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Correlation of binary coexistence curves of liquid–liquid equilibria over a wide temperature range using a new local composition model

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Abstract

A new local composition model with two energy parameters is used to correlate mutual solubility data over a wide temperature range for many mixtures. The energy parameters can be expressed by a quadratic function of temperature. Three types of coexistence curves are studied: **I**, systems with an upper critical solution temperature (UCST); **II**, systems with a UCST and a lower critical solution temperature (LCST); **III**, systems with a LCST. Prediction of the activity coefficients and excess molar enthalpies in the miscible region is discussed.

LIST OF SYMBOLS

a_{21}, a_{12}	binary energy parameters
A_{21}, B_{21}, C_{21}	coefficients of eqn. (9)
A_{12}, B_{12}, C_{12}	coefficients of eqn. (10)
g^E	excess molar Gibbs free energy
g^E_{comb}	combinatorial term of g^E function
n	index
r_i	molecular size parameter of pure component i
R	universal gas constant
T	absolute temperature
x_i	liquid-phase mole fraction of component i

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Greek letters

α, β	liquid phases in equilibrium
γ_i	activity coefficient of component i
τ_{21}, τ_{12}	binary parameters as defined by eqns. (7) and (8)
ϕ_i	segment fraction of component i
ϕ_i'	modified segment fraction of component i as defined by eqns. (3) and (4)
ρ_{12}	r_2/r_1

INTRODUCTION

Theoretical discussions of lower critical solution phenomena have been presented by several authors [1–7]. Most of these theories are quite complicated with only qualitative results and are of no practical use, even though some of them give a good agreement with experimental findings. In this paper we present a more practical approach to obtain a good description of three types of phase separation for many binary systems: **I**, systems with an upper critical solution temperature (UCST); **II**, systems with a UCST and a lower critical solution temperature (LCST); **III**, systems with a LCST. As part of a study on the performance of a new two-parameter local composition on phase equilibrium data reduction, we present some calculated results on mutual solubility data over a wide temperature range.

SOLUTION MODEL

Nagata [8] proposed the following model for the excess molar Gibbs free energy

$$\frac{g^{\mathrm{E}}}{RT} = x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} - x_1 \ln(\phi_1 + \phi_2\tau_{21}) - x_2 \ln(\phi_2 + \phi_1\tau_{12}) \qquad (1)$$

where ϕ is the segment fraction and τ is the binary adjustable parameter. Equation (1) has been successfully used to describe the thermodynamic properties of alcohol solutions with allowance for the association of alcohol molecules and the solvation of alcohol with active non-associating components. Equation (1) is equivalent to the Wilson equation, which is very useful only for completely miscible mixtures. In order to make the Wilson equation applicable to partially miscible mixtures, additional parameters can usually be included in the Wilson equation [9]. To apply eqn. (1) to partially miscible mixtures, we modify the combinatorial term of eqn. (1) as suggested by several investigations [10–14]

$$\frac{g^{\mathrm{E}}_{\mathrm{comb}}}{RT} = x_1 \ln\frac{\phi_1'}{x_1} + x_2 \ln\frac{\phi_2'}{x_2} \qquad (2)$$

where the modified segment fractions ϕ_1' and ϕ_2' are given by

$$\phi_1' = \frac{x_1 r_1^n}{x_1 r_1^n + x_2 r_2^n} \tag{3}$$

$$\phi_2' = \frac{x_2 r_2^n}{x_1 r_1^n + x_2 r_2^n} \tag{4}$$

The exponent n is taken as 2/3 or 3/4 and the pure component molecular size parameters r_i were obtained from Sørensen and Arlt [15].

The activity coefficients of two components are expressed as

$$\ln \gamma_1 = \ln \frac{\phi_1'}{x_1} + 1 - \frac{\phi_1'}{x_1} - \ln(\phi_1 + \phi_2\tau_{21}) - \left(1 - \frac{\phi_1}{x_1}\right) + \phi_2\left(\frac{\tau_{21}}{\phi_1 + \phi_2\tau_{21}} - \frac{\tau_{12}/\rho_{12}}{\phi_2 + \phi_1\tau_{12}}\right) \tag{5}$$

$$\ln \gamma_2 = \ln \frac{\phi_2'}{x_2} + 1 - \frac{\phi_2'}{x_2} - \ln(\phi_2 + \phi_1\tau_{12}) - \left(1 - \frac{\phi_2}{x_2}\right) + \phi_1\left(\frac{\tau_{12}}{\phi_2 + \phi_1\tau_{12}} - \frac{\rho_{12}\tau_{21}}{\phi_1 + \phi_2\tau_{21}}\right) \tag{6}$$

where $\rho_{12} = r_2/r_1$.

