

LIQUID-LIQUID EQUILIBRIUM DATA FOR TERNARY SYSTEMS CONTAINING ORGANIC ACID, HYDROCARBON AND WATER

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ABSTRACT

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Experimental LLE data are presented for the acetic acid-toluene-water system at 60, 70 and 80 °C and for the acetic acid-heptane-water, propionic acid-toluene-water, propionic acid-heptane-water and butanoic acid-toluene-water systems at 50, 60 and 70 °C. The data are correlated by means of the NRTL and UNIQUAC models and the relevant parameters are given. The UNIFAC method is used to predict the behaviour of the systems.

INTRODUCTION

Experimental data for the ternary system acetic acid-toluene-water are available in the literature over a relatively wide temperature range (Dackshinamurty et al., 1973; Rius Miro and Otero de la Granada, 1952; Salem, 1979), but unfortunately liquid-liquid equilibrium (LLE) data for systems containing longer-chain acids such as propionic and butanoic acid have been measured over narrow temperature ranges (Raya-Rao, 1956) or are not available at all.

Good experimental data over a wide temperature range are needed for parameter estimation in semiempirical models. The aim of this work was therefore to provide experimental LLE data for ternary systems containing acetic, propionic or butanoic acid together with water and one hydrocarbon, and then to correlate these data in order to obtain a set of parameters which can be used reliably in the design of separation processes.

The systems studied were acetic acid-toluene-water (A), acetic

TABLE 1

Experimental tie lines (mol %) for the system acetic acid-toluene-water (A) at 60, 70 and 80 °C

Water		Acetic acid		T (°C)
Phase 1	Phase 2	Phase 1	Phase 2	
82.57	1.53	16.87	4.58	60
67.04	2.56	32.05	13.52	
61.71	2.91	36.97	18.57	
50.04	4.82	47.25	29.49	70
83.81	1.48	15.62	4.32	
65.89	2.98	33.13	13.81	
54.12	4.74	40.99	20.93	80
47.98	7.98	48.01	32.75	
80.95	2.24	18.43	4.71	
66.44	2.21	32.15	13.89	
55.92	5.08	41.96	22.01	
46.88	8.53	48.19	34.22	

determinations of the conjugate phases were carried out. Tables 1-5 report the experimental liquid-liquid equilibrium data obtained, and Fig. 1 gives, as an example, a graphical representation of the influence of the acid on the equilibrium. It is interesting here to note the reduction of the miscibility gap

TABLE 2

Experimental tie lines (mol %) for the system acetic acid-heptane-water (B) at 50, 60 and 70 °C

Water		Acetic acid		T (°C)
Phase 1	Phase 2	Phase 1	Phase 2	
84.16	0.84	15.75	1.52	50
75.42	0.91	24.49	2.03	
61.38	1.93	38.52	8.38	
43.77	2.01	55.55	15.42	60
40.13	2.09	58.96	16.25	
83.47	1.52	16.41	1.90	
74.02	2.12	25.93	3.68	70
59.81	2.25	39.78	8.56	
45.93	2.51	53.52	15.03	
42.10	2.67	57.29	16.51	
80.58	1.61	19.30	2.03	
72.41	2.05	27.49	3.98	
60.99	2.06	38.91	8.91	
48.81	2.11	50.63	12.27	
45.17	2.80	53.98	16.52	

TABLE 3

Experimental tie lines (mol %) for the system propionic acid–toluene–water (C) at 50, 60 and 70 °C

Water		Propionic acid		T (°C)
Phase 1	Phase 2	Phase 1	Phase 2	
95.63	3.01	4.15	17.24	50
91.32	5.86	8.32	23.34	
86.48	11.22	13.16	30.21	
77.19	18.07	21.74	35.70	
72.27	24.31	25.20	39.93	60
94.82	4.02	4.96	14.86	
92.81	6.71	6.88	21.01	
87.50	10.50	12.11	27.87	
78.87	19.24	20.01	33.82	70
72.64	24.71	24.40	38.36	
95.01	4.57	4.73	14.91	
93.41	7.58	6.27	19.07	
88.32	11.54	11.26	25.52	
79.37	19.89	19.22	31.82	
73.53	25.04	23.30	35.89	

TABLE 4

Experimental tie lines (mol %) for the system propionic acid–heptane–water (D) at 50, 60 and 70 °C

