PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIA USING THE NRTL AND THE UNIQUAC MODELS

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Abstract— The experimental binodal curve, tie line data, plait point data and the tie lines and plit point, calculated by liquid models for following six ternary liquid-liquid equilibria systems: monochlorobenzene-water-acetone, cyclohexane-water-acetone, ethylacetate-water-acetone. chloroform-water-acetone, methylisobutylketone-water-acetone, and n-hexane-water-acetone were reported at 10°C.

Experimental tie line data were correlated to test consistency with Othmer-Tobias equation [15]

And those data were also correlated with the NRTL, the UNIQUAC, and the modified UNIQUAC models respectively and the parameters in each model were estimated to predict the value of tie lines by least-squares methods.

INSTRUCTION

The measurements and predictions of multicomponent liquid-liquid equilibria were very important for the design of solvent extraction processes.

Therefore the various equations represented as the excess Gibbs free energy function have been generally used to solve solvent extraction problems by many research workers [1-6].

They have attempted to predict more acculately the compositions of the splitting phase appearing in those processes.

In addition to their various researches, most of the data reported in literature for ternary system (solvent-water-acetone) were things that were determined at higher temperature than room temperature, but the data that were determined at temperature below it were little known.

Therefore the data below room temperature were reported and predicted in this work.

There are two methods in predicting the multicomponent liquid-liquid equilibria.

One of those methods is to extend to multicomponent liquid-liquid equilibria the binary interaction parameters estimated by using the liquid model from the vapor-liquid equilbria data and mutual solubility data of binary systems.

Another is that the parameters in liquid models are

estimated by using the only experimental tie line data, and the compositions of tie line are calculated during procedure of parameter estimation.

And the liquid models which was used in those researches were based on the concept of local composition such as the NRTL [19] model, or based on the concept of Guggenheim's quasi-chemical theory such as the UNIQUAC [17] and the modified UNIQUAC [18] models, or based on the concept of group contribution such as the UNIFAC [8] and ASOG [4] models.

On the other hand, there are various minimization methods in estimation of the parameters in liquid models and prediction of compositions of splitting phase on ternary liquid-liquid equilibria.

One of those methods is the minimization for the chemical potential difference of each component of splitting phase (so called isoactivity method), and it was used by most research workers.

Another is based on the concept that the necessary and sufficient condition of equilibrium is that the mixing Gibbs free energy of mixture is minimum on equilibrium (so called △G-minimization method), and it was used by Varhegyi and Eon [2], Sorensen et al. [16], etc.

The two methods are equally excellent, and they gave the similar results.

In this work the liquid-liquid equilibria data of the six ternary systems (solvent-water-acetone) were provided at 10°C, and they were correlated with the NRTL, the UNIQUAC, the modified UNIQUAC models.

And △G-minimization method was used to estimate

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the parameters in the NRTL, the UNIQUAC, and the modified UNIQUAC models represented as excess Gibbs free energy, and the composition of tie lines on ternary liquid-liquid equilibria were predicted from the only experimental tie line data.

EXPERIMENTAL

Binodal curves and tie lines for ternary (solvent(1)-water(2)-acetone(3) systems were determined by cloud point titrator similiar to that described by Haddad and Edmister [9] at 10°C.
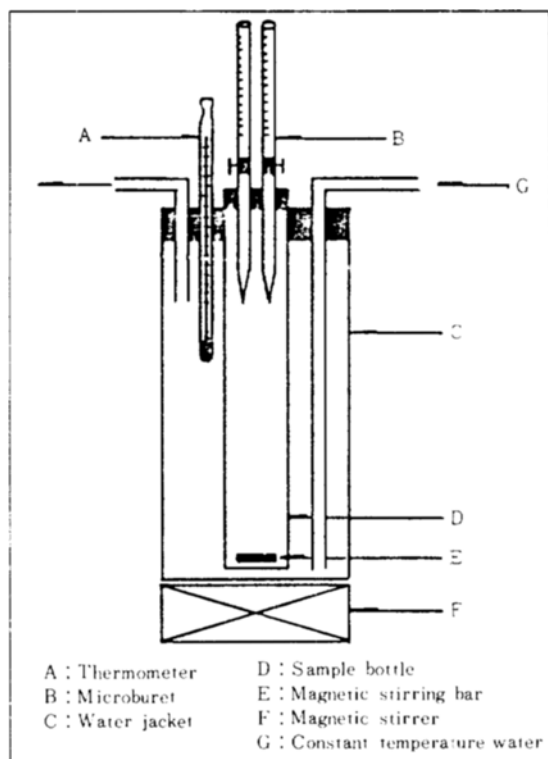
The apparatus was consisted of constant water bath (± 0.1C), microburet (0.1 ml minimum scale), sample bottle (about 200 ml), and clear water jacket as shown in Fig. 1.

Binodal curves were determined by applying method that was described by Othmer et al. [11].

Binodal curves were boundaries between miscible and partially miscible range, and were sharpened by titration liquids.