The binary parameters τ_{ij} are related to the energy parameters a_{ij}

$$\tau_{21} = \exp(-a_{21}/T) \tag{7}$$

$$\tau_{12} = \exp(-a_{12}/T) \tag{8}$$

We assume that the energy parameters can be expressed by a quadratic function of temperature

$$a_{21} = A_{21} + B_{21}T + C_{21}T^2 \tag{9}$$

$$a_{12} = A_{12} + B_{12}T + C_{12}T^2 \tag{10}$$

CALCULATED RESULTS

The mutual solubility points are calculated by solving the thermodynamic relations of isoactivity for components in equilibrated liquid phases

$$(x_1\gamma_1)^\alpha = (x_1\gamma_1)^\beta \tag{11}$$

$$(x_2\gamma_2)^\alpha = (x_2\gamma_2)^\beta \tag{12}$$

where the superscripts α and β indicate two liquid phases. All the

TABLE 1

Values of pure-component molecular size parameters

Component	r	Component	r
Aniline	3.7165	Guaiacol	4.5306
Benzene	3.1878	*n*-Hexadecane	11.2438
1-Butanol	3.4543	*n*-Hexane	4.4998
2-Butanone	3.2479	2-Isobutoxyethanol	5.0462
2-Butoxyethanol	5.0470	Methanol	1.4311
Cyclohexane	4.0464	*m*-Methylaniline	4.4515
Diethylene glycol	4.0013	3-Methylpyridine	3.7343
2,6-Dimethylpyridine	4.4693	Nicotine	6.4898
Dipropylamine	5.0324	Phenol	3.5517
Ethanol	2.1055	Propionic aldehyde	2.5735
Ethylbutylamine	5.0324	1-Propoxy-2-propanol	5.0462
1-Ethyl-3-isopropyl-glycerol ether	6.6381	2-Propoxy-1-propanol	5.0462
Furfural	3.1680	Tetrahydrofuran	2.9415
Glycerol	3.5857	Water	0.9200

experimental values studied in this work were taken from Ochi et al. [16], Skrzecz [17], and the compilations of Sørensen and Arlt [15] and of Macedo and Rasmussen [18]. The experimental data of Ochi et al. were smoothed by Ochi. Table 1 shows the values of the pure-component molecular size parameters and Table 2 gives the calculated results for 23 binary systems. Both values of the index, $n = 2/3$ and $n = 3/4$, give nearly the same results except for the glycerol + *m*-methylaniline and tetrahydrofuran + water systems which show closed-loop coexistence curves (type **II**). For these two systems, an index value $n = 3/4$ improves significantly the deviations between the experimental values and calculated results. Figures 1–3 compare the calculated results with the experimental values for selected systems. As shown in Fig. 2 for the 2,6-dimethylpyridine + water and

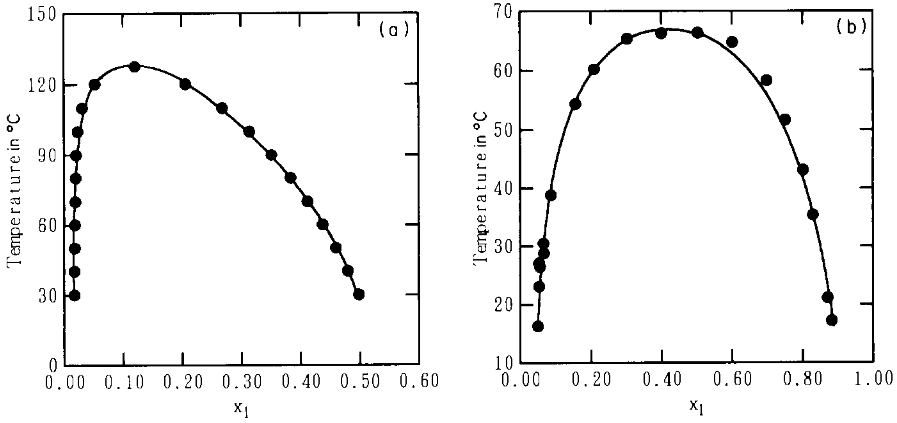

Fig. 1. Calculated liquid–liquid equilibria for two systems with an upper critical solution temperature: ●, experimental; ——, calculated using the exponent $n = 3/4$. (a) 1-Butanol + water, Ochi et al. (1990) [16]. (b) Furfural + cyclohexane, Pennington (1953) [15].

