the original mixture vs. the concentrations of the four components. In order to carry out the representation, a tetrahedral projection is made onto a plane parallel to the edges that do not meet. This representation is appropriate for the interpolation of equilibrium data suitable for equilibrium stage calculations for quaternary systems (*8*).

Glossary

C	chloroform
E	ethanol
F	objective function
L	ethanol level (defined as $L = X_E$ in the initial mixture)
M	chloroform–toluene mixture (defined as $M = X_C/(X_C + X_T)$ in the initial mixture)
N	number of tie lines
T	toluene
W	water
x	mole fraction
X	weight percentage
X', X''	coordinates
Y', Y''	coordinates

Superscript

$\wedge$	calculated

Subscripts

i	component
j	phase
k	tie line

Registry No. E, 64-17-5; C, 67-66-3; T, 108-88-3.

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Effect of Temperature on Liquid–Liquid Equilibria for Three Systems Containing Acetic Acid–Water–Toluene, Propionic Acid–Water–Cyclohexane, Propionic Acid–Water–Toluene at Atmospheric Pressure

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This study on the effect of temperature on the liquid–liquid equilibria on various ternary systems was instigated by a need for equilibrium data at various temperatures for the system propionic acid–water–toluene. The data for this system were required for a pilot plant study which operated as part of a fundamental investigation of liquid–liquid extraction operation, in the Department of Chemical and Petroleum Engineering of the University of Calgary. Two other systems, namely propionic acid–water–cyclohexane and acetic acid–water–toluene, were subsequently studied to further aid in the observation on temperature effects on equilibria. Measurements were made at (a) 5, 10, 20, 30, and 50 °C for the acetic acid–water–toluene system, (b) 2, 5, 10, 20, and 30 °C for the propionic acid–water–cyclohexane system, and (c) 5, 20, 35 , and 50 °C for the propionic acid–water–toluene system. The data obtained were then compared to equilibria predicted by the UNIFAC activity coefficient model.

Experimental Section

Materials. All chemicals used were from the Fisher Scientific Co. The manufacturers specifications are as follows: acetic acid purity more than 99.8% ($\rho_{20} = 1.049$ g/cm^3), toluene more than 99.0 mol % pure ($\rho_{20} = 0.866$ g/cm^3), propionic acid 0.01% residue after evaporation, 0.25% water ($\rho_{20} = 0.992$ g/cm^3), cyclohexane purity greater than 99 mol % ($\rho_{20} = 0.779$ g/cm^3). The water used was distilled and deionized in the laboratory.

Equipment. The following were used: constant temperature bath, Haake D3-6, ±0.02 °C; gas chromatograph, Shimadzu GC-8A; GC packing, Poropak Q. The burets used comply with, Type, Style Class A Tech. specification NNN-B-789. The thermometers used meet NBS specifications ±0.05 °C.

Procedure. The procedure for determining the mutual solubility (binodal) curves was that of Othmer (*1*). For the determination of the tie line data the following method was used.

Twenty milliliters of solvent and an equal amount of diluent (by weight) are taken in a flask. Five milliliters of solute is then added and the mixture is vigorously shaken, placed in a constant temperature bath, and allowed to settle. A small sample (1 μL) of each layer is removed with a glass syringe and injected into the gas chromatograph to determine the acid concentration. Another 5 mL of acid is added, the mixture is shaken, placed in the constant temperature bath, and allowed to settle. Again the acid concentration for each layer is determined by gas chromatograph. This procedure is repeated with progressively smaller additions of solute until only a single phase exists; i.e., the mixture is in the completely soluble region above the line of mutual solubility.

This is shown in Figure 1 where L represents equal amounts of solvent and diluent. Acid is added to percentage equal to the length of line OL. Two layers are present. Analysis of solvent layer gives a weight percent of acid equal to the distance YL. Y is projected to the left to an intersection with the mutual solubility line at P, which is thus the solvent end of the

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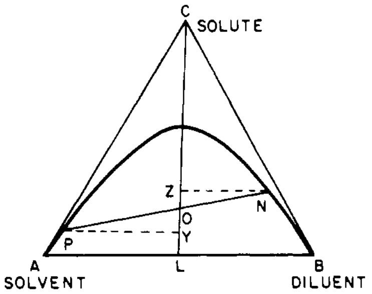

Figure 1.

