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Representation of mutual solubility data over a wide temperature range using a modified Wilson equation

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Abstract

A modified Wilson equation having four constants is used to describe the temperature dependence of mutual solubility data. The energy parameters are expressed by a quadratic function of temperature. The twenty-three systems studied are classified into three groups: (1) ten systems have an upper consolute temperature; (2) ten systems show a closed envelope of partial miscibility; (3) three systems have a lower consolute temperature. Calculated values are in close agreement with experimental results. For four selected systems in homogeneous regions, the method predicted the activity coefficients well and estimated excess molar enthalpies rather qualitatively.

INTRODUCTION

The original Wilson equation has been modified by several investigators to describe phase equilibria for partially miscible mixtures, as summarized by Novák et al. [1]. Novák et al. [2] used their modified Wilson equation for the description of temperature dependence of mutual solubility using the linear temperature dependence of the three parameters involved in the equation. One of the present authors applied Hiranuma's modification of the Wilson equation [3] to the prediction and correlation of ternary liquid-liquid equilibria [4,5]. This work aims to show the performance of Hiranuma's modification in the correlation of mutual solubilities over a wide temperature range using the quadratic temperature dependence of the energy parameters, which had been employed in the simultaneous correlation of the excess Gibbs free energy and excess molar enthalpy data by means of the original Wilson equation [6,7].

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SOLUTION MODEL

The modified Wilson equation [3] gives the activity coefficients of two components:

$$\ln \gamma_1 = -\ln(x_1 + \alpha_{12}\Lambda_{12}x_2) + x_2\left(\frac{\alpha_{12}\Lambda_{12}}{x_1 + \alpha_{12}\Lambda_{12}x_2} - \frac{\alpha_{21}\Lambda_{21}}{\alpha_{21}\Lambda_{21}x_1 + x_2}\right) + \ln(x_1 + \alpha_{12}x_2) - x_2\left(\frac{\alpha_{12}}{x_1 + \alpha_{12}x_2} - \frac{\alpha_{21}}{\alpha_{21}x_1 + x_2}\right) \quad (1)$$