TABLE 2

Calculated results for binary coexistence curves of liquid–liquid equilibria

No.	Type [a]	System (1 + 2)	Temperature range °C	Index [b]	Average abs. dev. mol.%	Parameters			References
						A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
1	I	Aniline + *n*-hexane	40.00–68.00	A	0.10	3013.270	−5.3193	0.0009	16
						−23517.039	156.0484	−0.2452	
				B	0.10	2874.314	−4.3025	−0.0023	
						−23630.476	156.9102	−0.2463	
2	I	1-Butanol + water	30.00–120.00	A	0.05	−746.010	7.7042	−0.0123	16
						−4734.346	30.2779	−0.0413	
				B	0.06	−850.303	8.5792	−0.0135	
						−4871.085	31.4610	−0.0432	
3	I	2-Butanone + water	0.00–140.00	A	0.50	307.403	2.6424	−0.0049	16
						−5303.982	31.3702	−0.0422	
				B	0.45	193.148	3.5123	−0.0060	
						−5460.938	32.6178	−0.0440	
4	I	Diethylene glycol + benzene	30.00–80.00	A	1.02	−3580.927	25.5253	−0.0360	16
						−9075.718	68.0095	−0.1086	
				B	0.42	−3611.960	25.8476	−0.0363	
						−9122.338	68.7153	−0.1100	
5	I	Ethanol + *n*-hexadecane	25.00–52.10	A	1.71	7038.561	−42.0434	0.0607	19
						−28334.100	190.8129	−0.3121	
				B	1.59	7500.396	−44.7295	0.0656	
						−28043.191	190.1607	−0.3129	
6	I	Furfural + cyclohexane	16.30–66.30	A	0.13	−1376.336	18.4322	−0.0350	15
						−7933.519	63.1901	−0.1062	
				B	0.13	−1435.540	18.9680	−0.0357	
						−7986.555	63.6902	−0.1068	
7	I	Methanol + cyclohexane	29.19–45.14	A	1.85	−3654.467	28.1998	−0.0517	15
						−26403.899	184.0484	−0.3079	
				B	1.85	−4260.206	32.5080	−0.0587	
						−26945.815	187.9478	−0.3144	

TABLE 2 Continued

No.	Type [a]	System (1 + 2)	Temperature range °C	Index [b]	Average abs. dev. mol.%	Parameters			References
						A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
8	**I**	Methanol + *n*-hexane	−18.15–32.85	A	0.45	21.746	3.6213	−0.0116	17
						−990.151	19.4626	−0.0433	
				B	0.48	−14.627	4.2667	−0.0128	
						−1030.932	20.1297	−0.0446	
9	**I**	Phenol + *n*-hexane	30.00–52.00	A	0.02	−3614.430	32.9790	−0.0590	16
						17031.168	−91.6590	0.1319	
				B	0.02	−3658.009	33.4368	−0.0596	
						16975.821	−91.1229	0.1312	
10	**II**	2-Butoxy-ethanol + water	50.00–130.00	A	0.03	−3994.957	22.7995	−0.0304	16
						−1451.655	12.0208	−0.0156	
				B	0.03	−4470.479	25.5670	−0.0340	
						−2259.033	16.5260	−0.0217	
11	**II**	2,6-Dimethylpyridine + water	45.30–164.90	A	1.49	−4516.455	24.9948	−0.0319	15
						2305.654	−9.7204	0.0143	
				B	1.43	−4942.922	27.4051	−0.0348	
						1470.828	−5.1914	0.0083	
12	**II**	Glycerol + guaiacol	39.50–83.50	A	1.86	−28537.074	174.4488	−0.2566	15
						−3658.704	25.1270	−0.0325	
				B	1.86	−28599.030	174.9365	−0.2571	
						−3763.692	25.8909	−0.0335	
13	**II**	Glycerol + *m*-methylaniline	6.70–120.50	A	110.58	−10782.975	69.4397	−0.0998	15
						−4946.528	33.3150	−0.0437	
				B	13.51	−10861.059	69.7927	−0.0993	
						−5048.500	34.3095	−0.0455	
14	**II**	2-Isobutoxy-ethanol + water	24.60–150.20	A	1.19	−4837.173	28.2932	−0.0383	15
						4900.773	−26.0347	0.0385	
				B	1.27	−5374.052	31.5004	−0.0426	
						3885.234	−20.2445	0.0306	
	III		26.21–38.10	A	0.02	−960.865	3.2466	0.0021	15
						−44001.154	291.3727	−0.4761	

