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APPLICATION OF NRTL AND UNIQUAC MODELS TO LIQUID-LIQUID SYSTEMS WITH HALOGEN SALTS (Part I)

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Abstract— Binodal curves, tie lines, and plait points for benzene-halogen salt solutions-n-propanol systems were determined, and Othmer-Tobias equation was employed for a system without salt and Eisen-Joffe equation for systems with salt to test consistency. Halogen salt solutions were prepared with aqueous solution of 5% KF, 5% NaCl, 5% NaBr and 5% NaI, respectively.

Compositions of two splitting phases on liquid-liquid equilibria (L-L-E) condition were calculated and the parameters were estimated by correlating experimental tie lines with the NRTL and the UNIQUAC (or modified UNIQUAC) models.

The effects of addition of four halogen salts (KF, NaCl, NaBr, NaI) to benzene-water-n-propanol system were considered.

INTRODUCTION

Applications of a liquid model to phase equilibrium data and their prediction are very important in the design of equipments for separation processes in chemical industry. Various researches have been proceeded for representing the thermodynamic phase equilibria of multicomponent systems with and/or without salts up to date.

Many researches [1-3] have been carried out to predict phase equilibrium data without salts by correlating them with various models such as Wilson [4], NRTL [5], UNIQUAC [6], ASOG [7] and UNIFAC [8].

Furthermore attempts that would represent phase equilibrium data thermodynamically have been done for electrolyte systems more than binary system with salt. A representative theory that could describe thermodynamic behaviour of electrolyte systems was electrostatic one, and it was based on the variation of dielectric constant of electrolyte systems. Debye and McAulay [9] derived an equation of activity coefficients of nonelectrolyte in dilute aqueous electrolyte systems on the basis of that theory, and recently significant developments in the estimation of the molality-mean ionic activity coefficients for aqueous electrolyte systems have been made by Meissner [10], Bromley [11], Pitzer [12-15], and Cruz and Renon [16]. And Chen et al. [17,18] also applied electrostatic forces to represent excess Gibbs energy for single solvent-electrolyte and single solvent-fused electrolytes systems.

On the other hand, Sander et al. [19] revised the parameters of the UNIQUAC model as temperature dependence terms and suggested a thermodynamic equation to consider the salt effect on vapor-liquid equilibria (V-L-E).

Studies of above enumeration were all analyses of the salt effect on V-L-E for binary systems or ternary systems with salt, but models that could predict the salt effect on L-L-E, quaternary systems with salts, seldom were seen, and few researches [20-24] only reported experimental data and considered the salt effect on L-L-E.

But Choi et al. [25] assumed that quaternary systems of L-L-E with salt were converted to ternary systems of L-L-E without salt if salt were excluded as much as salt concentration on the binodal curve, and represented quaternary L-L-E systems as excess Gibbs energy to consider the effect of NaCl on monochlorobenzene-water-acetone system.

In this work, the effect of addition of four halogen salts to benzene-water-n-propanol system were considered, and L-L-E data were correlated with liquid models, and the parameters in those liquid models were estimated, and the compositions of each phase in splitting phase on L-L-E were predicted.

EXPERIMENTAL

Binodal curves and tie lines for quaternary systems with halogen salts were determined by a cloud point titrator similiar to that described by Haddad and Edmister [26] at 25°C. The apparatus was consisted of

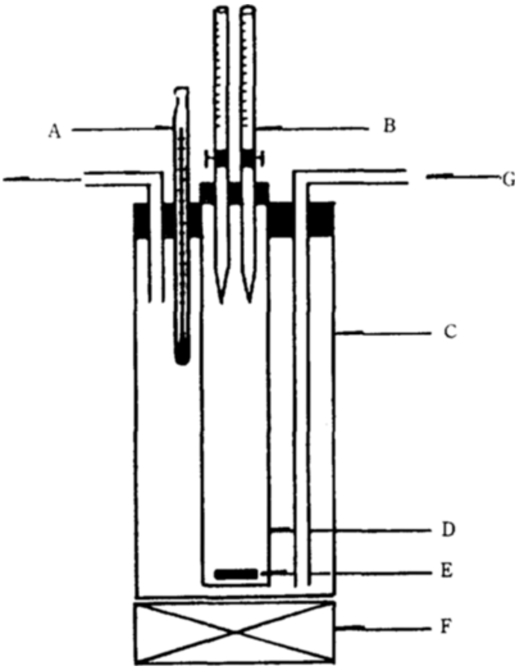

Fig. 1. Cloud-point titrator for liquid-liquid equilibria.