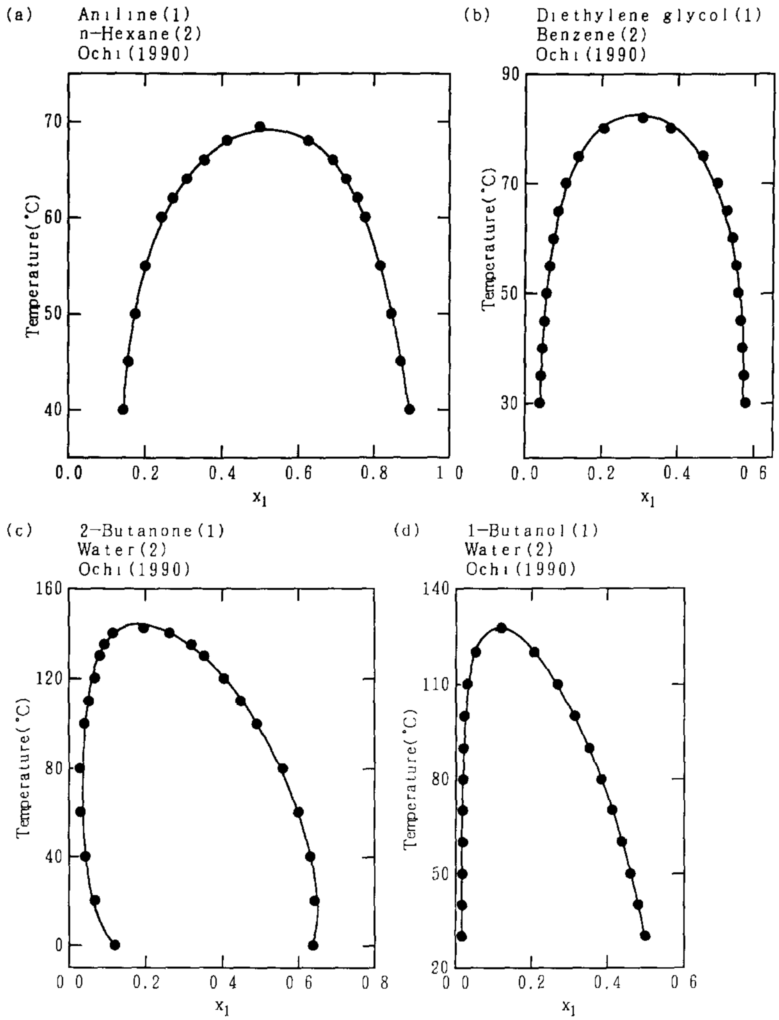

Fig. 1. Calculated liquid–liquid equilibrium curves for systems having an upper consolute temperature: ●, experimental (data smoothed by Ochi); ———, calculated. (a) Aniline–*n*-hexane; (b) diethylene glycol–benzene; (c) 2-butanone–water; (d) 1-butanol–water.

$$\ln \gamma_2 = -\ln(x_2 + \alpha_{21}\Lambda_{21}x_1) + x_1\left(\frac{\alpha_{21}\Lambda_{21}}{x_2 + \alpha_{21}\Lambda_{21}x_1} - \frac{\alpha_{12}\Lambda_{12}}{\alpha_{12}\Lambda_{12}x_2 + x_1}\right)$$

$$+ \ln(x_2 + \alpha_{21}x_1) - x_1\left(\frac{\alpha_{21}}{x_2 + \alpha_{21}x_1} - \frac{\alpha_{12}}{\alpha_{12}x_2 + x_1}\right) \quad (2)$$

$$\Lambda_{12} = \frac{V_2^{\mathrm{L}}}{V_1^{\mathrm{L}}} \exp\left(-\frac{a_{12}}{T}\right) \qquad \Lambda_{21} = \frac{V_1^{\mathrm{L}}}{V_2^{\mathrm{L}}} \exp\left(-\frac{a_{21}}{T}\right) \quad (3)$$

where x_i is the liquid phase mole fraction of component i, V_i^{L} is the liquid molar volume of pure component i and α_{ij} and a_{ij} are binary parameters.

The energy parameters a_{12} and a_{21} are expressed by a quadratic function of temperature:

$$a_{12} = A_{12} + B_{12}T + C_{12}T^2 \quad (4)$$

$$a_{21} = A_{21} + B_{21}T + C_{21}T^2 \quad (5)$$

The modified Wilson equation was fitted to mutual solubility data using the following thermodynamic relations for two components:

$$(x_1\gamma_1)^{\mathrm{I}} = (x_1\gamma_1)^{\mathrm{II}} \quad (6)$$

$$(x_2\gamma_2)^{\mathrm{I}} = (x_2\gamma_2)^{\mathrm{II}} \quad (7)$$

where the superscripts I and II denote conjugated liquid phases.

TABLE 1

Values of r for pure components

Component	r	Component	r
Aniline	3.7165	n-Hexadecane	11.2438
Benzene	3.1878	n-Hexane	4.4998
1-Butanol	3.4543	n-Heptane	5.1742
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	2.1005	1-Propoxy-2-propanol	5.0462
1-Ethyl-3-isopropyl		2-Propoxy-1-propanol	5.0462
glycerol ether	6.6381	Tetrahydrofuran	2.9415
Furfural	3.1680	Triethylamine	5.0118
Glycerol	3.5857	Water	0.9200
Guaiacol	4.5306		

