v_i	liquid molar volume of component *i*
x_i	mole fraction of component *i* in the liquid phase
n	number of data
E_{x_3}	local deviation between experimental and calculated values; $E_{x_3} = (x_{3,\mathrm{exptl}} - x_{3,\mathrm{calcd}})/x_{3,\mathrm{exptl}}$
$\bar{E}_{x_3}$	mean deviation; $\bar{E}_{x_3} = (1/n)\sum_1^n \lvert E_{x_3}\rvert$
$E_{x_3,\mathrm{max}}$	maximum absolute deviation for x_3
R	gas constant, cal/(mol K)
t	temperature, °C
T	temperature, K
Δc_p	difference between specific heat of the liquid and of the solid, cal/(mol K)
ΔH	enthalpy of fusion, cal/mol
γ	activity coefficient

Subscripts

1	relative to acetone
2	relative to ethanol
3	relative to acetic acid
t	at triple point
exptl	experimental
calcd	calculated

Registry No. Acetic acid, 64-19-7; ethanol, 64-17-5; acetone, 67-64-1.

Literature Cited

(1) Carta, R.; Dernini, S. *J. Chem. Eng. Data* **1983**, *28*, 328.
(2) Fredeslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(3) Gmehling, J.; Rasmussen, P.; Fredeslund, A. *Chem. Eng. Technol.* **1980**, *52*, 724.
(4) Gmehling, J.; Anderson, T. F.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 269.
(5) Martin, A.; Wu, P. L.; Adjei, A.; Beerbower, A.; Prausnitz, J. M.; *Pharm. Sci.* **1981**, *70*, 1260.
(6) Carta, R.; Dernini, S.; De Santis, R. *J. Chem. Eng. Data* **1979**, *24*, 100.
(7) Wilson, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(8) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(9) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(10) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(11) Weast, R. C. "Handbook of Chemistry and Physics"; Chemical Rubber Co.: Cleveland, OH, 1971; Section C.
(12) Gmehling, J.; Onken, U. "Vapor-liquid Equilibrium Data Collection"; Dechema Chemistry Data Series: Frankfurt 1977; Vol. 1/2a.
(13) Gmehling, J.; Onken, U.; Grenzheuser, P. "Vapor-liquid Equilibrium Data Collection"; Dechema Chemistry Data Series: Frankfurt 1982, Vol. 1/5.

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Quaternary Liquid–Liquid Equilibrium: Water–Ethanol–Chloroform–Toluene at 25 °C. Experimental Determination and Graphical and Analytical Correlation of Equilibrium Data

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Mutual solubility and tie line data at 25 °C and atmospheric pressure are presented for the quaternary system water–ethanol–chloroform–toluene. The obtained results have been correlated by the graphical method of Ruiz and Prats and by the UNIQUAC equation.

Introduction

In this work, liquid–liquid equilibrium (LLE) data for the quaternary system water (W)–ethanol (E)–chloroform (C)–toluene (T) are measured at 25 °C and atmospheric pressure. This system contains two pairs of partly miscible compounds: W–C and W–T. The experimental results have been obtained by applying a systematic method of selection of the points to be measured as reported in previous paper (*1*). This method permits the heterogeneous region to be fully characterized as well as allows graphical representation (method of Ruiz and Prats (*2*)) and analytical correlation (UNIQUAC (*3*)) of the equilibrium data in a form suitable for the interpolation of quaternary tie lines.

Experimental Section

All chemicals (analytical reagent grade) were supplied by Merck. The contents of volatile impurities were determined by gas chromatographic analysis. With the exception of chloroform, all the compounds contained negligible amounts of impurities (less than 0.1%). Chloroform was stabilized with ethanol in a percentage varying from 0.7% to 0.8%; the ethanol was removed by extraction with water.

Data for the binodal curves of the component ternary and quaternary systems were determined by using the cloud point method. The experimental device was that used by Ruiz and Prats (*4*).

Equilibrium data were obtained by preparing mixtures of known overall composition, intense stirring, and setting for at least 2 h at constant temperature (25 ± 0.1 °C). At the end of each experiment, samples were taken from both phases and analyzed by means of gas chromatography. Good separation of the four components was obtained on a 2 m × $^1/_8$ in. column packed with Chromosorb 101 100/120. The column temperature was 170 °C and detection was carried out by thermal conductivity. The detector current was 100 mA at a helium flow rate of 40 mL/min. To obtain quantitative results we applied the internal standard method, 1-propanol being the standard compound used for this purpose. The relative accuracy of the weight fraction measurements was 1%.