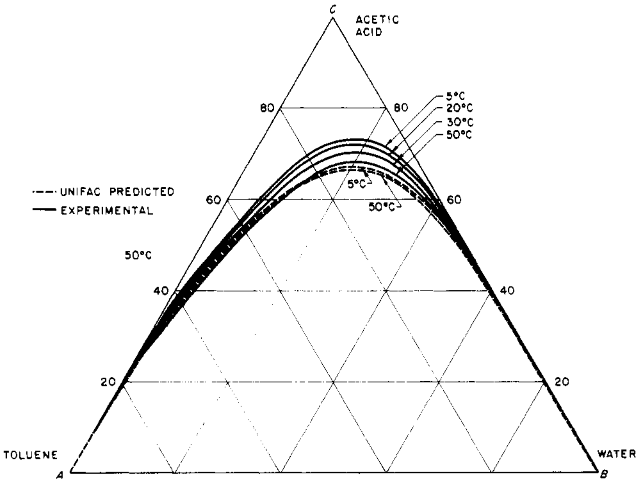

Figure 2. Acetic acid–water–toluene isotherms (wt %).

tie line. Similarly, the diluent layer when analyzed gives a weight percent of acid equal to the distance LZ. Z is projected to the right to an intersection with mutual solubility line at N, the diluent end of the line. Other tie lines are similarly determined. Since the point O is known, only the point P or N would have to be determined to fix the tie line. Determination of both serves as a check, since all three points must lie on the tie line. Although we were mostly concerned with relative effects of temperature on the equilibria of the tested systems, every possible measure was taken to ensure that errors were within the tolerances and that results were repeatable.

Results and Discussion

The solubility curve and tie line data for the acetic acid–water–toluene system at 5, 10, 20, 30, and 50 °C appear in Tables I and II, respectively. Tables III and IV show the solubility curve and tie line data at 2, 5, 10, 20, and 30 °C for the propionic acid–water–cyclohexane system. The solubility curve and tie line data for the propionic acid–water–toluene system at 5, 20, 35, and 50 °C are shown in Tables V and VI, respectively. The plait points were estimated by the method of Treybal et al. (*2*) and appear at the bottom of the mutual solubility tables.

Isotherms for all three systems at each of the experimental temperatures are shown on ternary diagrams of Figures 2–4. The trend of the two-phase region is to decrease in size with increase in temperature in all three systems. The effect of temperature is most noticeable at the higher solute concentrations. At lower solute concentrations the solubility is relatively unaffected by the changes in temperature encountered. Figures 5–7 show the corresponding distribution curves for each system at each temperature.

The standard deviation of the equilibrium data is estimated to be ±1%. Measurements were repeated where possible to ensure that the error would lie within the equipment specification. To further confirm the accuracy of our experimental method the data for the acetic acid–water–toluene system at 30 °C were compared to the published data of Dakshinamurty et al. (*3*). It was found that our experimental data corresponded well with that of Dakshinamurty's as shown in Figure 8.

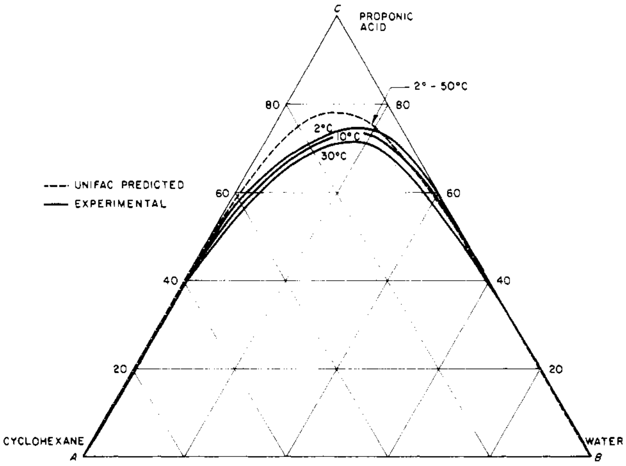

Figure 3. Propionic acid–water–cyclohexane isotherms (wt %).

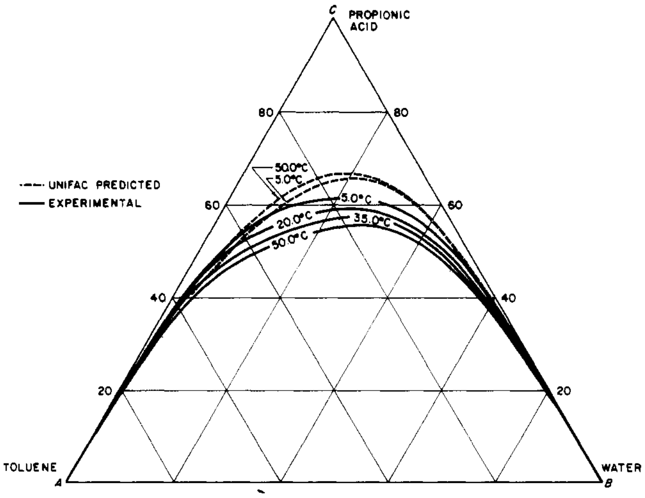

Figure 4. Propionic acid–water–toluene isotherms (wt %).

