_{ij}/(cal mol^{-1} K^{-1})	b_{ji}/(cal mol^{-1} K^{-1})
water (2)–benzene (3)	0.2	2692.74	3307.26	−11.501	10.607
water (2)–toluene (3)	0.2	2631.38	3783.84	−0.874	22.374
water (2)–*m*-xylene (3)	0.2	2895.39	4856.16	−9.432	9.604
water (2)–*p*-xylene (3)	0.2	2556.90	5149.00	0.0	0.0
water (2)–ethylbenzene (3)	0.2	3025.01	4667.66	−14.187	18.360
acetonitrile (1)–benzene (3)	0.3	143.62	548.74	3.290	−3.305
acetonitrile (1)–toluene (3)	0.3	378.41	36.83	9.491	−2.421
acetonitrile (1)–*m*-xylene (3)	0.3	−566.06	1140.48	16.615	−11.468
acetonitrile (1)–*p*-xylene (3)	0.3	−208.13	798.70	14.872	−8.981
acetonitrile (1)–ethylbenzene (3)	0.3	363.69	632.87	3.408	−4.182
acetonitrile (1)–water (2)	0.3	604.06	797.80	−2.421	6.920

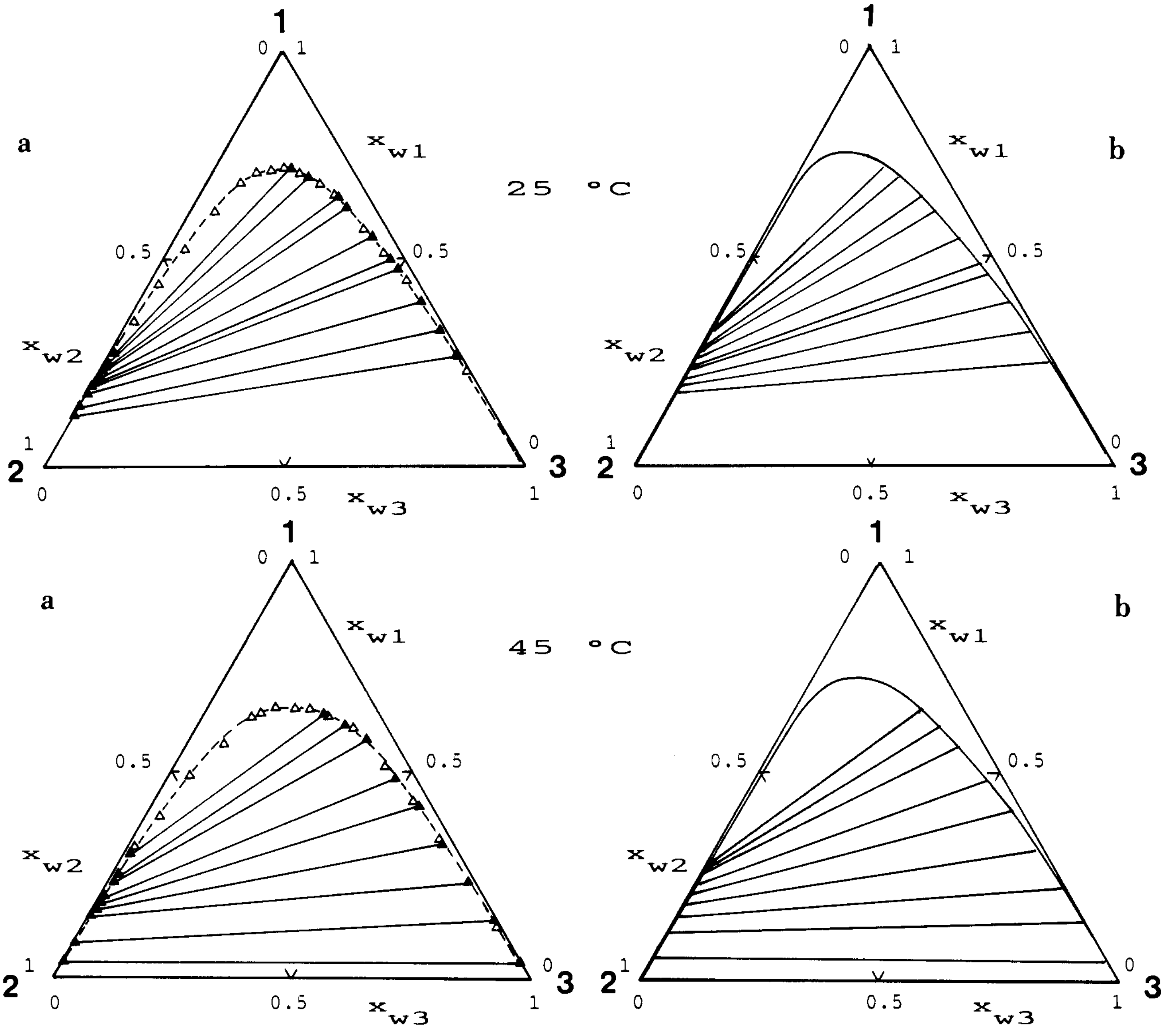

Figure 1. Ternary liquid–liquid equilibria for the acetonitrile (1) + water (2) + benzene (3) system at 25 and 45 °C, x_w, mass fractions: (a) △, experimental binodal curve, and ▲, experimental tie line; (b) calculated binodal curve and tie lines.

prediction of binodal curves and of tie lines appears to be satisfactory, as shown in Figure 1 for the system acetonitrile–water–benzene. Similar diagrams are obtained for the other four systems.

The binodal curve data and the tie-line data indicate that all the aromatic hydrocarbons investigated can be used in the liquid–liquid extraction of acetonitrile. The immiscibility region slightly increases for the solvents studied in the order benzene > toluene > *m*-xylene ≈ *p*-xylene ≈ ethylbenzene.

The distribution coefficients of acetonitrile between solvent and aqueous layers are shown in Figure 2. The order of solvents is benzene > toluene > *m*-xylene ≈ *p*-xylene ≈ ethylbenzene.

The selectivities are reported in Figure 3, as mass fractions of acetonitrile on a solvent-free basis. Ethylbenzene and the xylenes appear to be more selective than toluene and benzene.

By increasing the temperature from 25 to 45 °C, both selectivity and distribution coefficient values slightly decrease, and