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

Table 1. The physical properties of chemicals used.

Chemicals	Source	B.P (°C)	Density (25°C)	Solubility (20°C)
A		100.0	0.9999	
B	Merck GR	56.2	0.7998	
C	Merck GR	80.1	0.8737	
D	Merck GR	1517.0	2.4815	95.0
E	Merck GR	1465.0	2.1642^{20}	35.9
F	Merck GR	1447.0	3.2050^{18}	90.0
G	Merck GR	1304.0	3.6670^{0}	178.0

A: water, B: n-propanol, C: benzene, D: KF,
E: NaCl,
F: NaBr, G: NaI
Solubility of salt: basis in 100 parts water

microburet (0.1 m*l* minimum scale), sample bottle (about 200 m*l*), clear water jacket, and was circulated by constant temperature water from water bath as shown in Fig. 1.

Binodal curves were determined by applying the method that was described by Othmer et al. [27]. And those curves were boundaries of partially miscible and entirely miscible range.

The determination of tie line data was carried out by modifying cross-section method [28] that plotted the refractive indices of mixtures against the concentration of n-propanol in benzene (1)-halogen salt solutions (2)-n-propanol (3) system at a constant ratio of the remaining benzene (1)-halogen salt solution (2).

Determination of plait points was carried out by the method of Treybal et al. [29] on Hand's coordinates [30].

The above experimental method was well described in the previous papers of Choi et al. [25,31,32].

RESULTS

1. Experimental Data

Experimental binodal curve data, tie line data and plait point data for benzene (1)-halogen salt solutions (2)-n-propanol (3) systems with KF, NaCl, NaBr and NaI were reported on Table 2, Table 3, Table 4, respectively. Tie lines more than twenty sets were necessary to estimate the parameters in the liquid models (NRTL etc.). In this work, only five sets of those data that decribed partially miscible L-L-E were reported representatively on Table 3.

It is necessary that consistency of experimental tie line data should be tested to correlate with the NRTL, UNIQUAC and modified UNIQUAC models. Therefore those data were correlated with the Othmer and Tobias equation [33] for the system without salt and with the Eisen and Joffe equation [20] for systems with salts, and represented on Fig. 2 showed nearly linear correlations for benzene-halogen salt solutions-n-propanol systems. Therefore it was indirectly tested that the experimental data were consistent since the tie line data were satisfactorily correlated with their equations.

The Othmer-Tobias and Eisen-Joffe equation used in this work have the following forms.

(a) Othmer and Tobias equation

$$\mathrm{Log}\left(\frac{1-x_{22}}{x_{22}}\right) = m\ \mathrm{Log}\left(\frac{1-x_{11}}{x_{11}}\right) + n \qquad (1)$$

(b) Eisen and Joffe equation

$$\mathrm{Log}\frac{x_{31}}{x_{11}} = \mathrm{Log}\ A + B\ \mathrm{Log}\frac{x_{32}}{x_{22}} \qquad (2)$$

where

$$\mathrm{Log}\ A = a + b\ X_s$$

$$B = c + d\ X_s$$

2. Parameter Estimation from Tie Line Data

The experimental tie line data at 25°C were correlated with the NRTL, UNIQUAC and modified UNIQUAC models represented as excess Gibbs energy to estimate the parameters in each model and to calculate the compositions of tie lines in splitting phases by least-squares method, harmonizing with mixing Gibbs energy in liquid mixtures.

The expressions of excess and mixing Gibbs energy equations for multicomponent systems have following forms in liquid mixtures.

(a) NRTL model

$$\frac{G^E}{RT}=\sum_i x_i \frac{\sum_j x_j \tau'_{ji} G_{ji}}{\sum_j x_j G_{ji}} \qquad (3)$$

Table 2. Experimental binodal curve data for benzene(1)-halogen salt solutions(2)-n-propanol(3) systems at 25°C (wt.%).