Water		Propionic acid		T (°C)
Phase 1	Phase 2	Phase 1	Phase 2	
91.18	0.94	8.40	7.91	50
84.06	1.21	15.20	15.32	
74.02	2.75	25.07	25.46	
66.27	4.27	32.63	33.08	
57.92	6.69	40.23	40.33	60
51.52	8.51	45.61	46.01	
84.77	0.51	14.72	15.02	
75.85	2.89	23.24	23.41	
68.34	4.18	30.50	30.61	70
61.37	6.17	36.91	37.22	
53.04	8.62	44.10	44.45	
82.36	1.87	17.03	17.01	
72.70	3.82	26.28	26.56	
66.27	5.81	31.89	32.21	
60.30	7.20	37.62	38.07	
51.65	10.12	44.64	44.82	

TABLE 5

Experimental tie lines (mol %) for the system butanoic acid–toluene–water (E) at 50, 60 and 70 °C

Water		Butanoic acid		T (°C)
Phase 1	Phase 2	Phase 1	Phase 2	
97.88	11.43	2.01	26.15	50
97.09	20.51	2.77	33.91	
96.27	32.50	3.51	38.11	
95.84	41.01	4.11	40.02	
95.14	52.61	4.67	36.81	60
97.25	17.06	2.74	30.91	
96.32	25.41	3.46	37.11	
95.95	34.12	4.02	39.00	
95.09	52.11	4.71	38.27	70
94.79	61.83	5.11	32.87	
96.79	21.09	3.11	34.40	
96.18	29.23	3.49	39.01	
95.21	45.91	4.61	39.09	
94.08	68.49	5.91	28.04	
93.00	78.89	6.95	20.11	

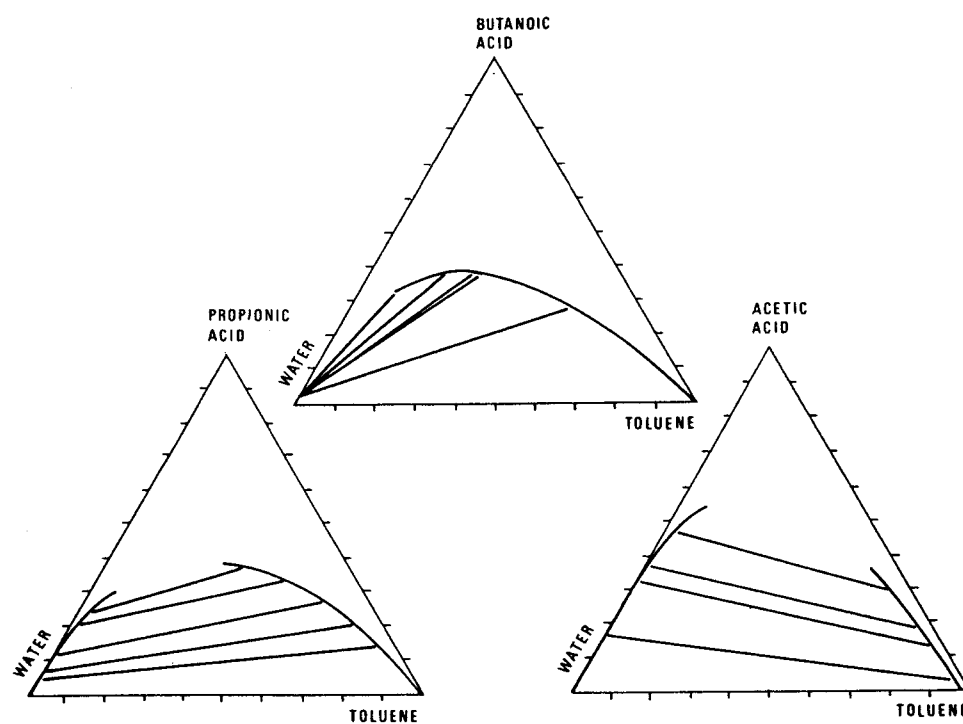


Fig. 1. Experimental LLE data at 60 °C: influence of organic acid.

and the varying slope of the tie lines as the number of carbon atoms in the acid increases.

DATA REDUCTION

The experimental data were correlated by means of two-parameter excess-free-energy models, namely, NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975). When using the NRTL model the parameter α was fixed at 0.2. The computer program used in the data reduction was that developed by Sørensen et al. (1979), with the objective function defined in terms of concentrations. The results are compared on the basis of a root-mean-square coefficient (RMS) defined as

$$\text{RMS} = 100 \left[\sum_k \min_i \sum_j (x_{ijk}^c - x_{ijk}^E)^2 / 6M \right]^{1/2}$$

$$i = 1, 2, 3; j = \text{I, II}; k = 1, \dots, M$$

which takes into account both the shape of the binodal curve and the slope of the tie lines.