15	**II**	3-Methylpyridine + water	49.40–152.50	A	4.35	−4809.518	26.6142	−0.0342	15
						4833.336	−22.4348	0.0314	
				B	4.20	−5311.647	29.1517	−0.0370	
						4072.856	−17.1223	0.0228	
16	**II**	Nicotine + water	61.50–233.00	A	0.78	−5101.490	25.7296	−0.0296	15
						−1141.343	7.9262	−0.0093	
				B	0.85	−5564.991	28.1244	−0.0322	
						−2581.797	15.0454	−0.0178	
17	**II**	1-Propoxy-2-propanol + water	34.50–171.70	A	2.23	−5079.552	29.0780	−0.0382	15
						3850.699	−21.5659	0.0330	
				B	2.51	−5468.383	31.2219	−0.0407	
						2815.458	−15.1198	0.0237	
18	**II**	2-Propoxy-1-propanol + water	42.80–162.00	A	0.51	−5746.131	32.2442	−0.0421	15
						5069.284	−26.5626	0.0378	
				B	0.44	−6265.755	35.3057	−0.0462	
						3820.268	−19.9219	0.0294	
19	**II**	Tetrahydrofuran + water	71.80–137.10	A	56.39	11412.625	−56.4410	0.0728	15
						−15466.810	81.2213	−0.1030	
				B	8.99	−1740.220	12.7051	−0.0170	
						−12283.193	64.4865	−0.0806	
20	**III**	Ethylbutylamine + water	10.00–40.00	A	1.13	2819.578	−24.4033	0.0529	15
						−35.650	9.5729	−0.0228	
				B	1.13	2493.755	−22.7687	0.0516	
						514.551	5.6900	−0.0159	
21	**III**	1-Ethyl-3-isopropyl-glycerol ether + water	34.10–78.40	A	0.94	−17372.032	104.7535	−0.1543	15
						27574.976	−169.6086	0.2612	
				B	0.88	−17802.020	107.1155	−0.1569	
						23216.972	−143.1999	0.2217	
22	**III**	Dipropylamine + water	−4.80–74.80	A	0.35	−1004.398	1.9776	0.0088	15
						8704.477	−57.8219	0.1030	
				B	0.32	−1393.614	4.3551	0.0058	
						8113.831	−54.8817	01.004	
23	**III**	Propionicaldehyde + water	15.00–40.00	A	0.21	11195.116	−71.7580	0.1239	18
						−9998.857	61.5274	−0.0916	
				B	0.23	10631.100	−68.1934	0.1187	
						−10104.271	62.3861	−0.0927	

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[a] **I**, system with an upper critical solution temperature; **II**, system with a closed curve of partial miscibility; **III**, mutual solubility increases with decreasing temperature.

1-propoxy-2-propanol + water systems, the present method is superior to the model of Yu and Nishiumi, who incorporated an equilibrium constant due to the hydrogen bonds between solvent and solute [7].

To check the physical significance of the parameters obtained, the activity coefficients and excess molar enthalpies in the miscible regions for a few selected systems were predicted using the coefficients given in Table 2. Figures 4–6 present a comparison of the experimental values and calculated results. For the methanol + cyclohexane or *n*-hexane and 1-butanol + water systems, the predicted activity coefficients agree well with the experimental values. However, for the ethanol + *n*-hexadecane system, the estimated results are considerably lower than the experimental values. Prediction of the excess molar enthalpies of the two systems gives very good results for the 1-butanol + water system and shows slightly higher values, but