TABLE 2

Calculated results for mutual solubility data

No.	Type [a]	System (1–2)	Temperature range (°C)	Average abs. dev. (mol.%)	Parameter					Ref.
					α_{21}	α_{12}	A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
1	1	Aniline–	40.00– 68.00	0.08	1.1	1.1	−20408.817	133.9109	−0.2116	10
		n-hexane					7459.221	−35.3973	0.0448	
2	1	1-Butanol–	30.00–120.00	0.04	1.5	1.0	−4644.085	30.1655	−0.0383	10
		water					−331.509	4.9935	−0.0060	
				0.03	3.0	1.0	−4362.232	26.5905	−0.0331	
							−92.513	3.0895	−0.0034	
3	1	2-Butanone–	0.00–140.00	0.20	1.5	1.1	−6005.353	35.0501	0.0443	10
		water					−145.742	4.3049	−0.0054	
				0.84	3.0	1.1	−3772.717	19.6286	−0.0221	
							523.870	0.5385	−0.0007	
4	1	Diethylene	30.00– 80.00	0.44	1.1	1.0	−8366.269	62.6654	−0.1017	10
		glycol –					−2930.061	20.5108	−0.0297	
		benzene								
5	1	Ethanol–	25.00– 52.10	4.32	1.1	1.0	−10796.681	79.2761	−0.1328	12
		n-hexadecane					19863.971	−123.2174	0.1986	
7	1	Furfural–	16.30– 66.30	0.14	1.1	1.1	−6750.593	53.5357	−0.0920	13
		cyclohexane					83.534	7.0811	−0.0179	
8	1	Methanol–	29.19– 45.14	2.57	1.1	1.0	−27527.795	193.1788	−0.3255	14
		cyclohexane					−4034.638	33.1875	−0.0606	
9	1	Methanol–	18.00– 50.00	0.02	1.1	1.0	−1428.588	23.7821	−0.0504	15
		n-heptane					14.777	5.5055	−0.0124	
10	1	Phenol–	30.00– 52.00	0.03	1.1	1.1	18019.337	−100.6701	0.1461	10
		n-hexane					−3012.106	26.3897	−0.0483	
11	2	2-Butoxy	50.00–130.00	0.02	1.5	1.0	−2528.633	20.0504	−0.0239	10
		ethanol–					−1434.450	10.0614	−0.0110	
		water		0.02	3.0	1.0	−1148.055	11.6811	−0.0134	
							−947.417	7.0808	−0.0072	

12	2	2,6-Dimethyl pyridine– water	45.30–164.90	2.87	1.5	1.1	2185.511	−6.6248	0.0121	16
							−1448.107	9.6592	−0.0102	
				2.45	3.0	1.1	3624.928	−14.6885	0.0212	
							−1026.800	7.1843	−0.0072	
13	2	Glycerol– guaiacol	39.50– 83.50	1.91	1.1	1.0	−2955.430	19.8312	−0.0262	17
							−28684.974	174.5408	−0.2580	
14	2	Glycerol– *m*-methyl aniline	6.70–120.50	10.68	1.1	1.0	−5120.061	33.4341	−0.0460	18
							−11604.286	73.2827	−0.1062	
15	2	2-Isobutoxy ethanol– water	24.60–150.20	4.61	1.5	1.0	−3522.185	23.3400	−0.0267	19
							−1111.789	8.5378	−0.0090	
				4.55	3.0	1.0	−2485.011	16.2430	−0.0173	
							−748.500	6.1741	−0.0061	
16	2	3-Methyl pyridine– water	49.40–152.50	5.67	1.5	1.1	5491.791	−24.4547	0.0361	16
							−1584.748	10.2503	−0.0113	
17	2	Nicotine– water	61.50–233.00	2.50	1.5	1.1	5528.116	−18.3911	0.0223	20
							−1627.384	10.2694	−0.0095	
				2.45	3.0	1.1	8830.744	−34.5675	0.0401	
							−1150.553	7.7147	−0.0067	
18	2	1-Propoxy- 2-propanol– water	34.50–171.70	2.44	1.5	1.0	2936.783	−12.8379	0.0214	21
							−1766.796	11.8187	−0.0129	
				2.36	3.0	1.0	4644.812	−23.8472	0.0371	
							−1278.933	8.8761	−0.0094	
19	2	2-Propoxy- 1-propanol– water	42.80–162.00	4.78	1.5	1.0	17478.707	−88.7201	0.1202	21
							−2089.642	13.5031	−0.0152	
				0.39	3.0	1.0	5768.201	−29.8117	0.0451	
							−1420.276	9.6380	−0.0105	
20	2	Tetrahydro furan– water	71.80–137.10	2.33	4.0	1.1	−3078.112	11.9029	−0.0083	22
							−1564.659	11.3267	−0.0148	