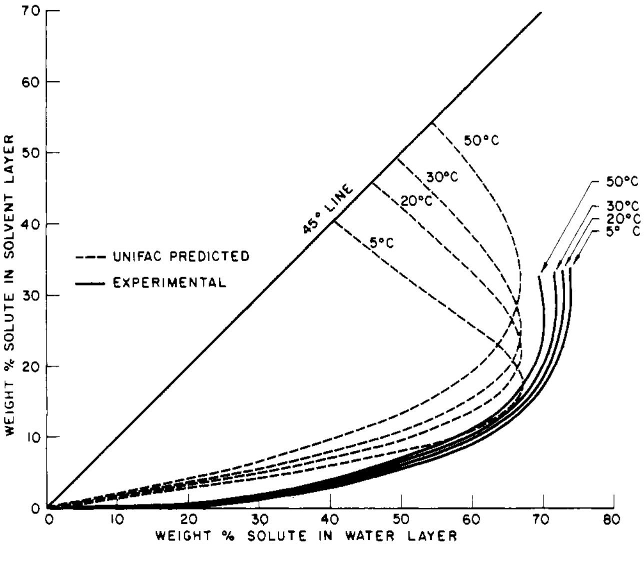

Figure 5. Distribution diagram for acetic acid–water–toluene system.

It is of interest to note the temperature dependence of the propionic acid–water–toluene system in particular. At 5.0 °C

Table I. Mutual Solubility Data for Acetic Acid-Water-Toluene System

5 °C			10 °C			20 °C			30 °C			50 °C		
toluene	water	acetic acid	toluene	water	acetic acid	toluene	water	acetic acid	toluene	water	acetic acid	toluene	water	acetic acid
0.85	49.26	49.88	0.79	46.06	53.15	0.82	47.32	51.86	0.88	50.98	48.13	1.00	57.60	41.39
1.67	38.67	59.64	1.79	37.33	60.88	1.79	37.63	60.58	1.92	40.25	57.83	2.17	45.64	52.19
2.68	30.95	66.37	2.79	32.19	65.02	2.82	32.64	64.54	3.03	35.10	61.87	3.35	38.66	57.99
4.07	26.91	69.02	4.19	27.65	68.16	4.25	28.10	67.65	4.56	30.09	65.35	4.92	32.45	62.63
5.15	23.77	71.08	5.27	24.35	70.38	5.47	25.29	69.24	5.80	26.78	67.42	6.26	28.94	64.80
6.82	20.98	72.20	7.00	21.55	71.45	7.14	21.98	70.88	7.50	23.06	69.44	8.14	25.03	66.83
8.31	19.20	72.49	8.44	19.49	72.07	8.65	19.98	71.37	9.09	20.99	69.62	10.17	22.17	67.66
9.78	17.38	72.84	10.06	17.87	72.07	10.64	18.20	71.15	10.92	18.69	70.39	11.80	20.19	68.00
11.13	16.07	72.80	11.42	16.48	72.10	11.73	16.92	71.35	12.31	17.77	69.92	14.01	18.39	67.60
12.87	14.86	72.27	13.14	15.17	71.69	13.39	15.47	71.14	14.10	16.28	69.62	15.21	17.56	67.23
14.77	13.65	71.58	14.99	13.86	71.15	15.42	14.25	70.33	16.16	14.93	68.91	17.08	16.28	66.64
16.33	12.57	71.09	16.98	12.75	70.27	17.42	13.07	69.51	17.99	13.81	68.20	19.70	14.79	65.51
18.43	11.70	69.87	20.93	10.87	68.20	21.62	11.23	67.15	22.49	11.70	65.81	24.29	12.62	63.09
20.61	10.71	68.68	24.01	9.70	66.29	24.72	9.99	65.29	25.97	10.49	63.54	27.58	11.46	60.96
23.66	9.56	66.78	28.43	8.37	63.20	29.24	8.61	62.15	30.93	8.93	60.13	33.24	9.60	57.16
28.18	8.14	63.68	33.80	6.83	59.37	34.51	6.97	58.52	36.25	7.32	56.43	38.99	7.88	53.13
45.94	3.98	50.08	46.72	4.05	49.23	46.84	4.06	49.10	49.82	4.32	45.86	53.01	4.59	42.40
57.96	2.01	40.03	56.78	2.30	40.92	58.59	2.37	39.04	60.52	2.44	37.04	64.30	2.60	33.10
64.25	1.11	34.64	66.31	1.15	32.54	68.24	1.18	30.57	67.13	1.55	31.32	75.06	1.30	23.64
39.37[a]	5.51[a]	55.12[a]	41.50[a]	4.39[a]	54.11[a]	42.23[a]	5.15[a]	52.62[a]	43.12[a]	5.80[a]	51.08[a]	46.03[a]	6.05[a]	47.12[a]

[a] Plait point composition.

