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Representation of closed-loop mutual solubility data for some binary aqueous mixtures using a chemical model

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Abstract

A chemical model is presented to reproduce the temperature dependence of binodal curves in some aqueous mixtures. The model assumes solvation equilibrium between solute and solvent, the Flory–Huggins equation for molecular size difference, and the NRTL equation whose energy parameters are assumed to be temperature dependent for molecular interaction. The calculated binodal curves agree well with the experimental results for the aqueous mixtures studied.

LIST OF SYMBOLS

$A_{12}, B_{12}, C_{12}, D_{12}$	coefficients of eqn. (16)
$A_{21}, B_{21}, C_{21}, D_{21}$	coefficients of eqn. (17)
a_{12}, a_{21}	binary interaction parameters for S–W pair
C	constant of eqn. (8)
G^E	excess Gibbs free energy
ΔH	enthalpy of formation of chemical complex S_1W_i
K	solvation constant as defined by eqn. (5)
i	degree of solvation
R	universal gas constant
r_I	molecular size parameter of component I
S	solute
S_1	solute monomer
T	absolute temperature
x_I	liquid-phase mole fraction of component I

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V	true molar volume of mixture
W	solvent
W_1	solvent monomer

Greek letters

γ_I	activity coefficient of component I
τ_{12}, τ_{21}	binary parameters as defined by eqn. (2)
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
ρ	r_W/r_S

Subscripts

S, W	solute and solvent (=water)
S_1W_t	chemical complex S_1W_t
chem	chemical
phys	physical

INTRODUCTION

Solution non-ideality is often explained in terms of physical or chemical models. Sometimes chemical models are useful for mixtures where molecular self-association or cross-association i.e. solvation, takes place. Conventional chemical models, except for the ideal chemical solution model, include two contribution terms: chemical and physical. Recently, Yu and Nishiumi [1] presented a chemical model in which the physical contribution is expressed by the NRTL equation [2] to describe the temperature dependence of mutual solubility data for some aqueous mixtures. These authors reproduced well the data of lower critical solution temperature (LCST), but failed to describe adequately the upper part of closed binodal curves, probably because temperature-independent energy parameters were used.

In this paper, we modify the chemical model of Yu and Nishiumi by introducing the temperature-dependent energy parameters of the NRTL equation in order to obtain a good representation of the closed loop of coexistence curves for the three mixtures studied by Yu and Nishiumi.

MODEL DESCRIPTION

We briefly describe the model used in this paper. The excess Gibbs free energy G^E is expressed as the sum of the Flory–Huggins and NRTL equations

$$\frac{G^{E}}{RT} = -x_1 \ln \Phi_1 - x_2 \ln \Phi_2 + x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \tag{1}$$

where Φ is the volume fraction and the binary NRTL parameters are defined by

$$\tau_{21} = a_{21}/T \qquad \tau_{12} = a_{12}/T \tag{2}$$

and

$$G_{21} = \exp(-\tau_{21}\alpha_{21}) \qquad G_{12} = \exp(-\tau_{12}\alpha_{12}) \tag{3}$$

The non-randomness parameters $\alpha_{12} = \alpha_{21}$ are taken here as 0.2.

Chemical contribution

We assume the following solvation equilibrium due to hydrogen bond formation between solvent (W) and solute (S) molecules, in the same way as Yu and Nishiumi

$$S_1 + iW_1 = S_1W_i \tag{4}$$

and the equilibrium constant K is defined by

$$K = \frac{\Phi_{S_1W_i}}{\Phi_{S_1}(\Phi_{W_1})^{i}} \tag{5}$$

where $\Phi_{S_1W_i}$, Φ_{S_1} and Φ_{W_1} are the volume fractions of the chemical species S_1W_i, S_1 and W_1.

The overall volume fractions of solvent W and solute S are related to those of the chemical species

$$\begin{aligned}\Phi_W &= \Phi_{W_1} + \frac{\Phi_{S_1W_i} i r_W}{r_S + i r_W} \\ &= \Phi_{W_1} + \frac{K\Phi_{S_1}(\Phi_{W_1})^{i} i\rho}{1 + i\rho}\end{aligned} \tag{6}$$

$$\begin{aligned}\Phi_S &= \Phi_{S_1} + \frac{\Phi_{S_1W_i} r_S}{r_S + i r_W} \\ &= \Phi_{S_1} + \frac{K\Phi_{S_1}(\Phi_{W_1})^{i}}{1 + i\rho}\end{aligned} \tag{7}$$

where ρ is the ratio of the molecular size parameter of solvent r_W to that of solute r_S ($\rho = r_W/r_S$).