The results obtained were reported on table 2.

Tie lines between splitting phase on ternary liquid-liquid equilibria were determined by cross section method [12].

A : Thermometer   D : Sample bottle
B : Microburet   E : Magnetic stirring bar
C : Water jacket   F : Magnetic stirrer
                       G : Constant temperature water

Fig. 1. Cloud-point titrator for liquid-liquid equilibria.

Table 1. The physical properties of chemicals used.

Chemicals	Source	B. P (°C)	Density (10 °C)
A		100. 0	0. 9997
B	Merck	56. 2	0. 8000
C	Merck	132. 0	1. 1155
D	Merck	80. 7	0. 7858
E	Merck	77. 2	0. 9103
F	Merck	61. 2	1. 4978
G	Merck	118. 0	0. 8086
H	Merck	69. 0	0. 6806

(A) water, (B) acetone, (C) monochlorobenzene
(D) cyclohexane, (E) ethylacetate, (F) chloroform
(G) methylisobutylketone, (H) n-hexane.

It consists in plotting the refractive index of a mixture against concentration of acetone of solvent (1)-water (2)-acetone (3) system at a constant ratio of the remaining solvent (1)-water (2).

That is, a series of mixture that a constant ratios of the solvent and water fixed to (a) 70:30, (b) 50:50, (c) 30:70, were prepared, and acetone was increasingly added to each point.

The mixtures were allowed to settle for about 3-4 hours to reach liquid-liquid equilibria after vigorous agitation during about 10 min.

The mixtures were respectively seperated to two phases and samples of each phase were withdrawn from whether the upper phase or the lower phase with syringe, and refractive indices were measured and were plotted according to concentration of acetone.

In this work the samples were withdrawn from lower phase.

Refractive indices were measured with an Abbé refractometer calibrated to 0.001 and the accuracy of composition measurements was estimated to be within ± 0.005 weight fraction.

If arbitrary values of the refractive indices were chosen from the above diagram, they would indicate concentrations of acetone for the three fixed points ((a), (b), (c)).

Concentrations of acetone taken from the diagram were again plotted according to path between acetone and three fixed points in triangular coordinates representing binodal curves.

Since the composition of equilibrium phases on the tie line is constant, their refractive index values must also be constant.

Hence, three points representing the constant refractive indices were connected and intersected with binodal curve, and their points were the compositions of

Table 2. Experimental binodal curve data for ternary solvent(1)-water(2)-acetone(3) system at 10℃.(Wt. %)

Solvent (A)	Water	Acetone	Solvent (B)	Water	Acetone	Solvent (C)	Water	Acetone
100.00	0.00		100.00	0.00		96.86	3.14	
83.25	0.36	16.39	79.87	0.43	20.60	88.13	3.88	7.99
71.76	0.78	27.46	67.46	0.67	31.87	78.63	5.19	16.78
62.66	1.36	35.98	58.46	1.19	40.34	66.28	7.37	26.35
53.04	2.38	44.57	44.04	2.63	53.33	57.52	10.01	32.47
45.65	3.56	50.80	32.13	5.02	62.86	50.03	13.68	36.29
35.20	6.25	58.55	12.27	14.91	72.82	38.48	23.20	38.32
23.56	12.85	63.59	6.62	21.30	72.07	32.12	30.20	37.63
16.51	20.52	62.97	3.09	29.56	67.35	27.06	36.32	36.62
11.80	28.31	60.61	1.08	40.12	58.80	21.30	44.22	34.48
6.21	37.08	56.71	0.43	49.17	50.40	16.28	52.90	30.82
1.21	58.56	40.24	0.14	61.37	38.49	12.71	62.11	25.18
0.61	65.91	33.48	0.08	70.59	29.33	10.12	73.65	16.23
0.28	73.71	26.00	0.04	82.30	17.66	8.49	83.47	8.04
0.15	99.85		0.00	100.00		7.85	92.15	

Solvent (D)	Water	Acetone	Solvent (E)	Water	Acetone	Solvent (F)	Water	Acetone
99.98	0.02		97.97	2.03		100.00	0.00	
88.07	0.33	11.60	83.30	2.89	13.81	86.36	0.25	13.39
67.57	1.24	31.19	72.29	3.74	23.97	71.66	0.56	27.78
59.81	1.80	38.39	59.85	5.42	34.73	54.11	0.79	45.10
49.93	3.00	47.07	44.41	9.57	46.02	42.62	2.02	55.36
41.39	4.67	53.95	33.84	15.63	50.52	27.38	5.22	67.40
29.40	9.39	61.21	30.70	18.39	50.91	16.68	9.83	73.49
22.32	15.10	62.58	27.60	21.50	50.90	10.96	13.57	75.47
16.50	22.37	61.13	20.53	30.12	49.35	6.10	20.00	73.90
8.16	36.17	55.67	13.06	41.01	45.93	2.27	29.39	68.34
4.02	47.91	48.07	8.24	50.98	40.78	1.18	35.98	62.84
2.26	58.21	39.53	4.35	66.43	29.22	0.94	48.18	50.88
1.33	73.18	25.49	3.36	75.50	21.14	0.53	65.10	34.37
1.14	90.95	7.91	2.93	85.15	11.92	0.18	81.02	18.80
2.56	97.44		2.44	97.56		0.00	100.00	