TABLE 2 (continued)

No.	Type [a]	System (1–2)	Temperature range (°C)	Average abs. dev. (mol.%)	Parameter					Ref.
					α_{21}	α_{12}	A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	
21	3	1-Ethyl- 3-isopropyl glycerol ether– water	34.10–78.40	0.60	1.5	1.1	20983.665 −3351.991	−126.2541 21.8445	0.1995 −0.0282	23
22	3	Dipropylamine– water	−4.80–74.80	0.58	1.5	1.1	7413.201 955.044	−46.6701 −6.7979	0.0866 0.0195	24
				0.66	3.0	1.1	7218.649 1143.540	−43.9686 −7.8285	0.0769 0.0199	
23	3	Triethylamine– water	18.72–69.20	87.31	1.5	1.1	51501.864 −111156.584	−326.1815 669.0591	0.5217 −0.9814	25
				72.55	3.0	1.1	89897.124 −110842.599	−564.3476 667.4978	0.8872 −0.9806	

[a] 1, system has an upper critical solution temperature; 2, system has a closed curve of partial miscibility; 3, mutual solubility increases with decreasing temperature.

SYSTEMS STUDIED

All mutual experimental data for the systems studied in this work were collected from Sørensen and Arlt [8], Macedo and Rasmussen [9] and Ochi et al. [10]. We used the smoothed data of ref. 10. Twenty-three systems have been classified into three groups: (1) ten systems with an upper consolute temperature; (2) ten systems having both upper and lower consolute temperatures; (3) three systems with a lower consolute temperature.