Salt	Benzene	Water	n-Propanol	No-salt	Salt	Benzene	Water	n-Propanol	NaBr
0%	100.00	0.00		0.00	5%	100.00	0.00		0.00
	89.00	1.11	9.89	0.00		83.85	0.95	15.15	0.05
	75.83	3.63	20.54	0.00		62.61	2.85	34.39	0.15
	68.32	4.54	27.14	0.00		49.78	4.43	45.56	0.23
	51.23	8.02	40.75	0.00		41.00	6.14	52.54	0.32
	34.01	13.59	52.40	0.00		30.02	9.04	60.46	0.48
	27.36	17.33	55.31	0.00		21.83	13.07	64.41	0.69
	21.21	21.80	56.99	0.00		16.91	16.91	65.29	0.89
	17.10	25.90	57.00	0.00		12.38	23.46	62.92	1.24
	12.93	30.78	56.29	0.00		8.42	31.69	58.23	1.67
	8.57	41.05	50.38	0.00		6.51	39.23	52.20	2.06
	4.28	60.37	35.35	0.00		5.29	46.30	45.97	2.44
	1.37	77.89	20.74	0.00		3.74	56.36	36.93	2.97
	0.08	89.52	10.40	0.00		2.68	63.23	30.76	3.33
		100.00	0.00	0.00		1.91	86.27	7.28	4.54

Salt	Benzene	Water	n-Propanol	KF	Salt	Benzene	Water	n-Propanol	NaI
5%	100.00	0.00		0.00	5%	100.00	0.00		0.00
	83.08	1.62	15.21	0.09		82.93	1.80	15.18	0.09
	62.52	2.98	34.34	0.16		67.44	3.32	29.01	0.18
	49.83	4.32	45.62	0.23		54.69	4.52	40.55	0.24
	33.26	5.56	60.89	0.29		39.56	6.09	54.03	0.32
	23.51	7.24	68.87	0.38		33.96	6.86	58.82	0.36
	12.47	9.29	77.75	0.49		23.17	8.64	67.74	0.45
	4.24	11.19	83.98	0.59		13.16	16.61	74.62	0.61
		11.93	87.44	0.63		8.21	15.44	75.54	0.81
	0.00	95.00		5.00		3.69	18.29	77.06	0.96
	0.30	92.48	2.35	4.87		2.02	22.12	74.70	1.16
	0.58	89.82	4.87	4.73		1.79	28.61	68.09	1.51
	0.80	87.24	7.37	4.59		1.44	51.96	43.87	2.73
	0.64	81.44	13.63	4.29		1.17	63.38	32.11	3.34
		72.25	23.95	3.80		0.75	81.25	13.72	4.28

Table 2. Continued.

Salt	Ben-zene	Water	n-Pro-panol	NaCl
5%	100.00	0.00		0.00
	83.88	0.72	15.36	0.04
	71.78	1.71	26.32	0.09
	62.37	2.37	35.14	0.12
	49.44	5.03	45.26	0.27
	40.27	7.72	51.60	0.41
	26.49	14.55	58.19	0.77
	23.06	16.93	59.12	0.89
	17.52	23.01	58.26	1.21
	15.01	26.17	57.44	1.38
	11.54	32.26	54.49	1.70
	8.12	41.12	48.60	2.16
	4.39	55.33	37.37	2.91
	1.31	70.98	23.97	3.74
	0.60	81.38	13.74	4.28

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

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

$$\tau'_{ji} = (g_{ji} - g_{ii})/RT \tag{5}$$

(b) modified UNIQUAC model (or UNIQUAC)

$$G^E = G^E(\text{combinatorial}) + G^E(\text{residual}) \tag{6}$$

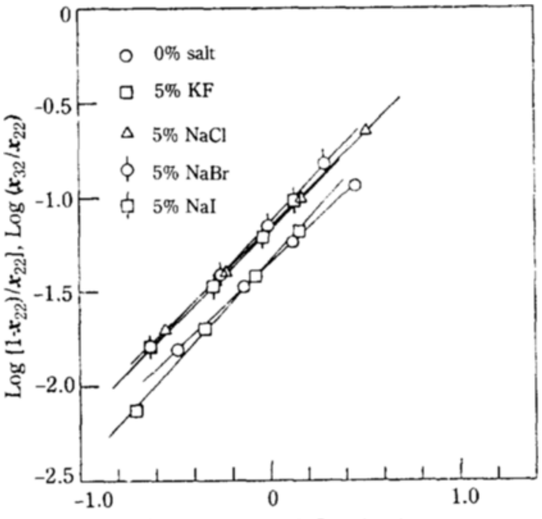

Fig. 2. Othmer-Tobias and Eisen-Joffe correlation for benzene(1)-halogen salt solutions(2)-n-propanol (3) systems at 25°C.