Table II. Tie Line Data for Acetic Acid-Water-Toluene System Acid Concentration

5 °C		10 °C		20 °C		30 °C		50 °C	
solvent[a]	water[a]	solvent	water	solvent	water	solvent	water	solvent	water
1.06	24.40	1.04	24.44	0.79	24.40	1.21	24.49	1.27	24.89
3.30	38.08	3.42	37.54	3.10	36.51	3.42	37.64	3.45	37.95
5.51	50.13	5.70	47.50	5.54	46.48	5.45	47.10	5.91	47.46
7.84	53.64	7.68	53.80	7.69	53.51	7.89	53.23	7.88	54.29
10.12	59.66	9.95	57.16	9.57	60.21	9.90	58.33	10.37	58.23
11.57	63.83	11.87	62.17	12.07	62.03	12.23	62.18	12.59	64.95
14.19	64.85	14.06	65.32	14.04	65.90	14.48	65.28	14.66	63.96
16.22	70.40	16.35	67.51	16.29	67.77	16.43	66.79	17.24	65.89
18.43	69.10	18.43	69.49	18.75	68.69	18.76	69.00	19.79	67.02
22.51	70.98	21.63	70.97	21.97	70.32	22.73	69.82	23.91	68.91
25.95	72.19	24.98	72.21	25.49	71.41	26.19	70.68	27.58	69.10
31.20	73.27	28.70	72.67	28.95	71.64	30.08	70.87	31.26	68.66
33.59	72.62	31.73	72.73	32.77	71.72	33.05	70.35		
		34.12	72.32						

[a] Refers to solvent and water layers.

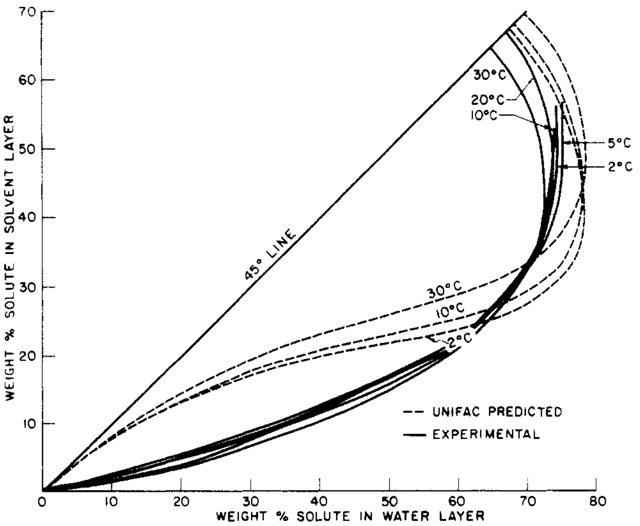

Figure 6. Distribution diagram for propionic acid-water-cyclohexane system.

the system exhibits solutropic behavior, having two changes in the direction of the slope of the tie lines. The distribution diagram in Figure 7 shows the transition in behavior from 50 to 5 °C.

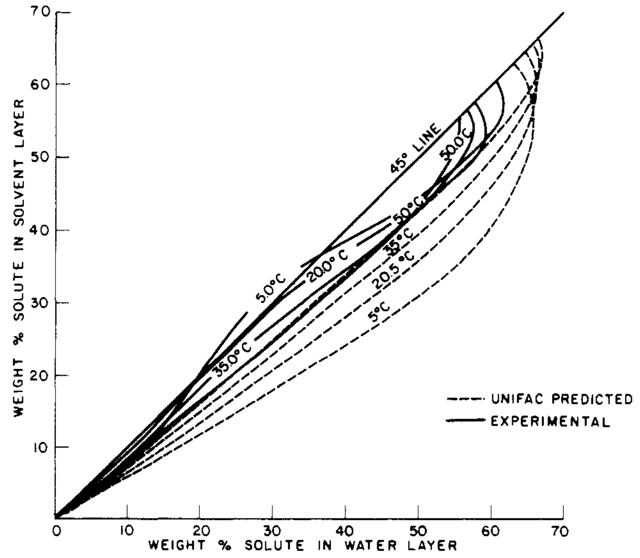

Figure 7. Distribution diagram for propionic acid-water-toluene system.