(A) monochlorobeneze, (B) cyclohexane, (C) ethylacetate, (D) chloroform, (E) methylisobutylketone, (F) n-hexane

Table 3. Experimental tie line data for solvent (1)-water(2)-acetone(3) system at 10℃. (mole %)

Solvent	Solvent Layer			Water Layer		
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.5371	0.0409	0.4218	0.0004	0.9233	0.0764
A	0.3401	0.1046	0.5554	0.0014	0.8601	0.1385
	0.2417	0.1602	0.5982	0.0037	0.8051	0.1911
	0.1520	0.2544	0.5936	0.0107	0.7232	0.2661
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7961	0.0026	0.2012	0.0006	0.8627	0.1367
B	0.5935	0.0150	0.3915	0.0026	0.7105	0.2868
	0.4334	0.0443	0.5223	0.0126	0.5717	0.4156
	0.3190	0.0833	0.5977	0.0347	0.4567	0.5086
	1.8631	0.1369	0.0000	0.0171	0.9829	0.0000
	0.6042	0.1843	0.2115	0.0236	0.9337	0.0427
C	0.4767	0.2377	0.2856	0.0292	0.8997	0.0711
	0.3602	0.3152	0.3246	0.0374	0.8573	0.1053
	0.2465	0.4403	0.3132	0.0532	0.7991	0.1477
	0.9989	0.0013	0.0000	0.0039	0.9961	0.0000
	0.3355	0.0979	0.5666	0.0022	0.9781	0.0197
D	0.2103	0.1798	0.6099	0.0021	0.9612	0.0367
	0.1206	0.3186	0.5608	0.0019	0.9357	0.0623
	0.0536	0.5209	0.4255	0.0039	0.8887	0.1075
	0.8966	0.1034	0.0000	0.0045	0.9955	0.0000
	0.5014	0.1719	0.3268	0.0066	0.9477	0.0457
E	0.3273	0.2426	0.4302	0.0087	0.9003	0.0910
	0.2458	0.3044	0.4498	0.0112	0.8661	0.1228
	0.1589	0.4268	0.4142	0.0173	0.8163	0.1664
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4288	0.0355	0.5358	0.0002	0.9752	0.0246
F	0.2505	0.0946	0.6548	0.0009	0.9372	0.0619
	0.1432	0.1926	0.6642	0.0023	0.8862	0.2115
	0.0692	0.3159	0.6149	0.0030	0.8070	0.1900

(A) monochlorobenzene, (B) cyclohexane, (C) ethylacetate, (D) chloroform, (E) methylisobutylketone, (F) n-hexane.

tie lines.

A few tie lines that could represent the partially miscibility in the results obtained by above methods were reported on the table 3.

The determination of plait points for the six solvent(1)-water(2)-acetone(3) systems was carried out by the method of Treybal et al. [13] on Hand's [14] coordinates.

The method was described in detail in the work studied by Choi and Rhim [10].

The plait points obtained by above method were reported on the table 4.

Tie lines and plait points determined by this method were used to estimated the parameters in liquid models by converting weight fraction into mole fraction.

All the chemicals used were reagent grade and were used directly without any further purification, and water was used by redistilling.

The physical properties of these chemicals were reported on the table 1.

RESULTS

1. Consistency of Experimental Tie Line Data

The six ternary systems studied at 10°C were following:

(A) monochlorobenzene(1)-water(2)-acetone(3).
(B) cyclohexane(1)-water(2)-acetone(3).
(C) ethylacetate(1)-water(2)-acetone(3).
(D) chloroform(1)-water(2)-acetone(3).
(E) methylisobutylketone(1)-water(2)-acetone(3).

Table 4. Experimental plait point data for solvent(1)-water(2)-acetone(3) system at 10℃.

(mole %)

System	Solvent	Water	Acetone
A	0.0482	0.5246	0.4272
B	0.1414	0.2375	0.6211
C	0.1123	0.6609	0.2268
D	0.0096	0.7536	0.2341
E	0.0456	0.6964	0.2580
F	0.0081	0.5878	0.4041

System: (A) monochlorobenzene (1)-water (2)-acetone (3)
(B) cyclohexane (1)-water (2)-acetone (3)
(C) ethylacetate (1)-water (2)-acetone (3)
(D) chloroform (1)-water (2)-acetone (3)
(E) methylisobutylketone (1)-water (2)-acetone (3)
(F) n-hexane (1)-water (2)-acetone (3)

(F) n-Hexane(1)-water(2)-acetone(3).

The experimental tie line data for six ternary systems were correlated to test consistency by the method of Othmer and Tobias [15] and were represented on the Fig. 2.