Table 3. Experimental tie line data for benzene (1)-halogen salt solutions (2)-n-propanol (3) systems at 25°C.

salt-free basis (mole %)

Salt	Benzene 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
	0.7564	0.0745	0.1691	0.0003	0.9849	0.0147
	0.5817	0.1368	0.2815	0.0007	0.9680	0.0313
	0.4340	0.2129	0.3531	0.0021	0.9451	0.0528
	0.2630	0.3174	0.4196	0.0057	0.8972	0.0970
B	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.8025	0.0424	0.1551	0.0005	0.9921	0.0074
	0.6288	0.0895	0.2818	0.0010	0.9795	0.0194
	0.4896	0.1023	0.4081	0.0016	0.9618	0.0366
	0.3585	0.1380	0.5034	0.0014	0.9383	0.0603
C	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7308	0.0635	0.2056	0.0011	0.9794	0.0195
	0.5621	0.1141	0.3238	0.0018	0.9593	0.0389
	0.3293	0.1876	0.4831	0.0029	0.9057	0.0914
	0.1762	0.2514	0.5724	0.0059	0.8077	0.1864
D	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7806	0.0383	0.1812	0.0007	0.9832	0.0160
	0.6004	0.0717	0.3279	0.0021	0.9605	0.0374
	0.4419	0.1287	0.4294	0.0051	0.9292	0.0657
	0.2606	0.2305	0.5089	0.0091	0.8597	0.1312
E	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7806	0.0383	0.1812	0.0006	0.9837	0.0156
	0.6129	0.0787	0.3084	0.0016	0.9655	0.0329
	0.4555	0.1266	0.4178	0.0027	0.9395	0.0577
	0.3418	0.1937	0.4645	0.0053	0.9076	0.0871

A: 0% salt, B: 5% KF, C: 5% NaCl, D: 5% NaBr, E: 5% NaI

$$G^E/RT\,(\text{com.}) = \sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{Z}{2}\sum_i q_i x_i \ln\frac{\theta_i}{\phi_i} \tag{7}$$

$$G^E/RT\,(\text{res.}) = -\sum_i q'_i x_i \ln\left(\sum_j \theta'_j \tau_{ji}\right) \tag{8}$$

$$\phi_i = r_i x_i / \sum_j (r_j x_j) \tag{9}$$

$$\theta_i = q_i x_i / \sum_j (q_j x_j) \tag{10}$$

$$\theta'_i = q'_i x_i / \sum_j (q_j x_j) \tag{11}$$

$$\tau_{ji} = \mathrm{Exp}(-(U_{ji} - U_{ii})/RT) \tag{12}$$

when q' is equal to q, the modified UNIQUAC model is reduced to the UNIQUAC model.

Table 4. Experimental plait point data for benzene (1)-halogen salt solutions (2)-n-propanol (3) systems at 25°C.

salt-free basis (mole %)

System	Benzene	Water	n-Propanol
A	0.0563	0.6158	0.3279
B	0.0133	0.4658	0.5209
C	0.0505	0.5656	0.3839
D	0.0519	0.6300	0.3181

A: benzene (1)-water (2)-n-propanol (3)
B: benzene (1)-5% NaCl solution (2)-n-propanol (3)
C: benzene (1)-5% NaBr solution (2)-n-propanol (3)
D: benzene (1)-5% NaI solution (2)-n-propanol (3)

(c) mixing Gibbs energy equation

$$\frac{\Delta G^M}{RT}=\frac{G^E}{RT}+\frac{\Delta G^{id}}{RT} \qquad (13)$$

where

$$\frac{\Delta G^{id}}{RT}=\sum_i x_i \ln x_i \qquad (14)$$

In this work an objective function was applied to above equations and minimized by addition of small increments to each initial parameters to estimate actual parameters by the direct search method of Hooke and Jeeves [34].