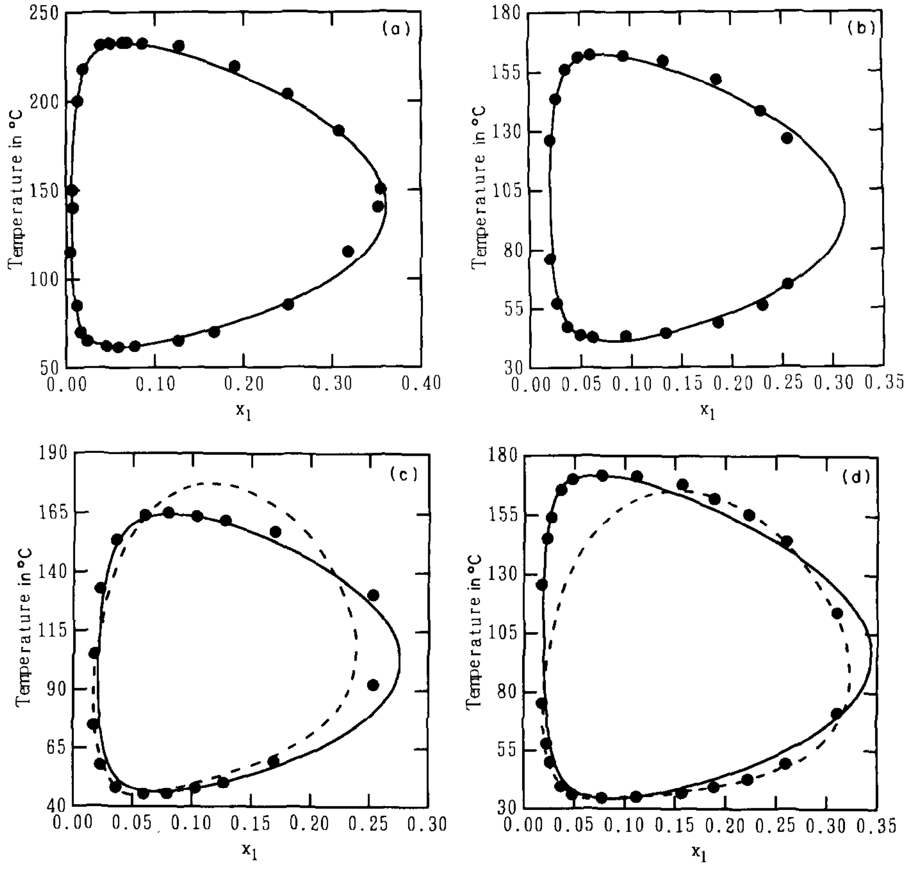

Fig. 2. Calculated liquid–liquid equilibria for four systems with both upper and lower critical solution temperatures: ●, experimental; ——, calculated by the present model with the exponent $n = 3/4$; – – –, calculated by the model of Yu and Nishiumi [7]. (a) Nicotine + water, Campbell (1958) [15]. (b) 2-Propoxy-1-propanol + water, Cox (1927) [15]. (c) 2,6-Dimethylpyridine + water, Flaschner (1909) [15]. (d) 1-Propoxy-2-propanol + water, Cox (1927) [15].

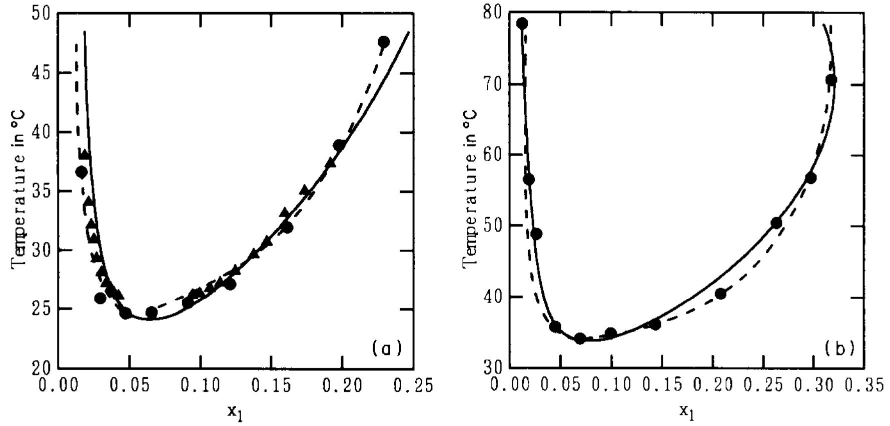

Fig. 3. Calculated liquid–liquid equilibria for two systems with a lower critical solution temperature: ●, ▲, experimental; ——, calculated by the present model with the exponent $n = 3/4$; – – –, calculated by the model of Yu and Nishiumi [7]. (a) 2-Isobutoxyethanol + water: ●, Cox (1926) [15]; ▲, Rudd (1960) [15]. (b) 1-Ethyl-3-isopropylglycerol ether + water, Davison (1966) [15].