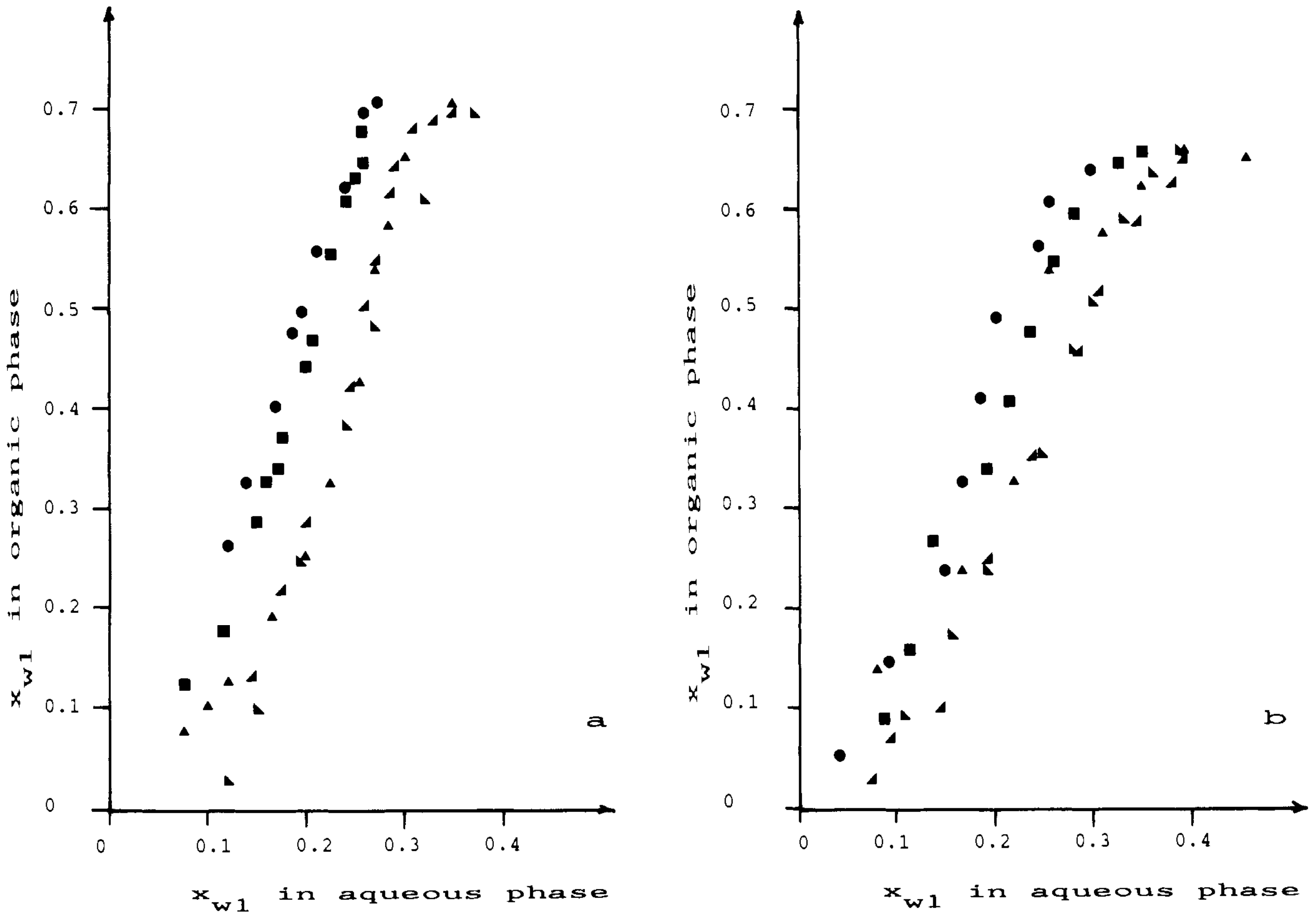

Figure 2. Experimental distribution coefficients of acetonitrile (1) + water (2) + solvent (3) system at (a) 25 °C and (b) 45 °C (x_{w1}, mass fractions). Solvent: ●, benzene; ■, toluene; ◣, *m*-xylene; ◢, *p*-xylene; ▲, ethylbenzene.

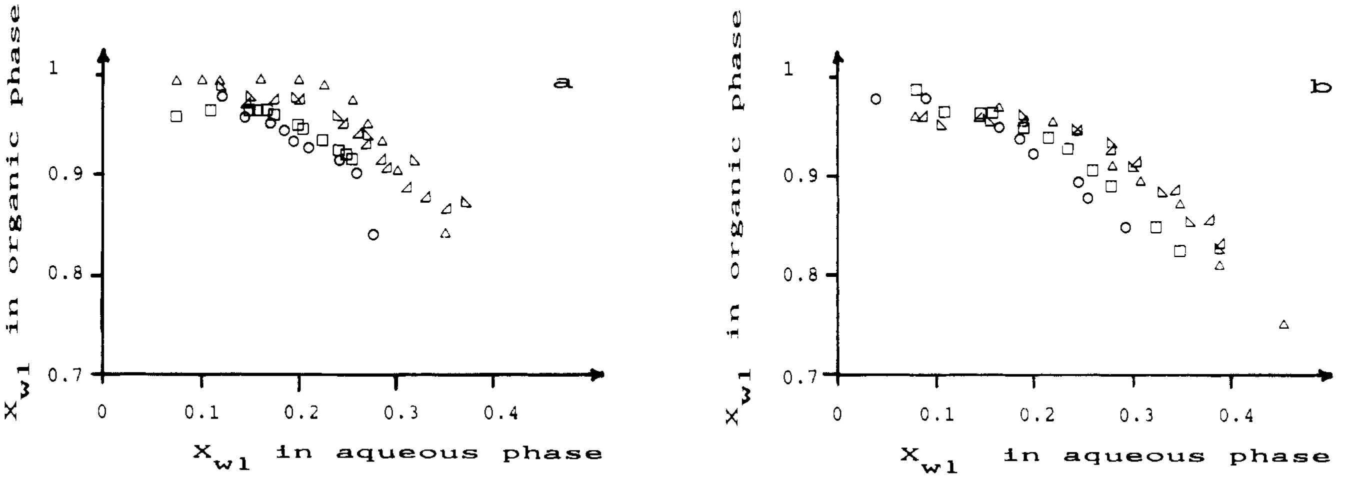

Figure 3. Experimental selectivity data for acetonitrile (1) + water (2) + solvent (3) system at (a) 25 °C and (b) 45 °C (X_{w1}, mass fractions on a solvent-free basis). Solvent: ○, benzene; □, toluene; ◺, *m*-xylene; ◿, *p*-xylene; △, ethylbenzene.

the differences between the solvents become less evident.