The temperature behavior of the UNIFAC (UNIQUAC functional-group activity coefficient) (*4*) model was also investigated, the results of which were compared to the data presented

Table III. Mutual Solubility Data for Propionic Acid-Water-Cyclohexane System

2 °C			5 °C			10 °C			20 °C			30 °C		
cyclohexane	water	propionic acid	cyclohexane	water	propionic acid	cyclohexane	water	propionic acid	cyclohexane	water	propionic acid	cyclohexane	water	propionic acid
0.57	48.47	50.96	0.58	49.78	49.64	0.67	57.62	41.71	0.50	63.55	35.94	0.53	68.28	31.17
1.31	33.63	65.01	1.40	36.04	62.56	1.37	43.93	54.70	0.79	50.68	48.53	0.85	54.67	44.48
2.37	30.40	67.23	2.46	31.59	65.95	2.08	35.92	62.00	1.34	43.09	55.56	1.41	45.63	52.95
3.59	26.32	70.09	3.73	26.60	69.67	4.55	25.91	69.54	2.51	33.85	63.64	1.93	41.40	56.68
5.55	21.95	72.50	5.63	22.26	72.11	6.46	22.12	71.42	3.67	31.00	65.33	2.39	38.31	59.29
8.31	17.78	73.91	8.52	17.93	73.55	8.02	19.61	72.37	3.94	28.84	67.22	2.80	35.92	61.28
10.38	15.68	73.94	10.55	15.94	73.51	9.47	18.01	72.52	5.28	24.69	70.03	3.29	33.76	62.95
13.14	13.50	73.36	13.36	13.72	72.93	11.85	15.61	72.54	6.53	22.36	71.10	4.09	29.95	65.96
15.34	12.15	72.51	15.48	12.34	72.18	13.67	14.04	71.53	7.63	20.63	71.74	5.60	26.16	68.24
16.75	11.31	71.94	17.00	11.49	71.51	15.57	12.90	70.83	8.36	19.52	72.12	6.82	23.35	69.83
17.50	10.96	71.54	17.74	11.11	71.15	17.22	11.95	70.13	12.51	15.25	72.24	8.50	20.78	70.72
18.01	10.73	71.26	18.25	10.87	70.87	20.14	10.33	69.53	13.43	14.65	71.92	10.25	18.42	71.33
20.27	9.76	69.97	20.51	9.87	69.61	23.08	8.89	68.03	15.06	13.53	71.41	11.20	17.26	71.54
22.61	8.71	68.68	22.94	8.84	68.22	27.58	7.08	65.33	16.46	12.68	70.86	12.51	16.14	71.36
25.81	7.46	66.73	26.16	7.56	66.28	30.36	5.85	63.79	18.22	11.69	70.00	14.34	14.72	70.94
28.54	6.41	65.05	28.85	6.48	64.67	32.91	5.28	61.81	20.30	10.68	69.02	16.70	13.09	69.91
31.85	5.31	62.84	31.97	5.34	62.69	38.67	3.72	57.61	23.76	9.16	67.07	20.98	11.04	67.98
37.47	3.61	58.92	38.10	3.67	58.23	50.32	1.61	48.06	28.69	7.37	63.94	24.52	9.44	66.04
49.08	1.57	49.35	49.36	1.58	49.06	60.39	0.77	38.84	34.27	5.50	60.23	29.50	7.57	62.92
57.94	0.74	41.32	58.37	0.75	40.88	26.43[a]	7.50[a]	66.07[a]	39.74	3.83	56.43	35.68	5.72	58.60
26.56[a]	7.06[a]	66.38[a]	24.66[a]	8.02[a]	67.32[a]				51.64	1.66	46.70	41.43	3.99	54.59
									60.62	0.78	38.60	54.32	1.74	43.93
									24.41[a]	8.95[a]	66.64[a]	64.35	0.83	34.82
												26.62[a]	8.65[a]	64.73[a]

[a] Plait point composition.

Table IV. Tie Line Data for Propionic Acid-Water-Cyclohexane System Acid Concentration

2 °C		5 °C		10 °C		20 °C		30 °C	
solvent[a]	water[a]	solvent	water	solvent	water	solvent	water	solvent	water
2.20	17.05	3.28	17.42	3.02	18.17	5.04	18.31	2.91	15.88
9.18	31.44	8.56	31.59	11.09	38.01	10.07	32.81	8.57	29.43
13.46	42.29	13.79	42.80	15.70	50.56	13.80	43.00	11.88	39.86
17.03	49.93	17.13	50.61	21.15	58.69	17.53	51.05	14.55	47.61
19.38	56.24	21.91	58.94	26.31	64.13	20.77	57.48	23.26	53.74
23.58	60.98	26.68	64.41	30.55	68.16	23.49	61.74	23.43	58.78
26.70	64.22	31.65	67.52	35.28	70.78	26.91	65.04	24.35	62.24
31.52	68.21	36.16	70.87	39.27	70.72	31.23	68.65	28.21	67.08
35.07	71.07	40.76	72.83	44.01	71.98	36.34	71.05	33.03	69.98
41.02	73.06	45.11	72.27	49.26	72.83	40.36	71.30	37.36	69.78
43.92	72.44	49.91	73.26	52.81	72.90	44.23	72.17	41.78	71.01
50.01	73.22	53.08	73.45			49.81	72.24	46.21	71.46
53.00	73.74	55.39	73.29			52.34	72.14		