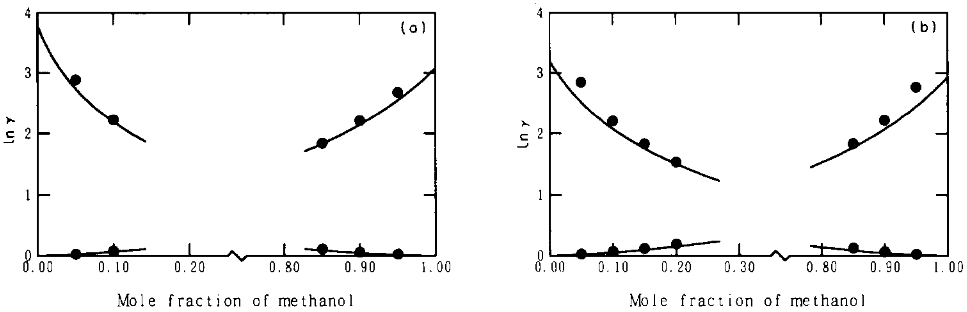

Fig. 4. Activity coefficients for (a) methanol + cyclohexane and (b) methanol + n-hexane: ●, experimental; data of Hwang and Robinson [20] at 25°C; ——, calculated using the exponent $n = 3/4$.

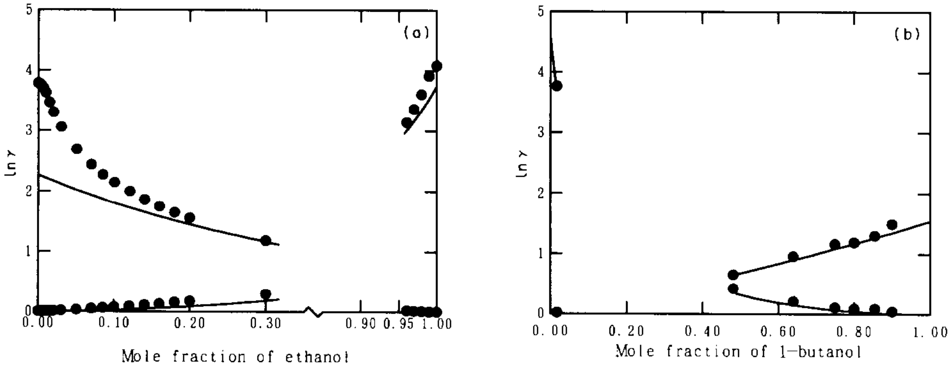

Fig. 5. Activity coefficients for (a) ethanol + n-hexadecane and (b) 1-butanol + water: ●, experimental. (a) Data of French et al. [19] at 25°C. (b) Data of Lyzlova et al. [21] at 35°C. ——, Calculated using the exponent $n = 3/4$.

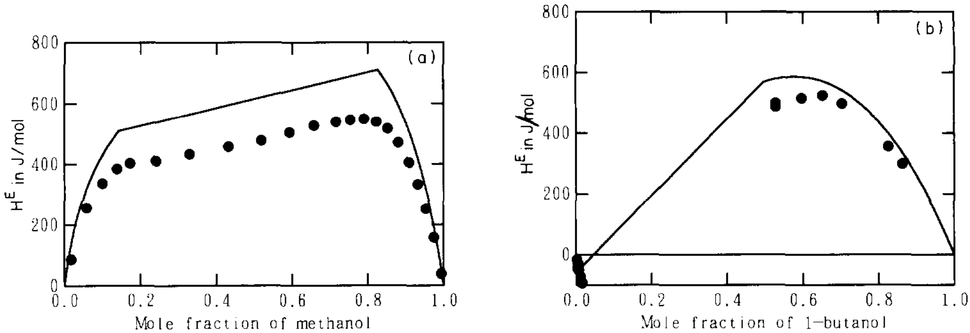

Fig. 6. Excess molar enthalpies for (a) methanol + cyclohexane and (b) 1-butanol + water: ●, experimental. (a) Data of Dai and Chao [22] at 25°C. (b) Data of Goodwin and Newsham [23] at 30°C. ——, Calculated using the exponent $n = 3/4$.

reproduces well the shape of the excess enthalpy curve for the methanol + cyclohexane system.

CONCLUSION

The capability of a new local composition model in reproducing the binary liquid–liquid equilibrium data of three different types over a wide temperature range has been studied. The model, called the extended-Wilson model, includes the modified Flory–Huggins term and the physical interaction term with two energy parameters, which are assumed to be a quadratic function of temperature. The model correlates well the experimental data points of the 23 systems studied.

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