Glossary

a_{ij}	parameter, eq 3, cal mol^{-1}
a_{ji}	parameter, eq 4, cal mol^{-1}
F_P	weighting factor for pressure deviations, eq 5
F_T	weighting factor for temperature deviations, eq 5
F_{y_i}	weighting factor for vapor-phase composition deviations of component *i*, eq 5
g_{ij}	energy of interaction between an *i–j* pair of molecules, cal mol^{-1}
G_{ij}	parameter of the NRTL equation, eq 2
b_{ij}	parameter, eq 3, cal mol^{-1} K^{-1}
b_{ji}	parameter, eq 4, cal mol^{-1} K^{-1}
M	total number of tie lines referred to both isotherms of each ternary system LLE data
N	total number of vapor–liquid equilibrium data of each binary system VLE data
P	pressure, kPa
R	gas constant, cal mol^{-1} K^{-1}
S	objective function, eq 5
T	temperature, K

x_i	liquid-phase mole fraction of component i
x_{wi}	liquid-phase mass fraction of component i
X_{wi}	liquid-phase mass fraction of component i on a solvent-free basis
y_i	vapor-phase mole fraction of component i
α_{ij}	parameter of the NRTL equation, eq 2
γ_i	activity coefficient of component i
τ_{ij}	parameter of the NRTL equation, eq 2
$\sigma(x_w)$	standard deviation, mass fraction

Subscripts

calc	calculated
exp	experimental
i,j	component indexes (1, acetonitrile; 2, water; 3, aromatic hydrocarbon)
j	phase index (1, aqueous; 2, organic)
k	tie-line index
m	running variable, eq 5
p,r	running variables, eq 2

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Vapor–Liquid Equilibria in the Carbon Dioxide + Ethanol and Carbon Dioxide + 1-Butanol Systems

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Vapor–liquid equilibrium data for CO_2 + ethanol mixtures at 314.5, 325.2, and 337.2 K and for CO_2 + 1-butanol mixtures at 314.8, 325.3, and 337.2 K have been measured by using a high pressure flow apparatus. The pressure in the experiments ranged from 4.633 to 11.776 MPa. Our results for the CO_2 + ethanol system are in good agreement with the recent results of Suzuki et al. and with the results of Panagiotopoulos. However, the results for the CO_2 + 1-butanol system are significantly different from those reported by King et al.

Introduction

CO_2 + alcohol systems are of interest because of their importance as supercritical fluid/cosolvent pairs in the separation of biomaterials (*1–4*). A knowledge of vapor–liquid equilibrium in these systems is therefore necessary for evaluating models for the extraction of biomaterials with supercritical fluid/cosolvent pairs. In spite of these interests, however, only the CO_2 + methanol (*5–8*) and CO_2 + ethanol (*8–11*) systems have been studied extensively. Surprisingly, the CO_2 + 1-propanol (*8*, *11*), CO_2 + 2-propanol (*11–12*), and CO_2 + 1-butanol (*13*) systems have received very little attention, and CO_2 + higher alcohol systems have not been studied at all.

We have constructed a flow apparatus to measure high-pressure vapor–liquid equilibria in systems containing CO_2 + alcohol and biomaterials in liquid solutions. A flow apparatus was chosen because large sample sizes could be generated for analysis, and this can be particularly valuable when dealing with components present in dilute concentrations. We are currently evaluating the CO_2 + ethanol, CO_2 + propanol, and CO_2 + 1-butanol systems for the supercritical extraction of pyrrolizidine alkaloids. We have therefore measured vapor–liquid equilibria in the CO_2 + ethanol and CO_2 + 1-butanol systems. The CO_2 + ethanol system was chosen as a test system to check the validity of the measurements from the new apparatus, since a number of investigators have reported data for this system at the conditions of interest. The only previously reported data for the CO_2 + 1-butanol system are those of King et al. (*13*) at 313.15 and 383.15 K. The CO_2 + 1-butanol system was studied in the present work because of a need for data at temperatures other than those previously reported.

Experimental Section

Experimental Apparatus. In the flow apparatus, two or more components are mixed thoroughly and continuously at constant temperature until vapor–liquid equilibrium is achieved. The vapor and liquid phases are then separated and analyzed to obtain the concentrations of the phases in equilibrium. A schematic diagram of the apparatus used in this work is shown in Figure 1, and a more detailed description is given below. The apparatus is similar to those described by Simnick et al. (*14*), Thies and Paulaitis (*15*), Inomata et al. (*16*), and Radosz et al. (*17*).

Liquid carbon dioxide was obtained from a cylinder equipped with an eductor tube and was compressed to the desired pressure by using a Milton Roy metering pump (Model 396–89). The inlet tube and the pump head were covered with an ice bath to ensure that the carbon dioxide remained liquid during the compression process. A regulator was used instead of the pump when the desired pressure was lower than the carbon dioxide cylinder pressure. Liquid ethanol and 1-butanol were compressed to the desired pressure by using another Milton Roy metering pump (Model 396–57).

The CO_2 and alcohol were pumped through a section of 0.125-in.-o.d. × 0.069-in.-i.d. stainless steel tubing, tubing coils, and two 0.1875-in.-o.d. × 0.132-in.-i.d. × 7-in. static mixers placed inside a constant-temperature air bath. Vapor–liquid

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