[a] Refers to solvent and water layers.

above. The UNIFAC model uses group interaction parameters for the prediction of equilibria for systems having components comprised of those groups. The group interaction parameters used in the calculation were those presented by Magnussen et al. (*5*) intended specifically for use in predicting liquid-liquid equilibria.

A computer program was employed to generate a series of tie lines that would facilitate the construction of solubility curves at required temperatures. The UNIFAC predicted isotherms are shown in Figures 2-4. It is found that UNIFAC achieved only moderate success in matching the binodal data using interaction parameters of Magnussen. Furthermore UNIFAC fails to follow the temperature behavior exhibited by the experimental data. The UNIFAC predicted isotherms for the system propionic acid-water-toluene tend to move in a direction opposite to that of the experimental isotherm with changes in temperature. This behavior was also observed in a comparison with the independent data of Dakshinamurty et al. (*6*) for the system acetic acid-water-ethyl butyrate shown in Figure 9. The UNIFAC isotherms for the other two systems did move in the same direction as the experimental data but only by such a small amount that they could not be resolved into separate curves on the ternary diagram (Figures 2 and 3).

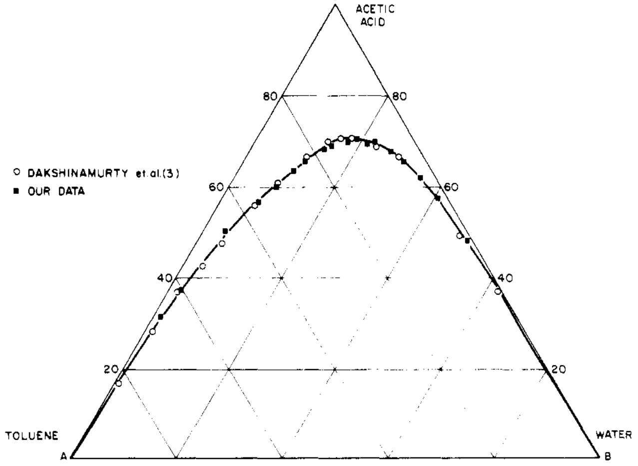

Figure 8. Phase equilibrium of acetic acid-water-toluene at 30 °C.

The tie line predictions also showed irregularities when compared with experimental data. This is most apparent in the propionic acid-water-toluene system illustrated by the distri-