The solvation equilibrium constant is expressed as

$$K = \exp(-\Delta H/RT + C) \tag{8}$$

where ΔH is the enthalpy of formation of the chemical complex S_1W_i and C is a constant.

From the Flory–Huggins equation for entropy, the activity coefficients of solute and solvent due to the solvation reaction are given by

$$\ln \gamma_{\mathrm{S,chem}} = \ln \frac{\Phi_{\mathrm{S}_1}}{x_{\mathrm{S}}} + 1 - \frac{r_{\mathrm{S}}}{V} \tag{9}$$

$$\ln \gamma_{\mathrm{W,chem}} = \ln \frac{\Phi_{\mathrm{W}_1}}{x_{\mathrm{W}}} + 1 - \frac{r_{\mathrm{W}}}{V} \tag{10}$$

where the true molar volume of the mixture V is expressed by

$$\begin{aligned} \frac{1}{V} &= \frac{\Phi_{\mathrm{S}_1}}{r_{\mathrm{S}}} + \frac{\Phi_{\mathrm{W}_1}}{r_{\mathrm{W}}} + \frac{\Phi_{\mathrm{S}_1\mathrm{W}_i}}{r_{\mathrm{S}} + i r_{\mathrm{W}}} \\ &= \frac{\Phi_{\mathrm{S}_1}}{r_{\mathrm{S}}} + \frac{\Phi_{\mathrm{W}_1}}{r_{\mathrm{W}}} + \frac{K\Phi_{\mathrm{S}_1}(\Phi_{\mathrm{W}_1})^i}{r_{\mathrm{S}} + i r_{\mathrm{W}}} \end{aligned} \tag{11}$$

Then, eqns. (9) and (10) become

$$\ln \gamma_{\mathrm{S,chem}} = \ln \frac{\Phi_{\mathrm{S}_1}}{x_{\mathrm{S}}} + 1 - \Phi_{\mathrm{S}_1} - \frac{\Phi_{\mathrm{W}_1}}{\rho} - \frac{K\Phi_{\mathrm{S}_1}(\Phi_{\mathrm{W}_1})^i}{1 + i\rho} \tag{12}$$

$$\ln \gamma_{\mathrm{W,chem}} = \ln \frac{\Phi_{\mathrm{W}_1}}{x_{\mathrm{W}}} + 1 - \Phi_{\mathrm{W}_1} - \rho\Phi_{\mathrm{S}_1} - \frac{\rho K\Phi_{\mathrm{S}_1}(\Phi_{\mathrm{W}_1})^i}{1 + i\rho} \tag{13}$$

Physical contribution

Each activity coefficient expression includes the physical contribution term given by

$$\ln \gamma_{\mathrm{S,phys}} = x_{\mathrm{W}}^2 \left[\frac{\tau_{21} G_{21}^2}{(x_{\mathrm{S}} + x_{\mathrm{W}} G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_{\mathrm{W}} + x_{\mathrm{S}} G_{12})^2} \right] \tag{14}$$

$$\ln \gamma_{\mathrm{W,phys}} = x_{\mathrm{S}}^2 \left[\frac{\tau_{12} G_{12}^2}{(x_{\mathrm{W}} + x_{\mathrm{S}} G_{12})^2} + \frac{\tau_{21} G_{21}}{(x_{\mathrm{S}} + x_{\mathrm{W}} G_{21})^2} \right] \tag{15}$$

Because the energy parameters of local composition models like the NRTL equation are generally temperature dependent [3], we assume that the temperature dependence of the energy parameters can be expressed by

TABLE 1

Values of molecular size parameters for pure components

Component	r_i	Component	r_i
Water	0.9200	1-Propoxy-2-propanol	5.0462
2-Isobutoxyethanol	5.0462	2,6-Dimethylpridine	4.4693

a cubic function of temperature

$$a_{12} = A_{12} + B_{12}T + C_{12}T^2 + D_{12}T^3 \tag{16}$$

$$a_{21} = A_{21} + B_{21}T + C_{21}T^2 + D_{21}T^3 \tag{17}$$

CALCULATED RESULTS

The mutual solubility curve is calculated by solving the thermodynamic equations of the liquid–liquid equilibrium

$$(x_S\gamma_S)^{\mathrm{I}} = (x_S\gamma^{S})^{\mathrm{II}} \tag{18}$$

$$(x_W\gamma_W)^{\mathrm{I}} = (x_W\gamma_W)^{\mathrm{II}} \tag{19}$$

where the superscripts I and II represent two liquid phases in equilibrium. Table 1 shows the values of pure component molecular size parameters taken from Sørensen and Arlt [4].