The methodology applied in selecting the points to be determined experimentally was as reported in a previous paper (*1*). The quaternary system water (W)–ethanol (E)–chloroform (C)–toluene (T) is represented schematically in Figure 1, using a regular tetrahedron. To characterize the solubility surface fully, ternary solubility curves for the systems W–E–T and W–E–C were determined experimentally, and also the four quaternary solubility curves which form the intersections of four

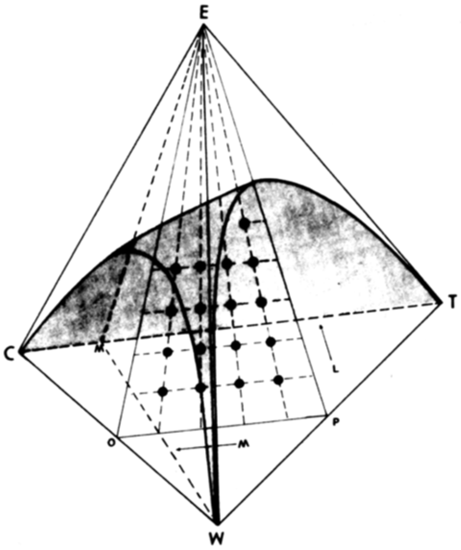

Figure 1. Qualitative representation of the solubility surface and initial mixtures for the quaternary system water (W)–ethanol (E)–chloroform (C)–toluene (T).

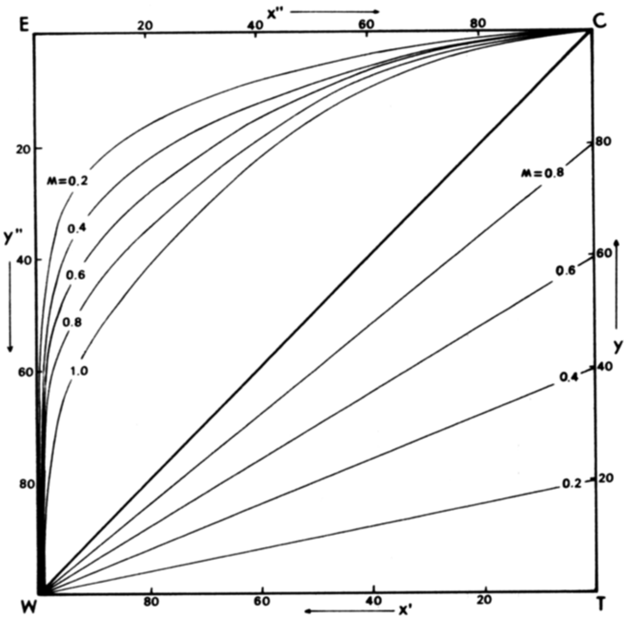

Figure 2. Solubility surface for the system water (W)–ethanol (E)–chloroform (C)–toluene (T) at 25 °C: method proposed by Frolov ($X' = 100X_W/(100 - X_E)$, $Y' = 100X_C/(100 - X_E)$, $X'' = 100X_C/(100 - X_T)$, and $Y'' = 100X_W/(100 - X_T)$).

equidistant planes (such as W–E–*M*) with the heterogeneous region. *M* represents the mixture chloroform–toluene, and its value is defined as $M = X_B/(X_B + X_C)$ where X_i is the weight percent of component *i*. The four quaternary planes have values of $M = 0.2$, 0.4, 0.6, and 0.8, while $M = 0.0$ denotes the ternary plane W–E–T and $M = 1.0$ the ternary plane W–E–C. The six resulting solubility curves may prove to be sufficient for the deduction of points over the solubility surface by interpolation.

Initial mixtures were selected to determine tie lines providing regular variation of composition within the heterogeneous region. Initial mixtures were selected such that $X_W = X_C + X_T$ in each W–E–*M* plane ($M = 0.0$, 0.2, 0.4, 0.6, 0.8, 1.0); the ethanol levels *L* were increased stepwise until the homogeneous region was reached. These initial mixtures have been represented schematically in Figure 1.