Table V. Mutual Solubility Data for Propionic Acid-Water-Toluene System

5 °C			20 °C			35 °C			50 °C		
toluene	water	propionic acid	toluene	water	propionic acid	toluene	water	propionic acid	toluene	water	propionic acid
2.2	49.7	48.2	0.9	68.5	30.6	2.3	57.6	40.1	2.0	65.5	32.6
3.8	44.9	51.3	1.1	62.0	37.0	2.8	54.1	43.1	3.4	55.3	41.3
4.4	42.6	53.0	2.8	51.3	45.9	3.5	50.9	45.6	4.4	50.5	45.2
5.3	39.6	55.1	3.4	48.4	48.2	4.4	47.9	47.7	5.7	46.1	48.2
6.4	36.8	56.8	4.5	45.1	50.5	6.1	42.8	51.1	7.6	41.2	51.2
7.5	34.4	58.1	5.6	41.6	52.8	7.9	38.5	53.6	9.3	37.9	52.8
8.5	32.5	59.0	6.3	40.0	53.7	9.8	34.8	55.4	10.9	35.0	54.0
9.6	30.6	59.8	7.4	37.6	55.0	12.0	31.5	56.5	12.7	32.4	54.9
10.5	29.5	60.1	8.5	35.2	56.4	13.2	29.7	57.1	14.5	30.1	55.4
11.1	28.6	60.4	9.3	33.6	57.0	13.8	28.9	57.3	16.4	28.0	55.6
11.9	27.4	60.7	10.2	32.2	57.6	14.1	28.7	57.2	18.4	26.0	55.6
12.9	26.1	61.0	11.6	30.3	58.2	15.0	27.6	57.4	20.5	24.2	55.3
14.1	24.6	61.3	12.5	29.0	58.5	15.8	26.8	57.3	21.1	23.7	55.2
17.5	21.3	61.2	13.6	28.0	58.4	16.1	26.4	57.5	22.3	22.7	55.1
19.3	19.4	61.2	14.4	26.4	59.2	17.9	24.7	57.5	23.0	22.0	55.0
22.1	17.3	60.6	16.3	24.3	59.4	18.6	24.0	57.4	24.3	21.0	24.7
23.2	16.4	60.4	18.0	22.7	59.3	19.8	22.9	57.3	26.1	19.5	54.4
24.5	15.3	60.2	20.4	20.4	59.2	22.1	21.1	56.9	27.8	18.2	54.0
26.1	14.1	59.7	22.6	18.7	58.7	24.6	19.2	56.3	31.0	16.2	52.8
28.6	11.6	59.8	25.0	17.0	58.0	31.6	14.2	54.2	33.9	14.3	51.8
31.0	10.4	58.6	28.8	14.4	56.9	37.8	10.3	51.9	36.6	12.7	50.7
32.3	9.6	58.2	31.4	12.3	56.3	41.7	8.2	50.1	40.3	10.5	49.2
34.5	8.1	57.3	34.2	10.7	55.1	45.2	6.8	47.9	43.8	8.5	47.7
36.4	7.2	56.4	37.7	8.3	54.0	48.6	5.5	45.9	46.5	7.3	46.2
38.6	6.2	55.2	40.2	6.9	52.9	52.3	4.2	43.5	49.2	6.1	44.7
39.7	5.7	54.6	48.8	3.6	47.6	56.3	3.4	40.3	54.2	4.6	41.2
44.5	4.6	51.0	53.9	2.3	43.8	59.7	2.7	37.6	57.4	3.7	38.9
49.1	3.1	47.8	77.7	2.2	20.0	62.1	2.3	35.6	63.4	2.6	34.0
27.4[a]	13.1[a]	59.5[a]	29.9[a]	13.6[a]	56.5[a]	27.7[a]	16.9[a]	55.5[a]	27.8[a]	18.2[a]	54.0[a]

[a] Plait point composition.

Table VI. Tie Line Data for Propionic Acid-Water-Toluene System Acid Concentration

5 °C		20 °C		35 °C		50 °C	
solvent[a]	water[a]	solvent	water	solvent	water	solvent	water
8.9	11.4	9.2	10.0	11.6	13.8	10.4	13.0
21.1	20.1	20.0	20.2	20.8	22.7	19.3	23.1
29.1	26.9	30.3	31.4	31.5	35.1	28.4	34.2
32.3	30.6	38.0	42.7	39.2	46.6	39.5	46.5
40.9	44.1	45.6	53.6	48.7	53.9	48.6	53.7
47.9	54.3						

[a] Refers to solvent and water layers.

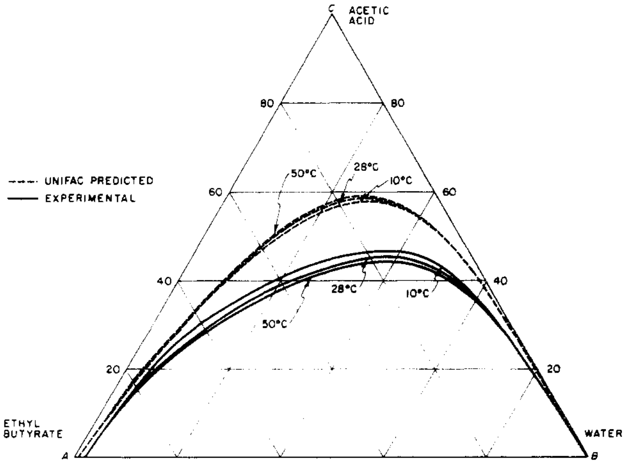

Figure 9. Acetic acid–water–ethyl butyrate isotherms.

bution diagram of Figure 7. As in the mutual solubility isotherms the distribution isotherms show opposite trends with respect to temperature. UNIFAC also fails to show the solutropic behavior of the system at 5.0 °C.

The distribution isotherms show slightly better agreement for the propionic acid–water–cyclohexane and the acetic acid–water–toluene system (Figures 5 and 6). The UNIFAC and the experimental distribution curves move in the same direction with respect to temperature, specially in the lower solute concentration region.

Conclusions

Temperature effects on the equilibria of the three ternary systems presented here were found to be significant within the limited temperature range of the experiments. The propionic acid–water–toluene system showed a transition to solutropic behavior with a reduction in temperature to 5 °C. The UNIFAC model was found to be incapable of predicting all of the trends relating to temperature effects on the ternary equilibria of the measured systems.

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Registry No. Acetic acid, 64-19-7; propionic acid, 79-09-4; toluene, 108-88-3; cyclohexane, 110-82-7.