Each initial parameter was determined to give physically meaningful binodal curves, and the initial values were different each other but same for all systems. And an objective function was stated in terms of concentration differences between the experimental and calculated mole fractions of tie lines and had following form.

$$F=\sum_i^n \min \sum_j^3 \sum_k^2 [x_{jk}^{exp}(i)-x_{jk}^{cal}(i)]^2 \qquad (15)$$

On the other hand, note that only the differences of g_{ji} (or U_{ji}) occur in eq. (3)-eq. (5) or eq. (6)-eq. (12), the value of G^E does not change if we add the same constant to each g_{ji} (or U_{ji}). This means that one of the g_{ji}(or U_{ji}) (ex: g_{11}, U_{11}) can be chosen arbitrarily and fixed during computation.

Therefore we shall assume g_{11} (or U_{11}) = 1000 cal/g-mole to be fixed and estimate the parameters in each model as following cases.

(a) In the case of correlation of tie line data with the NRTL, constraints were $50<g<9999$ and $0.001<\alpha<0.999$, and eight additional parameters (g_{22}, g_{33}, g_{12}, g_{13}, g_{23}, α_{12}, α_{13}, α_{23}) were estimated.

(b) In the case of correlation of them with the modified UNIQUAC (or UNIQUAC), constraints were $50<U<9999$, and five additional parameters (U_{22}, U_{33}, U_{12}, U_{13}, U_{23}) were estimated.

The values of r_i, q_i, q_i' for pure component used on computation were quoted in literature [35].

The values of the parameters estimatied by being correlated with the NRTL and modified UNIQUAC (or UNIQUAC) models were reported on Table 6. This table also included numerical values of the root-mean-square-deviation defined as

$$RMSD=100\left[\sum_i^n \min \sum_j^3 \sum_k^2 (x_{jk}^{cal}(i))^2/6n\right]^{1/2} \qquad (16)$$

And the calculated tie line data were reported on Table 7.

Finally the experimental plait points data for benzene-water (or 5% NaCl, 5% NaBr, 5% NaI)-n-propanol were calculated as the same procedure by each model and reported on Table 5.

Table 5. Plait points calculated by each model for benzene (1)-halogen salt solutions (2)-n-propanol(3) systems at 25°C.

(a) NRTL: salt-free basis (mole %)

System	Benzene	Water	n-Propanol
A	0.0352	0.6206	0.3262
B	0.0088	0.4708	0.5204
C	0.0325	0.5788	0.3887
D	0.0428	0.6194	0.3378

(b) UNIQUAC: salt-free basis (mole %)

System	Benzene	Water	n-Propanol
A	0.0634	0.6186	0.3180
B	0.0204	0.4620	0.5176
C	0.0674	0.5524	0.3802
D	0.0362	0.6344	0.3294

(c) modified UNIQUAC: salt-free basis (mole %)

System	Benzene	Water	n-Propanol
A	0.0577	0.6219	0.3204
B	0.0213	0.4633	0.5154
C	0.0672	0.5604	0.3724
D	0.0442	0.6285	0.3273

A: benzene (1)-water (2)-n-propanol (3)
B: benzene (1)-5% NaCl solution (2)-n-propanol (3)
C: benzene (1)-5% NaBr solution (2)-n-propanol (3)
D: benzene (1)-5% NaI solution (2)-n-propanol (3)

Table 6. Model parameters for benzene (1)-halogen salt solutions (2)-n-propanol (3) systems at 25°C.

(a) NRTL model

Salt	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
A	1000.00	1818.94	1224.91	7665.81	502.11	1906.05	0.226	0.029	0.071	0.2735
B	1000.00	1822.13	760.59	7538.36	510.90	1929.84	0.224	0.001	0.001	0.2329
C	1000.00	1446.66	1301.39	6977.41	914.36	1956.33	0.250	0.001	0.001	0.1892
D	1000.00	1612.51	1332.45	7827.78	572.54	1909.14	0.215	0.041	0.002	0.1863
E	1000.00	1482.76	1062.60	7128.69	576.96	1734.75	0.220	0.090	0.197	0.2112

(b) UNIQUAC model

Salt	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
A	1000.00	1783.20	1515.17	6536.96	295.78	1297.13	0.2910
B	1000.00	1720.80	1370.40	7006.26	950.08	1650.13	0.2464
C	1000.00	1748.80	1344.53	7312.61	1123.58	1683.79	0.4647
D	1000.00	1739.97	1273.31	7920.64	937.97	1592.01	0.1860
E	1000.00	1867.95	1222.38	6994.12	959.19	1669.46	0.1751