Table 6 shows the results of the fitting at the different temperatures for the acetic acid–water–toluene system: the high value of the correlation coefficient for the parameters in excess-Gibbs-energy models does not allow any conclusion about a possible temperature dependence of the parameters. The fact that any equation for G^E can provide only an approximation to the experimental data leads to nonuniqueness of the parameters: there are many sets of parameters which can represent the experimental data equally well within experimental uncertainties.

For this reason we fitted, for one system at a time, all the data at different temperatures (global fitting). This procedure gives a set of parameters

TABLE 6

Parameters (K) from individual fitting for the system acetic acid–water–toluene

T (°C)	RMS	Acid–water		Toluene–water		Toluene–acid	
<i>UNIQUAC</i>							
60	0.1931	–159.1	–269.5	663.8	371.9	–62.60	68.60
70	0.5031	–211.7	–361.2	762.1	172.2	213.2	203.3
80	0.5020	–283.6	–273.4	604.5	343.1	–60.20	40.43
<i>NRTL</i>							
60	0.4256	–330.6	–304.4	1378.7	799.3	802.5	–530.8
70	0.4659	182.9	–713.0	2000.3	828.6	760.2	–410.3
80	0.4635	–250.8	–571.5	1514.8	712.9	802.2	–591.2

TABLE 7
UNIQUAC parameters (K) for the binary systems investigated

Binary system	Global fitting		Sørensen's method	
Water-acetic acid	-339.45	-192.06	-124.34	-294.43
	6.6159	-393.03		
Water-toluene	187.99	788.59	444.52	659.24
	235.86	798.18		
	461.94	638.48		
Acetic acid-toluene	177.52	-183.00	16.051	33.800
Water-heptane	242.17	840.68	125.92	935.73
	78.429	1603.9		
Acetic acid-heptane	247.86	91.208	357.21	24.769
Water-propionic acid	-92.333	36.913	-305.85	273.28
	-324.16	201.11		
Propionic acid-toluene	-237.69	202.16	-312.60	212.27
Propionic acid-heptane	236.38	-224.03	147.17	-136.60
Butanoic acid-toluene	14873	21.447	25.097	11.951
Butanoic acid-water	-160.30	386.51	-158.24	382.97

(Tables 7 and 8) which can be used safely within the experimental temperature range and, as shown in Table 9, gives relatively good results in terms of the RMS values.

Sørensen and Arlt (1979) proposed a different data reduction method, in which different ternary liquid-liquid data sets with some common binary pairs are fitted simultaneously in order to ensure uniqueness of the parame-

TABLE 8
NRTL parameters (K) for the binary systems investigated

Binary system	Global fitting		Sørensen's method	
Water-acetic acid	72.266	-627.92	350.49	-708.16
	772.04	-887.04		
Water-toluene	2095.1	842.63	2112.2	944.03
	1866.8	825.91		
	1754.5	993.37		
Acetic acid-toluene	679.89	-389.34	765.82	-352.20
Water-heptane	2036.9	798.02	1997.9	748.89
	1762.0	1127.9		
Acetic acid-heptane	1411.7	-162.65	1285.8	-172.17
Water-propionic acid	-152.15	-303.65	-29.972	13.663
	174.46	-191.02		
Propionic acid-toluene	-318.05	-705.09	-595.69	167.71
Propionic acid-heptane	681.16	-463.02	615.42	-407.73
Butanoic acid-toluene	96.180	113.73	-51.277	106.25
Butanoic acid-water	-512.38	1609.8	-438.37	1432.8

TABLE 9
RMS values obtained using the different procedures

System	T ($^{\circ}\text{C}$)	UNIQUAC (individual)	NRTL (individual)	UNIQUAC (global)	NRTL (global)	UNIQUAC (Sørensen)	NRTL (Sørensen)
A	60	0.1931	0.4256	0.4782	0.5316	0.4966	0.5519
	70	0.5031	0.4659	0.5285	0.4687	0.5699	0.4705
	80	0.5020	0.4635	0.5591	0.5198	0.5890	0.5417
B	50	0.3601	0.3107	0.4012	0.5676	0.4563	0.6154
	60	0.1287	0.1067	0.2212	0.2417	0.2306	0.3079
	70	0.3907	0.3911	0.3986	0.4714	0.4194	0.4859
C	50	0.4431	0.4701	0.8380	0.9415	1.0366	1.0319
	60	0.3515	0.3511	0.3842	0.4467	0.6041	0.7087
	70	0.2996	0.2876	0.7509	0.8747	0.7834	1.1619
D	50	0.2813	0.2887	0.3436	0.3108	0.8142	0.7480
	60	0.2660	0.2715	0.3033	0.2990	0.8130	0.7948
	70	0.2268	0.3019	0.3083	0.3856	0.7184	0.6067
E	50	0.2219	0.2341	0.3178	0.4593	0.3271	1.2611
	60	0.2361	0.2775	0.2711	0.4114	0.2795	1.4658
	70	0.1871	0.2112	0.2386	1.0956	0.2430	2.7335

ters for all the binary systems involved. Table 9 summarizes the correlation results obtained using the three different data fitting procedures described above, namely, individual, global and Sørensen, for both models.