The Fig. 2 gave nearly linear correlations for six ternary systems and showed that the experimental data were consistent since the tie line data were satisfactorily correlated with their equation.

The equation proposed by Othmer and Tobias[15] was expressed as

$$\log\left(\frac{1-x_{22}}{x_{22}}\right) = m_1 \log\left(\frac{1-x_{11}}{x_{11}}\right) + n_1 \tag{1}$$

2. Parameter Estimation from Tie Line Data

To predict ternary liquid-liquid equilibria, the experimental tie line data determined at 10°C were correlated with NRTL [19], UNIQUAC [17], and modified UNIQUAC [18] model represented as the excess Gibbs free energy, harmonizing with the mixing Gibbs free energy equation.

The expression of the excess Gibbs free energy for a multicomponent mixture and the mixing Gibbs free energy equation have the following form.

(a) NRTL model

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j \tau'_{ji} G_{ji}}{\sum_j x_j G_{ji}} \tag{2}$$

$$\tau'_{ji} = (g_{ji} - g_{ii})/RT \tag{3}$$

where $g_{ji} = g_{ij}$

Fig. 2. Othmer-Tobias correlation for solvent (1)-water(2)-acetone(3) at 10℃.

$$G_{ji} = Exp(-\alpha_{ji} \tau'_{ji}) \tag{4}$$

where $\alpha_{ji} = \alpha_{ij}$

(b) UNIQUAC model

$$G^E = G^E (combinatorial) + G^E (residual) \tag{5}$$

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i}$$
$$- \sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right) \tag{6}$$

(c) modified UNIQUAC model

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i}$$
$$- \sum_i q'_i x_i \ln\left(\sum_j \theta'_j \tau_{ji}\right) \tag{7}$$

where following terms are common in (b) and (c)

$$\phi_i = r_i x_i / \sum_j (r_j x_j) \tag{8}$$

$$\theta_i = q_i x_i / \sum_j (q_j x_j) \tag{9}$$

$$\theta'_i = q'_i x_i / \sum_j (q'_j x_j) \tag{10}$$

$$\tau_{ji} = Exp[-(U_{ji} - U_{ii})/RT] \tag{11}$$

(d) mixing Gibbs free energy

$$\frac{\Delta G^M}{RT} = \frac{G^E}{RT} + \frac{\Delta G^{id}}{RT} \tag{12}$$

where

$$\frac{\Delta G^{id}}{RT} = \sum_i x_i \ln x_i \tag{13}$$

In this work a least-squares technique was used for estimating the parameters in each model from experimental tie line data.

An objective function was stated in terms of concentration difference between experimental mole fraction and calculated mole fraction of tie lines.

That had following form.

$$F = \sum_i^n \min \sum_j^3 \sum_k^2 [x_{jk}^{exp}(i) - x_{jk}^{cal}(i)]^2 \tag{14}$$

Small increments of parameters were added to each initial parameter to estimate actual parameters by the means of Hooke and Jeeves [20] algorithm.

Each initial parameter was determined to give physically meaningful binodal curve.

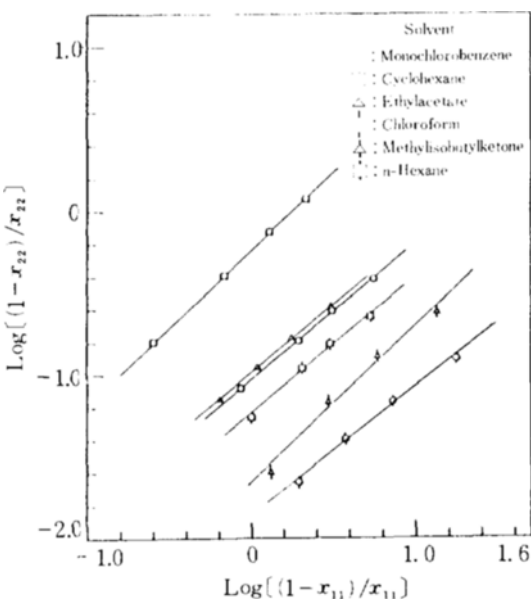If increments of parameters minimized the objective function, those would be accepted, otherwise rejected.

Therefore the actual parameters and tie lines were calculated at each step of the computation.

The parameter estimation method used in this work has been already described by Varhegyi and Eon [2].

But they estimated the parameters in the only NRTL model when α was changed.

In this work parameter estimation methods by the

UNIQUAC and the modified UNIQUAC models were added together with their research work, and parameter estimation methods were handled with following three cases.