(c) modified UNIQUAC model

Salt	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	RMSD
A	1000.00	2194.28	652.07	7082.15	187.73	1483.38	0.2042
B	1000.00	1511.62	326.08	7689.15	437.44	1310.05	0.2542
C	1000.00	2001.66	617.93	6506.87	766.05	1810.08	0.4110
D	1000.00	1916.81	617.57	9840.82	579.01	1591.16	0.1456
E	1000.00	2110.10	1130.58	7121.61	492.23	1643.82	0.1491

Constraint: $50 \leq U \leq 9999$, $50 \leq g \leq 9999$, $0.001 \leq \alpha \leq 0.999$

A: 0% salt, B: 5% KF, C: 5% NaCl, D: 5% NaBr, E: 5% NaI

Table 7. Tie lines calculated for benzene (1)-halogen salt solutions (2)-n-propanol (3) systems at 25°C.

(a) NRTL model: salt-free basis (mole %)

Salt	Benzene 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
	0.7511	0.0371	0.2118	0.0000	0.9862	0.0138
	0.5739	0.1246	0.3015	0.0001	0.9716	0.0283
	0.4312	0.2121	0.3567	0.0003	0.9491	0.0506
	0.2727	0.3252	0.4021	0.0021	0.8986	0.0993
B	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.8075	0.0143	0.1782	0.0000	0.9918	0.0081
	0.6275	0.0643	0.3082	0.0000	0.9812	0.0188
	0.4876	0.1103	0.4021	0.0001	0.9663	0.0336
	0.3555	0.1493	0.4952	0.0003	0.9422	0.0576
C	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7306	0.0442	0.2252	0.0001	0.9813	0.0186
	0.5591	0.1070	0.3339	0.0003	0.9645	0.0352
	0.3248	0.1915	0.4837	0.0020	0.9104	0.0876
	0.1631	0.2606	0.5763	0.0082	0.8150	0.1769
D	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7831	0.0164	0.2005	0.0000	0.9879	0.0120
	0.5959	0.0676	0.3365	0.0001	0.9681	0.0319
	0.4386	0.1307	0.4307	0.0004	0.9363	0.0633
	0.2633	0.2287	0.5080	0.0031	0.8624	0.1345
E	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7842	0.0135	0.2023	0.0000	0.9845	0.0154
	0.6114	0.0624	0.3263	0.0001	0.9659	0.0340
	0.4592	0.1355	0.4052	0.0004	0.9416	0.0580
	0.3467	0.2051	0.4482	0.0011	0.9127	0.0862

(b) UNIQUAC model: salt-free basis (mole %)

Salt	Benzene 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
	0.7546	0.0525	0.1929	0.0000	0.9957	0.0043
A	0.5710	0.1272	0.3018	0.0000	0.9754	0.0245
	0.4329	0.2070	0.3610	0.0003	0.9449	0.0549
	0.2814	0.3248	0.3939	0.0017	0.8934	0.1048
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.8081	0.0158	0.1761	0.0000	0.9940	0.0060
B	0.6409	0.0585	0.3006	0.0000	0.9820	0.0180
	0.4862	0.0885	0.4253	0.0000	0.9659	0.0341
	0.3596	0.1430	0.4974	0.0000	0.9399	0.0601
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7406	0.0263	0.2331	0.0000	0.9770	0.0230
C	0.5690	0.0638	0.3673	0.0000	0.9543	0.0457
	0.3331	0.1590	0.5079	0.0002	0.8969	0.1030
	0.1912	0.2654	0.5434	0.0012	0.8130	0.1858
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7790	0.0385	0.1825	0.0000	0.9865	0.0135
D	0.5900	0.0663	0.3436	0.0000	0.9698	0.0302
	0.4368	0.1242	0.4390	0.0001	0.9370	0.0629
	0.2635	0.2287	0.5078	0.0006	0.8650	0.1344
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7804	0.0254	0.1942	0.0000	0.9880	0.0120
E	0.6094	0.0665	0.3241	0.0000	0.9718	0.0282
	0.4510	0.1257	0.4234	0.0000	0.9462	0.0538
	0.3362	0.1877	0.4761	0.0001	0.9144	0.0855

(c) modified UNIQUAC model: salt-free basis (mole %)