Table I. Mutual Solubility Data (wt %) for Water (W)-Ethanol (E)-Toluene (T) at 25 °C

X_W	X_E	X_T	X_W	X_E	X_T	X_W	X_E	X_T
2.6	19.0	78.4	15.0	49.9	35.0	30.4	56.6	13.0
6.9	34.5	58.6	18.6	53.6	27.8	35.7	55.4	9.0
11.1	44.3	44.6	22.0	56.1	22.0	59.8	39.2	1.0
			26.0	56.7	17.3			

Table II. Quaternary Solubility Data (wt %) for Water (W)-Ethanol (E)-Chloroform (C)-Toluene (T) at 25 °C

X_W	X_E	X_C	X_T
	$M = 0.2$		
2.7	18.9	15.7	62.7
7.9	33.7	11.7	46.7
11.6	41.8	9.3	37.2
15.8	47.2	7.4	29.6
19.5	51.2	5.8	23.4
23.3	53.3	4.7	18.7
27.3	54.6	3.6	14.5
31.7	54.7	2.7	10.9
37.1	53.6	1.9	7.4
59.8	39.2	0.2	0.8
	$M = 0.4$		
2.9	18.8	31.3	47.0
8.9	32.9	23.3	34.9
12.3	38.7	19.6	29.4
16.7	44.3	15.6	23.4
20.8	48.8	12.5	18.7
24.7	50.7	9.9	14.8
28.9	52.3	7.6	11.5
33.1	52.7	5.7	8.5
39.1	51.1	3.9	5.9
59.7	38.8	0.6	0.9
	$M = 0.6$		
3.0	18.8	46.9	31.3
9.5	32.4	34.9	23.2
12.7	36.6	30.4	20.3
17.7	41.1	24.7	16.5
22.2	44.4	20.0	13.4
26.6	46.7	16.0	10.6
31.3	47.9	12.5	8.3
35.8	48.9	9.2	6.1
41.6	48.0	6.2	4.2
59.6	38.4	1.2	0.8
	$M = 0.8$		
3.0	18.8	62.6	15.6
9.9	32.1	46.4	11.6
13.0	35.1	41.6	10.4
18.4	38.5	34.5	8.6
23.6	40.9	28.4	7.1
28.8	42.3	23.1	5.8
34.0	43.3	18.1	4.5
39.1	44.1	13.4	3.4
45.0	43.7	9.0	2.3
59.4	37.6	2.4	0.6

Table III. Tie Line Data (wt %) for Water (W)-Chloroform (C)-Toluene (T) at 25 °C

	aqueous phase			organic phase		
M	X_W	X_C	X_T	X_W	X_C	X_T
0.0	99.9		0.052	0.059		99.9
0.2	99.9	0.07	0.048	0.054	19.9	80.1
0.4	99.8	0.17	0.032	0.057	39.8	60.2
0.6	99.7	0.30	0.020	0.064	59.6	40.3
0.8	99.5	0.46	0.006	0.079	79.8	20.1
1.0	99.3	0.70		0.090	99.9	

Results

Table I shows mutual solubility data for the ternary system water–ethanol–toluene at 25 °C. Quaternary solubility points concerning the planes $M = 0.2$, 0.4, 0.6, and 0.8 are shown in Table II. A qualitative representation of the solubility surface