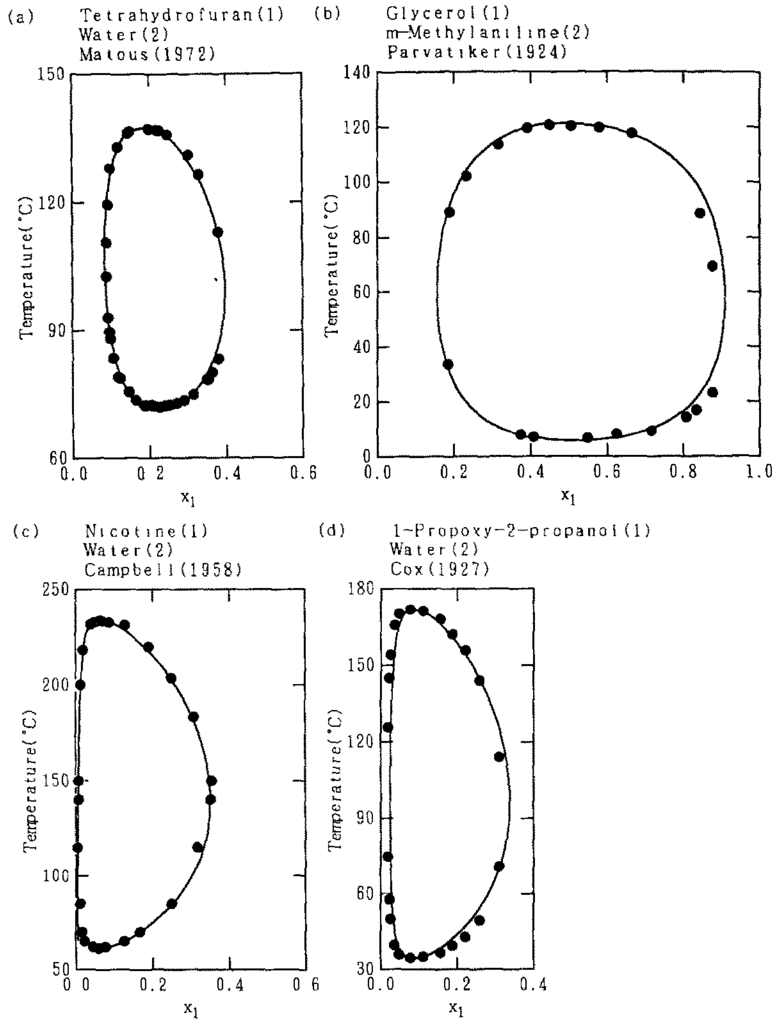

Fig. 2. Calculated liquid–liquid equilibrium curves for systems having both upper and lower consolute temperatures: ●, experimental; ——, calculated. (a) Tetrahydrofuran–water; (b) glycerol–*m*-methylaniline; (c) nicotine–water; (d) 1-propoxy-2-propanol–water.

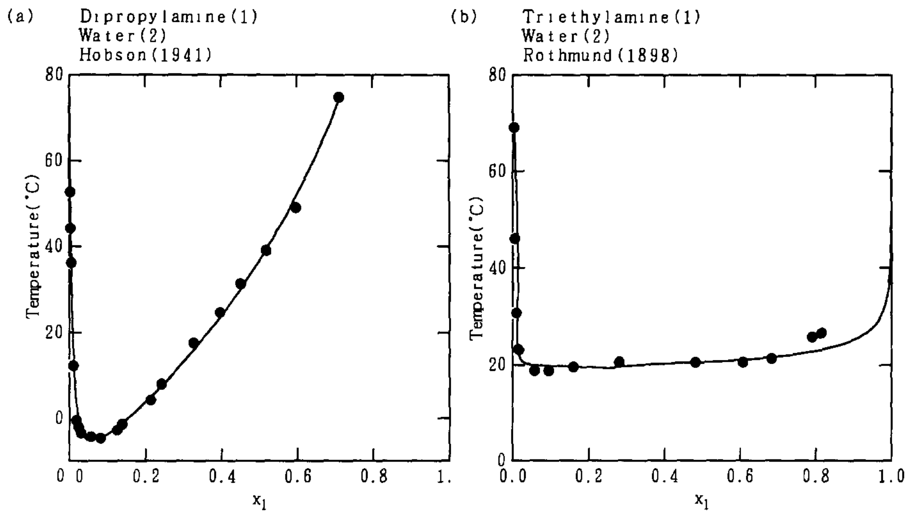

Fig. 3. Calculated liquid-liquid equilibrium curves for systems having a lower consolute temperature: ●, experimental; ———, calculated. (a) Dipropylamine-water; (b) triethylamine-water.

CALCULATED RESULTS

We used the molecular size parameter r_i of pure component i instead of V_i^L, because V_i^L data were not always available over a wide temperature range. Table 1 gives values of r_i taken from refs. 8 and 9. Values of α were assigned as recommended by Hiranuma [3,11]. Table 2 summarizes calculated results and some of them are shown in Figs. 1-3. In aqueous