(1) in the case of being correlated with the NRTL model, $g_{11} = 1000$ cal/g-mole of the nine parameters was fixed and the $(0 \leq \alpha_{ji} \leq 1$ j, $i = 1$, 2) constraint 3, was used in the calculation and the follwoing eight additional parameters were estimated.

$$g_{22}, g_{33}, g_{12}, g_{13}, g_{23}, \alpha_{12}, \alpha_{13}, \alpha_{23} \qquad (15)$$

(2) in the case of being correlated with the NRTL model. $g_{ll} = 1000$ cal/g-mole and $\alpha = 0.2$ recommanded by Renon and Prausnitz [19] in liquid-liquid equilibria were used in the calculation, and following five additional parameters were estimated.

$$g_{22}, g_{33}, g_{12}, g_{13}, g_{23} \qquad (16)$$

(3) in the case of the UNIQUAC, and the modified UNIQUAC model, $U_{ll} = 1000$ cal/g-mole value was fixed, and following five additional parameters were estimated.

$$U_{22}, U_{33}, U_{12}, U_{13}, U_{23} \qquad (17)$$

The values of r_i, q_i, q_i' for pure component used in computation were quoted in literature [21].

The values of the parameters estimated by being correlated with the NRTL, the UNIQUAC, and the modified UNIQUAC models were reported on table 6.

This table also included numerical values of the root-mean-square-deviation defined as

$$RMSD = 100 \left[\sum_i^n \min \sum_j^3 \sum_k^2 (x_{jk}^{exp}(i) - x_{jk}^{cal}(i))^2 / 6n \right]^{1/2}$$
$$(18)$$

And tie lines predicted by each model were reported on table 7.

Finally the experimental plait points were calculated as the same procedure by the NRTL, the UNIQUAC, and the modified UNIQUAC models respectively and predicted values were reported on table 5.

DISCUSSION

For prediction of the splitting phase compositions with only tie line data on liquid-liquid equilibria by li-

Table 5. Plaits points calculated by each model for solvent(1)- water(2)- acetone(3) system at 10℃. (mole %)

(a) NRTL model (α = changed)				(b) NRTL model (α = 0.2)			
System	Solvent	Water	Acetone	System	Solvent	Water	Acetone
A	0. 0485	0. 5237	0. 4278	A	0. 0487	0. 5229	0. 4284
B	0. 1418	0. 2372	0. 6210	B	0. 1420	0. 2368	0. 6212
C	0. 1201	0. 6541	0. 2258	C	0. 1210	0. 6530	0. 2260
D	0. 0102	0. 7498	0. 2400	D	0. 0116	0. 7488	0. 2396
E	0. 0485	0. 6952	0. 2563	E	0. 0473	0. 6954	0. 2573
F	0. 0092	0. 5850	0. 4058	F	0. 0105	0. 5834	0. 4061

(c) UNIQUAC model				(d) modified UNIQUAC			
System	Solvent	Water	Acetone	System	Solvent	Water	Acetone
A	0. 0448	0. 4912	0. 4635	A	0. 0467	0. 5024	0. 4509
B	0. 1370	0. 2336	0. 6294	B	0. 1344	0. 2454	0. 6202
C	0. 1430	0. 6212	0. 2368	C	0. 1421	0. 6108	0. 2471
D	0. 0237	0. 7268	0. 2495	D	0. 0184	0. 7325	0. 2491
E	0. 0586	0. 6626	0. 2788	E	0. 0475	0. 6739	0. 2786
F	0. 0096	0. 5602	0. 4302	F	0. 0091	0. 5783	0. 4126

System : (A) monochlorobenzene (1)-water (2)-acetone (3), (B) cyclohexane (1)-water (2)-acetone (3)
  (c) ethylacetate (1)-water (2)-acetone (3), (D) chlorobenzene (1)-water (2)-acetone (3)
  (E) methylisobutylketone (1)-water (2)-acetone (3), (F) n-hexane (1)-water (2)-acetone (3)

Table 6. Model parameters for solvent(1)-water(2)-acetone(3) system at 10℃.

(a)NRTL model $(\alpha = \text{changed})$

Solvent	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
A	1000.00	1255.18	1470.23	7326.82	981.40	1877.50	0.21	0.30	0.29	0.2182
B	1000.00	1781.22	1456.94	7003.42	1134.24	1697.81	0.14	0.08	0.15	0.0658
C	1000.00	1004.08	887.49	4903.64	1037.90	1518.96	0.30	0.09	0.02	1.0261
D	1000.00	1706.66	1387.43	6409.41	172.96	2066.98	0.11	0.99	0.48	0.3038
E	1000.00	1430.81	1468.09	7234.24	797.93	1775.92	0.21	0.51	0.28	0.6674
F	1000.00	1417.40	1229.69	6288.64	570.36	2081.55	0.17	0.98	0.41	0.1470

(b) NRTL model $(\alpha = 0.2)$

Solvent	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
A	1000.00	1419.58	1523.91	7482.16	995.79	1927.10	0.20	0.20	0.20	0.2802
B	1000.00	1188.73	2010.80	6124.52	1614.25	1848.05	0.20	0.20	0.20	0.1245
C	1000.00	1794.89	4609.77	6720.45	50.00	1088.88	0.20	0.20	0.20	1.1824
D	1000.00	2176.89	287.31	5463.51	64.86	2099.88	0.20	0.20	0.20	0.4601
E	1000.00	1539.07	1549.63	7660.23	168.73	1620.84	0.20	0.20	0.20	0.6515
F	1000.00	1268.27	1067.20	7860.64	676.80	2009.60	0.20	0.20	0.20	0.5481