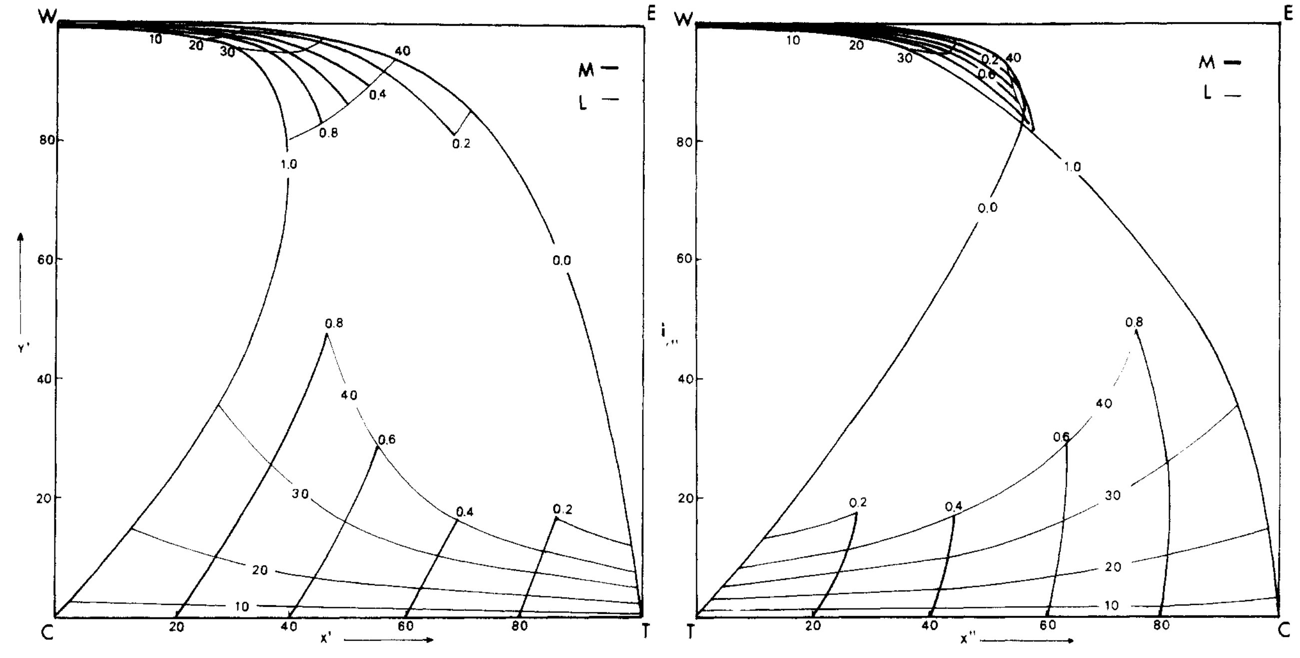

Figure 3. Equilibrium of the system water (W)–ethanol (E)–chloroform (C)–toluene (T) at 25 °C: (a) projection onto a plane parallel to the W–T and E–C edges ($X' = X_E + X_T$ and $Y' = X_E + X_W$); (b) projection on a plane parallel to the W–C and E–T edges ($X'' = X_E + X_C$ and $Y'' = X_E + X_W$).

Table IV. Tie Line Data (wt %) for Water (W)–Ethanol (E)–Toluene (T) at 25 °C

aqueous phase			organic phase		
X_W	X_E	X_T	X_W	X_E	X_T
87.0	12.9	0.09	0.06	0.61	99.3
81.9	18.0	0.12	0.09	0.95	99.0
75.5	24.5	0.19	0.13	1.61	98.3
72.5	27.2	0.31	0.15	2.12	97.7
67.8	31.8	0.44	0.21	2.76	97.0
63.9	35.4	0.69	0.22	3.39	96.4
54.5	43.6	1.94	0.34	4.99	94.7
53.6	44.3	2.17	0.37	5.28	94.3
52.0	45.6	2.46	0.39	5.55	94.1
41.8	52.2	5.98	0.65	7.68	91.7
40.8	52.7	6.56	0.72	8.54	90.7
37.5	54.4	8.09	0.88	8.85	90.3
29.0	56.6	14.4	1.21	12.0	86.8
23.3	56.5	20.1	1.87	14.9	83.3

is shown in Figure 1 using a regular tetrahedron. The quantitative representation of this surface using the Frolov (*5*) method is shown in Figure 2. This representation is appropriate for the interpolation of solubility surface points.

The tie lines for the ternary systems water–chloroform–toluene and water–ethanol–toluene appear in Tables III and IV. Mutual solubility and tie line data at 25 °C for the ternary system water–ethanol–chloroform were reported in a previous paper (*1*).

The compositions for the quaternary tie lines are shown in Table V. The values of *M* and *L* for the initial mixtures are also included.

Table V. Tie Line Data (wt %) for Water (W)–Ethanol (E)–Chloroform (C)–Toluene (T) at 25 °C

	aqueous phase				organic phase			
L	X_W	X_E	X_C	X_T	X_W	X_E	X_C	X_T
				$M = 0.2$				
10	82.4	17.4	0.11	0.09	0.15	1.23	19.9	78.7
20	68.0	31.3	0.33	0.38	0.23	3.64	19.3	76.9
30	54.3	42.9	1.08	1.79	0.65	7.47	17.3	74.6
40	41.8	50.4	2.39	5.41	1.10	10.7	15.4	72.8
50	27.6	54.0	4.17	14.2	1.93	15.3	12.2	70.6
				$M = 0.4$				
10	82.5	17.1	0.27	0.07	0.17	1.44	39.1	59.3
20	68.3	30.7	0.74	0.26	0.25	4.54	37.4	57.9
30	54.5	41.6	2.44	1.45	0.89	9.46	34.3	55.4
40	41.1	48.4	5.52	5.01	1.90	14.8	29.4	53.9
				$M = 0.6$				
10	82.6	16.9	0.45	0.04	0.18	1.72	58.6	39.6
20	68.7	29.9	1.29	0.18	0.47	6.33	55.4	37.8
30	55.1	39.9	3.85	1.10	1.81	14.3	48.6	35.4
40	40.5	45.8	9.50	4.18	5.39	23.9	39.5	31.2
				$M = 0.8$				
10	83.0	16.3	0.74	0.02	0.19	2.16	77.2	20.5
20	69.9	28.3	1.74	0.09	1.01	9.33	71.4	18.3
30	58.9	36.3	4.45	0.45	4.05	21.7	58.8	15.4
40	40.6	42.8	13.9	2.72	13.2	35.2	40.1	11.6