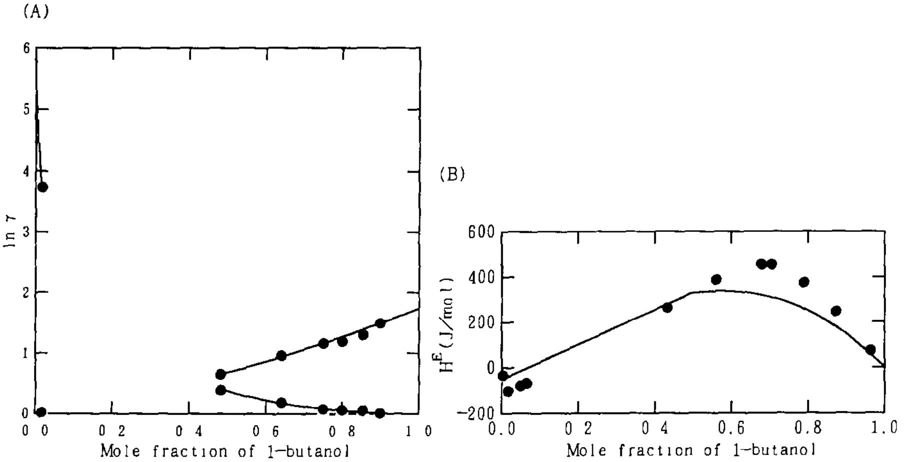

Fig. 4. Calculated activity coefficients and excess enthalpies for 1-butanol-water: ———, calculated. (A) ●, experimental activity coefficient data of Lyzlova et al. [26] at 35°C; (B) ●, experimental excess enthalpy data of Belousov and Ponner [27] at 30°C.

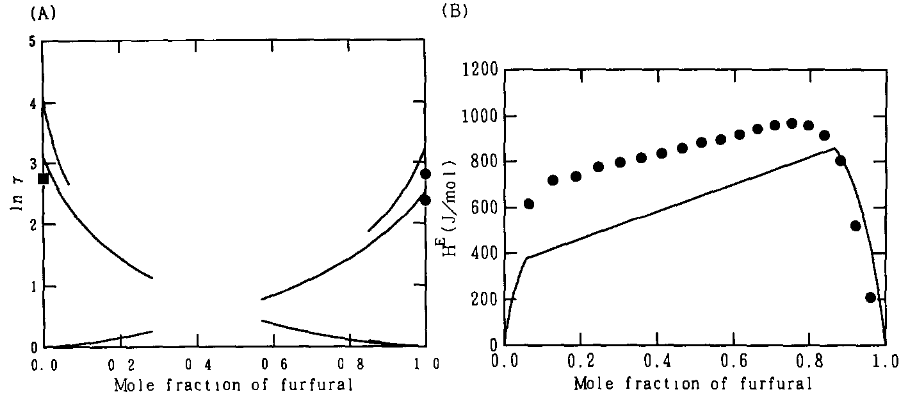

Fig. 5. Calculated activity coefficients and excess enthalpies for furfural–cyclohexane: ———, calculated. (A) ■, experimental activity coefficient, γ_1^∞ of Thomas et al. [28] at 64.4°C; ●, γ_2^∞ of Santacesaria et al. [29] at 30 and 64.4°C; (B) ●, experimental excess enthalpy data of Battler and Rowley [30] at 25°C.

solutions two values of α_w for water (1.5 and 3) gave the same results except for the 2-propoxy-1-propanol–water system with $\alpha_w = 3$ and the tetrahydrofuran–water system with $\alpha_w = 4$.

The method was applied to the prediction of activity coefficients and excess enthalpies in miscible regions by use of the parameters listed in Table 2. For the 1-butanol–water system (Fig. 4) the calculated activity coefficients agree excellently with the experimental results at 35°C and excess enthalpies are well predicted at 30°C. For the furfural–cyclohexane system (Fig. 5), agreement in limited activity coefficients is reasonably good