(c) UNIQUAC model

Solvent	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
A	1000.00	1732.27	1909.44	7000.00	945.68	1612.07	0.4876
B	1000.00	1501.62	1622.79	6972.96	1339.20	1528.28	0.3098
C	1000.00	2019.99	53.87	7058.04	291.24	1162.16	1.1075
D	1000.00	654.21	993.60	6493.00	143.47	2076.00	0.6828
E	1000.00	1867.00	1805.51	7681.32	480.06	1289.00	0.6124
F	1000.00	1808.00	1546.18	7015.22	834.07	1760.00	0.6294

(d) modified UNIQUAC model

Solvent	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
A	1000.00	1518.73	2072.65	6983.71	1193.67	1670.40	0.4596
B	1000.00	1123.14	1756.98	6573.55	1452.19	1470.54	0.4476
C	1000.00	2423.45	1325.60	5012.04	513.39	1353.47	1.2835
D	1000.00	50.00	1548.99	7913.02	50.91	2408.33	0.4801
E	1000.00	1920.00	1960.99	7160.00	814.32	1511.11	0.6712
F	1000.00	1407.76	1926.29	7002.51	1083.91	1737.96	0.6625

Constraints: $50 \leqq g \leqq 9999$, $50 \leqq U \leqq 9999$, $0 \leqq \alpha \leqq 1$ (A) monochlorobenzene, (B) cyclohexane, (C) ethylacetate (D) chloroform, (E) methylisobutylketone, (F) n-hexane.

Table 7. Tie lines predicted by each model for solvent(1)-water(2)-acetone(3) system at 10℃.
(mole %)

(a) NRTL model (α = changed)

Solvent	Solvent Layer			Water Layer		
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.5298	0.0433	0.4269	0.0005	0.9244	0.0751
A	0.3419	0.1170	0.5411	0.0024	0.8598	0.1378
	0.2483	0.1780	0.5737	0.0057	0.8044	0.1898
	0.1622	0.2629	0.5750	0.0138	0.7199	0.2663
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7910	0.0014	0.2076	0.0002	0.8650	0.1348
B	0.5960	0.0132	0.3908	0.0031	0.7090	0.2880
	0.4364	0.0439	0.5197	0.0140	0.5683	0.4176
	0.3202	0.0892	0.5906	0.0349	0.4569	0.5082
	0.8928	0.0097	0.0975	0.0009	0.9826	0.0165
	0.5871	0.1594	0.2534	0.0022	0.9565	0.0413
C	0.4665	0.2405	0.2930	0.0033	0.9406	0.0560
	0.3391	0.3025	0.3584	0.0064	0.9070	0.0865
	0.2290	0.4407	0.3303	0.0472	0.8043	0.1485
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.3295	0.0745	0.5961	0.0000	0.9770	0.0230
D	0.2130	0.1843	0.6027	0.0000	0.9668	0.0332
	0.1224	0.3251	0.5524	0.0000	0.9491	0.0508
	0.0641	0.5146	0.4213	0.0068	0.8732	0.1200
	0.9241	0.0006	0.0752	0.0000	0.9938	0.0062
	0.4928	0.1365	0.3706	0.0005	0.9425	0.0570
E	0.3381	0.2645	0.3974	0.0016	0.9109	0.0875
	0.2616	0.3362	0.4022	0.0033	0.8827	0.1139
	0.1698	0.4396	0.3907	0.0096	0.8254	0.1650
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4338	0.0284	0.5378	0.0001	0.9682	0.0318
F	0.2537	0.0967	0.6496	0.0002	0.9355	0.0643
	0.1402	0.1950	0.6648	0.0005	0.8915	0.1081
	0.0620	0.3189	0.6190	0.0013	0.8126	0.1861

(b) NRTL model (α = 0.2)