Table VI. UNIQUAC Interaction Parameters (K)

	W	E	C	T
W	0.0	−102.6	413.7	308.2
E	−316.8	0.0	104.4	−41.8
C	1375.9	−432.5	0.0	429.2
T	1326.9	342.1	−202.1	0.0

Correlation Using UNIQUAC

The equation UNIQUAC (*3*) slightly modified by Anderson and Prausnitz (*6*) was used to correlate the experimental data obtained for the quaternary system water–ethanol–chloroform–toluene at 25 °C. The pure component molecular structure constants for UNIQUAC equation are those given by Prausnitz et al. (*7*). The parameter estimation is carried out by minimizing the objective function defined as

$$F = \sum^{i} \sum^{j} \sum^{k} (x_{ijk} - \hat{x}_{ijk})^2$$

where *i* denotes component *i* (*i* = 1, 2, 3, 4), *j* denotes phase (*j* = 1, 2), and *k* denotes the tie line (*k* = 1, 2,..., *N*). *x* is the

Table VII. Calculated (C) and Experimental (E) LLE Data (Mole Fraction) for the Quaternary System Water (W)–Ethanol (E)–Chloroform (C)–Toluene (T) at 25 °C

	aqueous phase				organic phase			
	x_W	x_E	x_C	x_T	x_W	x_E	x_C	x_T
E[a]	0.999		0.0011		0.0057		0.994	
C[b]	0.999		0.0010		0.0043		0.996	
E	1.000			0.0001	0.0030			0.997
C	1.000			0.0001	0.0030			0.997
E	0.992		0.0007	0.0000	0.0049		0.750	0.245
C	0.999		0.0008	0.0000	0.0044		0.750	0.245
E	1.000		0.0005	0.0000	0.0038		0.531	0.465
C	0.999		0.0006	0.0001	0.0040		0.531	0.465
E	1.000		0.0003	0.0001	0.0032		0.337	0.660
C	0.999		0.0004	0.0001	0.0038		0.337	0.660
E	1.000		0.0001	0.0001	0.0030		0.161	0.837
C	1.000		0.0002	0.0001	0.0037		0.160	0.836
E	0.921	0.079		0.0003	0.0045	0.019		0.977
C	0.918	0.082		0.0005	0.0079	0.016		0.976
E	0.844	0.155		0.0011	0.0103	0.053		0.936
C	0.832	0.166		0.0012	0.0133	0.041		0.946
E	0.758	0.237		0.0053	0.0165	0.094		0.890
C	0.743	0.254		0.0029	0.0197	0.074		0.906
E	0.660	0.322		0.0184	0.0300	0.139		0.831
C	0.653	0.341		0.0060	0.0271	0.117		0.856
E	0.538	0.410		0.0520	0.0529	0.205		0.743
C	0.552	0.436		0.0124	0.0359	0.178		0.786
E	0.928	0.070	0.0017		0.0156	0.072	0.912	
C	0.941	0.057	0.0022		0.0414	0.084	0.874	
E	0.875	0.122	0.0032		0.0891	0.261	0.650	
C	0.847	0.146	0.0070		0.1262	0.236	0.638	
E	0.829	0.163	0.0082		0.2664	0.388	0.345	
C	0.757	0.225	0.0176		0.2365	0.351	0.412	
E	0.923	0.076	0.0002	0.0002	0.0079	0.025	0.158	0.809
C	0.930	0.069	0.0005	0.0003	0.0135	0.033	0.155	0.798
E	0.846	0.152	0.0006	0.0009	0.0117	0.073	0.149	0.767
C	0.853	0.145	0.0011	0.0009	0.0267	0.081	0.144	0.748
E	0.759	0.234	0.0023	0.0049	0.0313	0.141	0.126	0.702
C	0.762	0.233	0.0027	0.0023	0.0424	0.144	0.123	0.691
E	0.664	0.313	0.0057	0.0163	0.0504	0.192	0.106	0.652
C	0.684	0.307	0.0047	0.0047	0.0559	0.202	0.104	0.639
E	0.530	0.405	0.0121	0.0533	0.0820	0.254	0.078	0.586
C	0.581	0.399	0.0083	0.0111	0.0682	0.269	0.077	0.586
E	0.924	0.075	0.0005	0.0002	0.0093	0.031	0.324	0.636
C	0.939	0.059	0.0009	0.0003	0.0193	0.047	0.315	0.619
E	0.849	0.143	0.0014	0.0006	0.0132	0.094	0.297	0.596
C	0.870	0.127	0.0020	0.0006	0.0408	0.111	0.282	0.566
E	0.763	0.228	0.0052	0.0040	0.0436	0.180	0.251	0.526
C	0.784	0.210	0.0045	0.0016	0.0700	0.198	0.236	0.495
E	0.665	0.306	0.0135	0.0158	0.0839	0.255	0.196	0.465
C	0.700	0.288	0.0083	0.0038	0.0947	0.275	0.187	0.443
E	0.925	0.074	0.0008	0.0001	0.0103	0.039	0.507	0.444
C	0.946	0.052	0.0013	0.0002	0.0269	0.060	0.487	0.426
E	0.852	0.145	0.0024	0.0004	0.0252	0.132	0.447	0.395
C	0.874	0.123	0.0029	0.0004	0.0642	0.152	0.416	0.368
E	0.771	0.218	0.0081	0.0030	0.0837	0.258	0.338	0.320
C	0.783	0.209	0.0069	0.0013	0.1149	0.264	0.319	0.302
E	0.668	0.295	0.0236	0.0135	0.2012	0.349	0.222	0.227
C	0.694	0.289	0.0134	0.0035	0.1656	0.356	0.236	0.242
E	0.928	0.071	0.0013	0.0001	0.0114	0.051	0.698	0.240
C	0.950	0.048	0.0016	0.0001	0.0357	0.073	0.663	0.228
E	0.860	0.136	0.0032	0.0002	0.0531	0.192	0.567	0.188
C	0.870	0.125	0.0042	0.0003	0.0981	0.198	0.529	0.176
E	0.798	0.192	0.0091	0.0012	0.1659	0.348	0.363	0.123
C	0.773	0.215	0.0109	0.0009	0.1837	0.326	0.366	0.125
E	0.677	0.279	0.0350	0.0089	0.3742	0.390	0.172	0.064
C	0.680	0.295	0.0220	0.0028	0.2612	0.402	0.242	0.094