The RMS values obtained by means of Sørensen's method are relatively higher than those obtained by global fitting. The RMS values are considerably lower when one system is fitted at a single temperature.

PREDICTION

Table 10 shows predictions for literature systems not included in the data base, using the various sets of parameters obtained above. Experimental data

TABLE 10
Prediction of literature data by means of UNIQUAC parameters from global fitting for the systems acetic acid-toluene-water (A) and propionic acid-heptane-water (D)

Reference	System	T ($^{\circ}\text{C}$)	Tie lines	Prediction	Fitting
Woodman (1926)	A	25	8	1.9267	0.6500
Dakshinamurty et al. (1973)	A	60	8	3.3258	0.8600
Salem (1979)	A	60	10	3.8036	0.1304
Rius Miro and Otero de la Granada (1952)	A	75	4	1.8277	
Fuse and Iguchi (1971)	A	25	10	2.7860	1.0204
Rius Miro and Otero de la Granada (1952)	A	55	5	2.1150	1.0870
Kovaleva (1969)	D	25	7	1.7001	0.7161

at 25°C (Woodman, 1926; Fuse and Iguchi, 1971; Kovaleva, 1969) are predicted reasonably well, even though data at this temperature were not included in the parameter estimation. Experimental data at 55 and 75°C from a different source (Rius Miro and Otero de la Granada, 1952) are also predicted well. Some difficulties arise when considering the data of Salem (1979) and those of Dackshinamurty et al. (1973). In any case, the RMS values obtained in the predictions are within a reasonable range: an analysis of artificial systems (Kikic et al., 1983) shows that for a perfect model an RMS value of 0.8 corresponds to an uncertainty of 0.016 in the mole fractions. Group contribution methods may be applied to predict liquid-liquid equilibrium data. Magnussen et al. (1981) recently extended the UNIFAC method to LLE calculations and published relevant parameter tables. Figure 2 reports predictions for the propionic acid-toluene-water and butanoic acid-toluene-water systems at 60°C by means of the UNIFAC method using LLE parameters. The predicted two-phase regions are larger than the experimental ones, but the slope of the tie lines is predicted correctly.

In order to quantify the above prediction, Table 11 compares the tie lines calculated by means of the UNIFAC method with those calculated on the basis of the parameters obtained from fitting for the single system. The high RMS values result essentially from the poor prediction of the shape of the

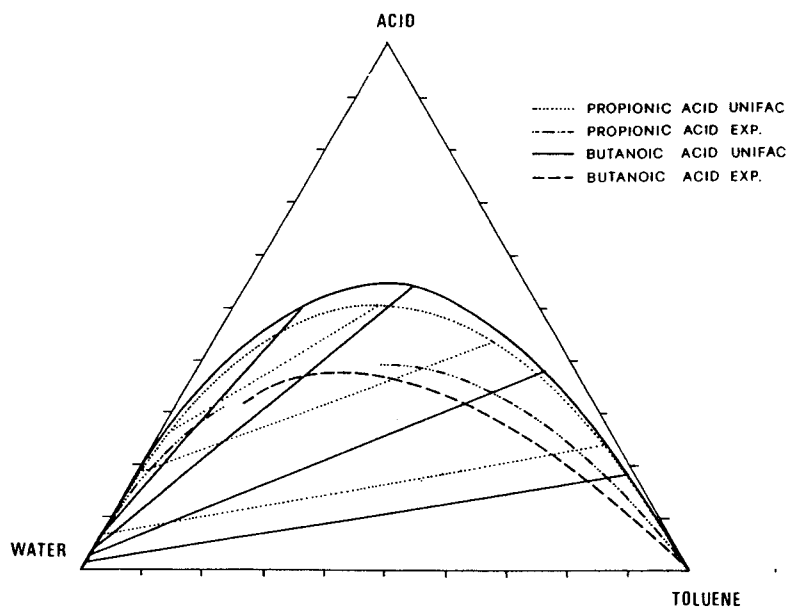


Fig. 2. Comparison between experimental binodal curves and binodal curves predicted by UNIFAC method.

TABLE 11
UNIFAC predictions

System	T (°C)	Number of experimental data	RMS
Propionic acid-toluene-water	60	5	5.0627
Butanoic acid-toluene-water	60	5	6.2132

binodal curve. Similar trends are observed for other temperatures and for the other systems.

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