Solvent	Solvent Layer			Water Layer		
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.5331	0.0491	0.4178	0.0003	0.9239	0.0757
A	0.3445	0.1245	0.5311	0.0020	0.8589	0.1391
	0.2508	0.1836	0.5656	0.0047	0.8045	0.1908
	0.1626	0.2665	0.5709	0.0116	0.7223	0.2661
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7956	0.0025	0.2019	0.0009	0.8627	0.1364
B	0.5926	0.0169	0.3905	0.0066	0.7077	0.2857
	0.4331	0.0468	0.5201	0.0207	0.5670	0.4123
	0.3205	0.0870	0.5924	0.0426	0.4533	0.5041
	0.9030	0.0040	0.0931	0.0000	0.9861	0.0139
	0.5982	0.1612	0.2406	0.0010	0.9367	0.0623
C	0.4904	0.2523	0.2573	0.0022	0.9168	0.0810
	0.3831	0.3491	0.2678	0.0056	0.8859	0.1084
	0.2616	0.4685	0.2699	0.0173	0.8318	0.1509
	0.9999	0.0000	0.0001	0.0000	1.0000	0.0000
	0.3387	0.1273	0.5340	0.0000	0.9794	0.0205
D	0.2112	0.1907	0.5981	0.0000	0.9675	0.0325
	0.0896	0.3179	0.5924	0.0020	0.9326	0.0654
	0.0594	0.5105	0.4301	0.0097	0.8588	0.1315
	0.9219	0.0006	0.0775	0.0000	0.9987	0.0013
	0.4875	0.1477	0.3747	0.0001	0.9580	0.0418
E	0.3340	0.2662	0.3998	0.0013	0.9143	0.0844
	0.2630	0.3346	0.4024	0.0034	0.8800	0.1166
	0.1770	0.4376	0.3854	0.0116	0.8164	0.1720
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4305	0.0476	0.5219	0.0000	0.9691	0.0309
F	0.2485	0.0829	0.6685	0.0001	0.9431	0.0568
	0.1454	0.1886	0.6659	0.0076	0.8793	0.1130
	0.1171	0.3176	0.5653	0.0188	0.8105	0.1708

(c) UNIQUAC model

Solvent	Solvent Layer			Water Layer		
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
A	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4894	0.0808	0.4298	0.0000	0.9300	0.0700
	0.3433	0.1416	0.5151	0.0002	0.8638	0.1360
	0.2559	0.1948	0.5493	0.0008	0.8053	0.1939
	0.1679	0.2708	0.5613	0.0032	0.7244	0.2724
B	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7803	0.0123	0.2074	0.0000	0.8676	0.1324
	0.5945	0.0346	0.3709	0.0008	0.7100	0.2892
	0.4364	0.0653	0.4983	0.0049	0.5739	0.4212
	0.3194	0.0999	0.5807	0.0147	0.4701	0.5152
C	0.8584	0.0503	0.0913	0.0000	0.9844	0.0156
	0.6136	0.1880	0.1984	0.0008	0.9429	0.0563
	0.4960	0.2696	0.2344	0.0026	0.9171	0.0803
	0.3840	0.3577	0.2583	0.0069	0.8852	0.1079
	0.2607	0.4704	0.2689	0.0184	0.8353	0.1462
D	0.9898	0.0102	0.0000	0.0002	0.9998	0.0000
	0.3373	0.1129	0.5498	0.0002	0.9704	0.0295
	0.2134	0.1753	0.6114	0.0002	0.9532	0.0466
	0.0731	0.3104	0.6164	0.0007	0.9195	0.0798
	0.0469	0.5072	0.4460	0.0062	0.8475	0.1463
E	0.9006	0.0167	0.0826	0.0000	0.9969	0.0031
	0.5036	0.1728	0.3267	0.0000	0.9510	0.0490
	0.3395	0.2665	0.3940	0.0002	0.9077	0.0921
	0.2668	0.3295	0.4036	0.0006	0.8851	0.1143
	0.1643	0.4344	0.4014	0.0025	0.8366	0.1609
F	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4237	0.0935	0.4828	0.0000	0.9803	0.0197
	0.2540	0.1538	0.5922	0.0000	0.9455	0.0545
	0.1589	0.2177	0.6233	0.0000	0.8842	0.1158
	0.0882	0.3002	0.6116	0.0001	0.8105	0.1894

continued

(d) modified UNIQUAC model

Solvent	Solvent Layer			Water Layer		
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
A	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.5166	0.0875	0.3959	0.0000	0.9384	0.0616
	0.3354	0.1562	0.5085	0.0002	0.8628	0.1371
	0.2481	0.2061	0.5458	0.0006	0.8034	0.1959
	0.1632	0.2748	0.5620	0.0027	0.7229	0.2744
B	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7670	0.0236	0.2094	0.0000	0.8713	0.1287
	0.5856	0.0493	0.3651	0.0008	0.7135	0.2857
	0.4364	0.0782	0.4854	0.0047	0.5735	0.4218
	0.3223	0.1090	0.5687	0.0141	0.4663	0.5196
C	0.8779	0.0632	0.0598	0.0002	0.9583	0.0414
	0.6238	0.2048	0.1713	0.0017	0.9274	0.0708
	0.5031	0.2850	0.2119	0.0035	0.9101	0.0864
	0.3858	0.3709	0.2433	0.0074	0.8871	0.1055
	0.2615	0.4797	0.2588	0.0177	0.8478	0.1345
D	0.9828	0.0172	0.0000	0.0001	0.9999	0.0000
	0.3369	0.1361	0.5270	0.0000	0.9813	0.0187
	0.2104	0.1905	0.5991	0.0000	0.9689	0.0311
	0.0594	0.5106	0.4299	0.0096	0.8596	0.1308
E	0.8942	0.0358	0.0699	0.0000	0.9955	0.0045
	0.5040	0.1929	0.3031	0.0000	0.9579	0.0421
	0.3273	0.2804	0.3923	0.0001	0.9197	0.0803
	0.2351	0.3573	0.4076	0.0003	0.8876	0.1121
	0.1560	0.4310	0.4131	0.0013	0.8453	0.1534
F	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.4251	0.0840	0.4909	0.0000	0.9869	0.0131
	0.2417	0.1418	0.6166	0.0000	0.9282	0.0718
	0.1549	0.2306	0.6144	0.0000	0.8992	0.1008
	0.0890	0.3271	0.5939	0.0001	0.8154	0.1845