Salt	Benzene 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
	0.7537	0.0590	0.1873	0.0000	0.9888	0.0112
A	0.5779	0.1247	0.2974	0.0000	0.9696	0.0303
	0.4325	0.2017	0.3658	0.0002	0.9429	0.0569
	0.2742	0.3222	0.4037	0.0014	0.8962	0.1024
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.8072	0.0214	0.1714	0.0000	0.9921	0.0079
B	0.6330	0.0521	0.3149	0.0000	0.9802	0.0198
	0.4886	0.0914	0.4200	0.0000	0.9638	0.0362
	0.3599	0.1442	0.4958	0.0001	0.9397	0.0603
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7375	0.0318	0.2307	0.0000	0.9799	0.0201
C	0.5649	0.0670	0.3681	0.0000	0.9620	0.0398
	0.3216	0.1590	0.5194	0.0001	0.9069	0.0930
	0.1862	0.2586	0.5552	0.0011	0.8115	0.1875
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7813	0.0303	0.1884	0.0000	0.9852	0.0148
D	0.5984	0.0709	0.3307	0.0000	0.9653	0.0347
	0.4392	0.1262	0.4346	0.0001	0.9358	0.0642
	0.2611	0.2296	0.5094	0.0006	0.8666	0.1328
	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000
	0.7794	0.0368	0.1837	0.0000	0.9864	0.0136
E	0.6114	0.0809	0.3078	0.0000	0.9690	0.0310
	0.4576	0.1402	0.4022	0.0001	0.9436	0.0563
	0.3442	0.2030	0.4528	0.0002	0.9148	0.0849

A: no salt, B: 5% KF, C: 5% NaCl, D: 5% NaBr, E: 5% NaI

DISCUSSION

All binodal curves that added 5% KF, 5% NaCl, 5% NaBr and 5% NaI to benzene-water-n-propanol system were illustrated on Fig. 3, and the distribution curves of n-propanol between benzene and water layer were illustrated on Fig. 4. We omitted the points of experimental data on the diagram of binodal curves illustrated on Fig. 3 to describe effectively the effect of salt addition to benzene-water-n-propanol.

Addition of the four halogen salts to above ternary

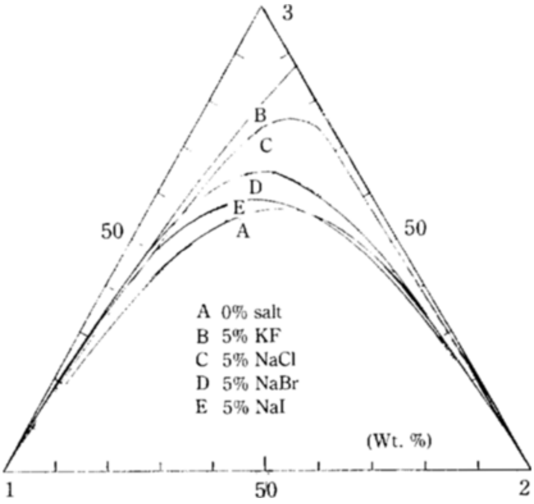

Fig. 3. Salt effect on binodal curve of benzene(1)-water(2)-n-propanol(3) system at 25°C.

system increased the region of heterogeneity in comparison with no-salt condition in the order of KF> Nacl>NaBr>NaI as shown on Fig. 3, and enhanced distribution of n-propanol (solute) in benzene layer as shown on Fig. 4.

On the other hand, it was assumed that quaternary L-L-E with salt were converted to ternary L-L-E without salt if salt were excluded as much as salt concentration.

The experimental tie line data of salt-free basis were correlated with the NRTL and modified UNIQUAC (or UNIQUAC) models under the above assumption. Experimental tie line data were compared with the compositions of tie lines calculated by above each model, and the comparable diagram for benzene-water-n-propanol system without salt was shown representatively on Fig. 5 and the others were similiar to that diagram.

As the result, experimental data were good identical within error range in comparison with calculated values as shown on Fig. 5.

The salt effects on L-L-E could be described by the interaction energy parameters between two components reported on Table 6. Those parameters (g_{13}, U_{13}) of each model between 1-3 molecule (benzene-n-propanol) for (B)-(E) systems with salts were increased more than that for (A) system without salt. The good extraction of solute (n-propanol) from water layer to solvent (benzene) layer was carried out from the above results in comparison with condition of no-salt.