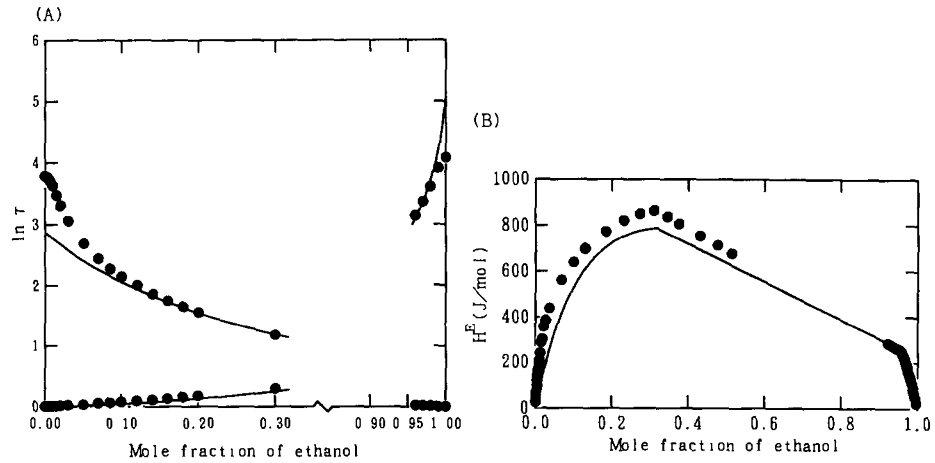

Fig. 6. Calculated activity coefficients and excess enthalpies for ethanol–*n*-hexadecane: ———, calculated. ●, Experimental data of French et al. [12] at 25°C for (A) activity coefficient and (B) excess enthalpy.

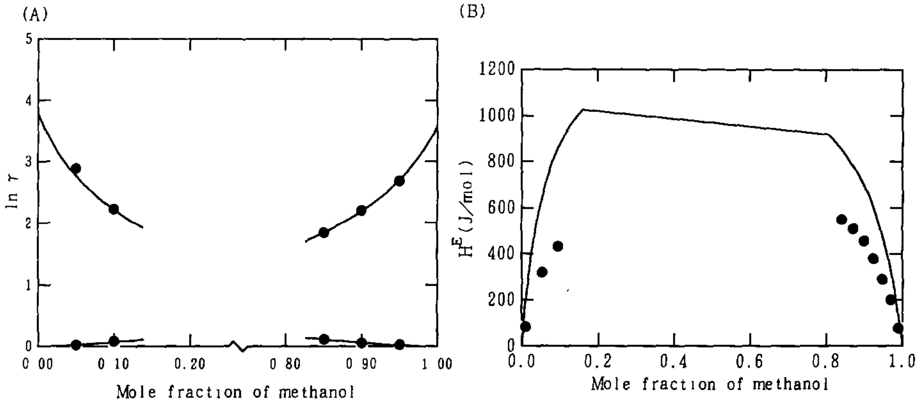

Fig. 7. Calculated activity coefficients and excess enthalpies for methanol–cyclohexane: ———, calculated. (A) ●, experimental activity coefficient data of Hwang and Robinson [31] at 25°C; (B) ●, experimental excess enthalpy data of Dai and Chao [32] at 30°C.

and excess enthalpies were estimated rather qualitatively. In the ethanol–*n*-hexadecane system (Fig. 6) the prediction of these properties can be considered very good. In the methanol–cyclohexane system (Fig. 7) the method predicts well the activity coefficients at 25°C, but the predicted excess enthalpies at 30°C are significantly higher than the experimental values.

We may conclude that the Hiranuma–Wilson equation reproduces well the mutual solubility data of the twenty-three systems studied by using the quadratic temperature dependence of the energy parameters, and predicts the activity coefficients in miscible regions with sufficient accuracy, but it provides a reasonable estimation of excess enthalpies.

LIST OF SYMBOLS

a_{ij}	binary interaction energy parameter
A_{ij}, B_{ij}, C_{ij}	coefficients related to a_{ij}
r_i	molecular size parameter of pure component *i*
T	absolute temperature
V_i^L	molar liquid volume of pure component *i*
x_i	liquid phase mole fraction of component *i*

Greek letters

α	binary parameter in eqns. (1) and (2)
γ_i	activity coefficient of component *i*
γ_i^∞	activity coefficient of component *i* at infinite dilution

Subscripts

i, *j*	components

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