(A) monochlorobenzene (B) cyclohexane (C) ethylacetate (D) chloroform (E) methylisobutylketone (F) n-hexane.

quid models, Triday [23] reported results predicted by the method of Sorensen et al. [16] for the ternary benzene(1)-water(2)-methanol(3) system.

His tie line data were correlated with the UNIQUAC model at 20°C, and RMSD value was 0.4870.

And Annesini et al. [24] also reported the results predicted by the same method for six propylene carbonate(1)-n-hexane(2)-benzene(or ethylbenzene)(3), pro-

pylene carbonate(1)-n-heptane(2)-toluene(or ethyl-benzene)(3), and propylene carbonate(1)-n-octane(2)-o-oxylene(or ethylbenzene)(3) systems.

Their tie line data were correlated with the NRTL ($\alpha = 0.2$) model and the UNIQUAC model at 20°C, and the RMSD values were 0.5147-0.6825 in the NRTL ($\alpha = 0.2$) model and were 0.6112-0.7409 in the UNI-QUAC model.

Though systems of this work were different from them, the results in this work could be compared with those of Triday's and Annesini's since the only experimental tie line data equally were correlated with same liquid models.

In this work the RMSD values were 0.1245-0.6515 in the NRTL model ($\alpha = 0.2$) and were 0.3098-0.6828 in the UNIQUAC model except ethylacetate(1)-water(2)-acetone(3) system as shown on table 5.

Therefore the final RMSD values were compared much with those results of Triday's and Annesini's.

On the other hand generally the NRTL model in the case of varying α value gave the RMSD values slightly lower than those of the same model in the case of fixing α value except (E) system, and the RMSD values in the NRTL model in the case of fixing α value were lower than those of the UNIQUAC, and the RMSD values in the UNIQUAC model were slightly better than those of the modified UNIQUAC model.

Such phenomena were appeared in the work of Annesini et al. [24] for prediction of liquid-liquid equilibria with the NRTL model and the UNIQUAC model.

But those differences were not significant since all the RMSD values were satisfactory within error range.

CONCLUSIONS

The tie line data determined at 10°C from binodal curve for the six ternary monochlorobenzene (or cyclohexane, ethylacetate, chloroform, methylisobutylketone, n-hexane) (1)-water (2)-acetone (3) systems were satisfatorily correlated with Othmer and Tobias equation.

Such tie line data also were correlated with the NRTL model in the case of varying or fixing α value, the UNIQUAC, and the modified UNIQUAC model, and the parameters in each model were estimated, and the tie lines were predicted.

As a result of correlating with each model, the tie lines predicted with the NRTL model in the case of varying or fixing α value, the UNIQUAC model, and the modified UNIQUAC model were good identical within 0.0658-1.0261, 0.2802-1.1824, 0.3098-1.1075, 0.4476-1.2835 RMSD values with the experimental tie line data.

NOMENCLATURE

F   : objective function defined by eq. (14).

G^E : excess Gibbs free energy (cal/g-mole)
ΔG^{id} : ideal Gibbs free energy (cal/g-mole)
ΔG^M : mixing Gibbs free energy (cal/g-mole)
G_{ji} : NRTL binary interaction parameter
g_{ij} : NRTL binary interaction parameter (cal/g-mole)
min   : minimum
m_1 : constant defined by Othmer-Tobias eq.(1)
n_1 : constant defined by Othmer-Tobiass eq. (1)
n   : number of exerimental tie line data.
q_i : area parameter of pure component i
q_i' : modified area parameter of pure component i
r_i : volume parameter of pure component i
R   : gas constant (cal/g-mole K)
T   : absolute temperature (K)
U_{ji} : UNIQUAC, modified UNIQUAC binary interaction parameter (cal/g-mole)
x_i : mole fraction of component i in the liquid phase
x_{jk} : tie line mole fraction of component j in k phase
$x_{jk}^{exp}(i)$: the i-th experimental tie line mole fraction of component j in k phase
$x_{jk}^{cal}(i)$: the i-th calculated tie line mole fraction of component j in k phase
Z   : lattice coordination number (set equal to 10)

Greek Letters

α_{ji} : nonrandomness parameter in NRTL eq.
ϕ_i : volume fraction defined by eq. (8)
θ_i : area fraction defined by eq. (9)
θ_i' : modified area fraction defined by eq. (10)
τ_{ji}' : NRTL binary interaction parameter
τ_{ji} : UNIQUAC, modified UNIQUAC binary interaction parameter

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