Unfortunately the order of salting-out of each halogen salt could not be determined with the only parameters estimated by each model, but such problem could be solved with the diagram of binodal curves on Fig. 3 or that of distribution curves on Fig. 4 as mentioned previously.

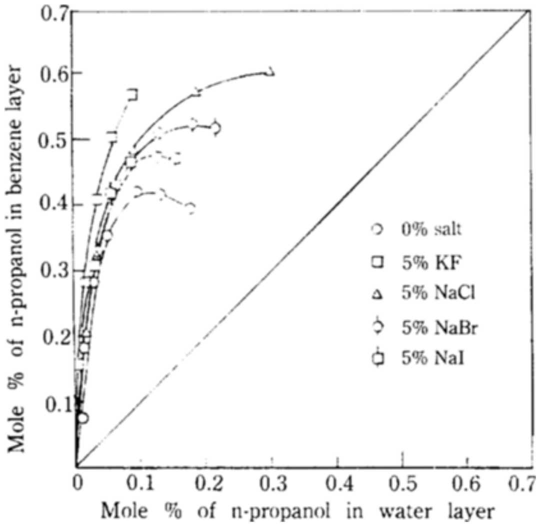

Fig. 4. Distribution of n-propanol between benzene and water layer at 25°C(salt-free basis).

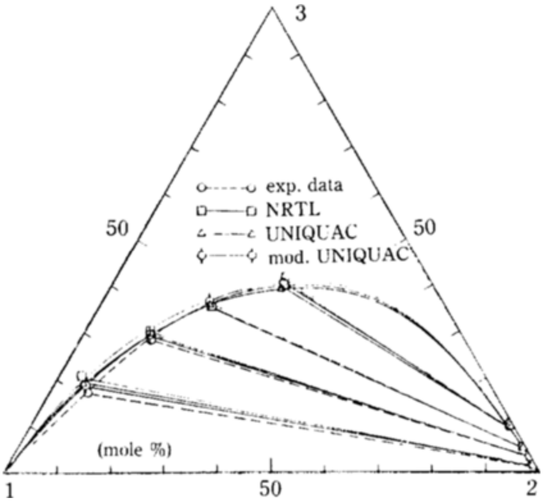

Fig. 5. Comparison of experimental and calculated tie lines for liquid-liquid equilibria of benzene (1)-water(2)-n-propanol(3) system at 25°C.

CONCLUSIONS

The experimental tie line data for benzene-water (or 5% halogen salt solutions)-n-propanol system were tested satisfactorily by being correlated with the Othmer-Tobias equation and the Eisen-Joffe equation.

The binodal curves and the distribution curves for benzene-halogen salt solutions-n-propanol systems were represented schematically, as a result, halogen salts increased the range of heterogeneity in the order of KF>NaCl>NaBr>NaI in comparison with benzene-water-n-propanol system without salt.

On the other hand, salting-out phenomena of halogen salts could be described by the interaction energy parameters estimated by correlating above tie line data with each liquid model, and the tie lines calculated by each model were good identical within the range of 0.1863-0.2735 RMSD for the NRTL, 0.1751-0.4647 RMSD for the UNIQUAC, and 0.1456-0.4110 RMSD for the modified UNIQUAC in comparison with the experimental tie line data respectively.

NOMENCLATURE

A-B : Eisen-Joffe constant
a-d : Eisen-Joffe constant
F : objective function
G^E : excess Gibbs energy (cal/g-mole)

ΔG^{id} : ideal Gibbs energy (cal/g-mole)
ΔG^{M} : mixing Gibbs energy (cal/g-mole)
G_{ji} : NRTL binary interaction parameter
g_{ji} : NRTL binary interaction parameter (cal/g-mole)
K : distribution coefficient
min : minimum
m : constant defined by Othmer-Tobias eq. (1)
n : constant defined by Othmer-Tobias eq. (1)
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 (or modified UNIQUAC) 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
X_S : salt concentration
Z : lattice coordination number (set equal to 10)

Greek Letters

α_{ji} : nonrandomness parameter in NRTL eq.
θ_i : area fraction defined by eq. (10)
θ_i' : modified area fraction defined by eq. (11)
ϕ_i : volume fraction defined by eq. (9)
τ_{ji}' : NRTL binary interaction parameter
τ_{ji} : UNIQUAC (or modified UNIQUAC) binary interaction parameter

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