[a] E = experimental. [b] C = calculated.

experimental composition (mole fraction) and $\hat{x}$ the calculated composition (mole fraction). These compositions have been predicted by setting the concentration in the global initial mixture equal to that in the middle of the corresponding experimental tie line. The 12 estimated UNIQUAC binary interaction parameters (two parameters per binary) are presented in Table VI. The absolute mean deviation between experimental and calculated LLE data is 1.9 mol %. The calculated and experimental LLE data (mole fraction) are shown in Table VII.

Graphical Correlation

The graphical method represents in many cases a viable alternative to computer methods requiring thermodynamic correlation of equilibria data. In this work, we have correlated the experimental compositions of the quaternary tie lines using the method of Ruiz and Prats (*2*). Figure 3 is the application of this method to this system and consists of a graphical representation of the variations of two parameters (*M* and *L*) of 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.

Literature Cited

(1) Ruiz, F.; Prats, D.; Gomis, V. *J. Chem. Eng. Data* **1984**, *29*, 147.
(2) Ruiz, F.; Prats, D. *Fluid Phase Equilib.* **1983**, *10*, 115.
(3) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(4) Ruiz, F.; Prats, D. *Fluid Phase Equilib.* **1983**, *10*, 77.
(5) Frolov, A. F. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1965**, *39*, 1538.
(6) Anderson, T. F.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 561.
(7) Prausnitz, J.; Anderson, T.; Grens, E.; Eckert, C.; Hsieh, R.; O'Conell, J. "Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980.
(8) Ruiz, F.; Prats, D.; Marcilla, A. *Fluid Phase Equilib.* **1984**, *15*, 257.

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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% (ρ_{20} = 1.049 g/cm^3), toluene more than 99.0 mol % pure (ρ_{20} = 0.866 g/cm^3), propionic acid 0.01% residue after evaporation, 0.25% water (ρ_{20} = 0.992 g/cm^3), cyclohexane purity greater than 99 mol % (ρ_{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