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Vapor Pressures of Nitric Acid and Water in the Systems HNO_3–H_2O and HNO_3–$Th(NO_3)_4$–H_2O at 50 °C[†]

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The equilibrium compositions of the vapor above nitric acid–water, thorium nitrate–water, and nitric acid–thorium nitrate–water mixtures at 50 °C have been studied as a function of solution concentration by using a transpiration technique. Nitric acid concentrations were varied from 0 to 20 *m* and thorium nitrate concentrations from 0 to 2.5 *m*. Our data for the nitric acid–water system have been combined with literature data to obtain parameters for Scatchard's ion-component model, and these parameters provide a satisfactory description of the system at 50 °C over a wide concentration range. The enhancement, at 50 °C, of the nitric acid vapor pressure by added thorium nitrate was found to be less than that previously determined at 25 °C. The data for the nitric acid–thorium nitrate–water system at 50 °C were fitted to a single multiparameter function.

Introduction

Recently, we reported values for vapor pressures of water (P_W) and nitric acid (P_N) above HNO_3–$Th(NO_3)_4$–H_2O solutions at 25 °C (*1*). It was shown that, although the Scatchard treatment (*2*) was satisfactory for representing the binary system data, an empirical expression provided a better representation of the ternary data obtained for a wide range of thorium nitrate and nitric acid concentrations. Experiments have now been completed for similar mixtures at 50 °C. Since there is marked disagreement between literature data (*3-6*) for the HNO_3–H_2O binary system, vapor pressures for this system have been redetermined. Water vapor pressures for the $Th(NO_3)_4$–H_2O binary system were not available and these have also been measured.

Table I. Solution Concentrations and Experimental (50 °C) Vapor Pressures for the Binary Systems

HNO_3–H_2O			$Th(NO_3)_4$–H_2O	
HNO_3[a]	P_W, kPa	P_N, Pa	$Th(NO_3)_4$[a]	P_W, kPa
0.496	12.04	0.06	0.25	12.22
0.496	12.16	0.06	0.25	12.25
0.745	11.95	0.11	0.50	12.05
0.745	11.92	0.13	0.50	11.98
0.978	11.92	0.22	0.75	11.46
0.978	11.99	0.23	0.75	11.73
1.46	11.74	0.51	0.75	11.50
1.46	11.75	0.53	1.00	11.44
1.96	11.44	0.98	1.00	11.44
1.96	11.52	1.04	1.25	11.15
2.92	10.87	2.36	1.25	11.10
2.92	10.87	2.37	1.52	10.65
3.90	10.46	5.87	1.52	10.88
3.90	10.49	6.07	1.52	10.61
4.86	9.89	10.5	2.07	10.15
4.86	9.92	11.1	2.07	10.14
4.86	9.92	10.8	2.58	9.14
4.86	9.95	11.0	2.58	9.18
6.44	9.10	24.5		
6.44	9.13	25.4		
7.95	8.44	47.3		
7.95	8.45	48.2		
10.0	7.58	84.8		
10.0	7.60	88.2		
12.1	6.75	145		
12.1	6.76	149		
20.1	4.74	581		
20.1	4.69	582		

[a] Concentration, in mol kg^{-1}.

Experimental Section

The details of the transpiration apparatus used to determine the vapor pressures of water and nitric acid have been described previously (*1*). Dried nitrogen was passed through two presaturators and a saturator containing solutions of a particular thorium nitrate and/or nitric acid concentration. The nitric acid and water in the gas stream were then condensed in a collector in a dry ice–acetone bath. The saturators and presaturators were thermostated in a bath at 50.00 ± 0.02 °C, and all portions of the presaturator–saturator system above the surface of the thermostating bath were heated to prevent vapor condensation. Three similar sets of apparatus were attached in series. The third set, used to determine the quantity of dry gas passed through the system, was thermostated at 25.0 °C and contained deionized water in the saturator and presaturators.

The thorium nitrate, nitric acid, and thorium nitrate–nitric acid mixtures were prepared from standardized concentrated stock solutions of thorium nitrate and nitric acid. Details of the preparation and analysis of the stock solutions have been given previously (*1*), as has the procedure for analyzing the material trapped in the collectors during a transpiration run. As discussed in ref 1, the errors in the water vapor pressure measurements were ≤2%, and for runs in which more than 1 mg of nitric acid was transpired, the estimated errors in the nitric acid vapor pressures were ≤5%. For runs in which less than 1 mg of nitric acid was transpired, the errors in the nitric acid vapor pressures increased markedly, being roughly inversely proportional to the quantity of nitric acid collected.

Results and Discussion

Tables I and II give our solution concentrations and experimentally determined vapor pressures for the HNO_3–H_2O,

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