Yu and Nishiumi studied only four aqueous systems. The first two systems have an LCST: 2-isobutoxyethanol + water and 1-ethylglycerol 3-isopropyl ether + water; and the other two systems have an LCST and an upper critical solution temperature (UCST): 1-propoxy-2-propanol + water and 2,6-dimethylpyridine + water. However, the 2-isobutoxyethanol + water system also has an UCST [4]. For the 1-ethylglycerol 3-isopropyl ether + water system, the temperature difference between the highest experimental data point and the lowest data point is 42°C, and Yu and Nishiumi reproduced well the experimental data of this system using their method. For the other three systems, the corresponding temperature differences are 79°C for 2-isobutoxyethanol + water, 140°C for 1-propoxy-2-propanol + water and 122°C for 2,6-dimethylpyridine + water. The solvation constant is temperature dependent and is mainly responsible for the temperature variation of the activity coefficients for 1-ethylglycerol 3-isopropyl ether + water. For the other three systems with both a UCST and an LCST, we should consider the temperature dependence of the energy parameters in the physical contribution term. We studied two cases for the temperature dependence of the energy parameters: cubic and quadratic. All the experimental data were taken from Sørensen and Arlt [4]. Table 2 gives the coefficients of eqns. (16) and (17), together with the values of i, $-\Delta H/R$ and C taken from Yu and Nishiumi.

TABLE 2

Values of binary solvation parameters, coefficients of energy parameters and absolute arithmetic mean deviations

System (1 + 2)	Temperature range/°C	i	$-(\Delta H/R)/$ K	C	Case[a]	Dev.[b] (mol.%)	Coefficients			
							A_{12} A_{21}	B_{12} B_{21}	C_{12} C_{21}	$D_{12} \times 10^3$ $D_{21} \times 10^3$
2-Isobutoxyethanol + water	24.6–150.2	2.6205	6013.1353	−17.6452	1	1.43	−10930.265	61.2410	−0.08838	
							10688.582	−46.7938	0.06876	
					2	0.99	52033.043	−470.0747	1.39775	−1.3769
							−9434.244	121.9507	−0.40415	0.4440
1-Propoxy-2-propanol + water	34.5–171.7	2.2937	5119.0628	−14.5812	1	1.41	−8297.684	45.9758	−0.06480	
							8423.627	−33.8865	0.04948	
					2	0.89	27982.671	−250.6113	0.73889	−0.7221
							1893.293	19.6029	−0.09902	0.1398
2,6-Dimethylpyridine + water	45.3–164.9	2.4158	5366.3187	−14.6612	1	1.05	−6622.123	35.6268	−0.05113	
							8623.050	−33.2815	0.04716	
					2	0.55	103654.950	−848.8338	2.29753	−2.0650
							−70216.735	598.7321	−1.63107	1.4763

[a] 1, quadratic temperature dependence of the energy parameters assumed; 2, cubic temperature dependence of the energy parameters assumed.

[b] Absolute arithmetic mean deviation.

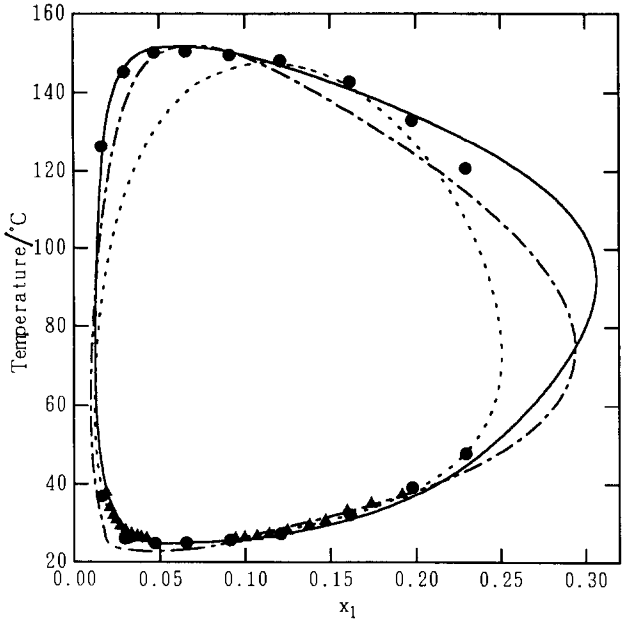

Fig. 1. Calculated and experimental coexistence curves for the 2-isobutoxyethanol(1) + water(2) system. Experimental: ●, ref. 5 data; ▲, ref. 6 data. Calculated: – – –, by Yu and Nishiumi [1]; ——, by this work with cubic temperature-dependent energy parameter; ·······, by this work with quadratic temperature-dependent energy parameter.

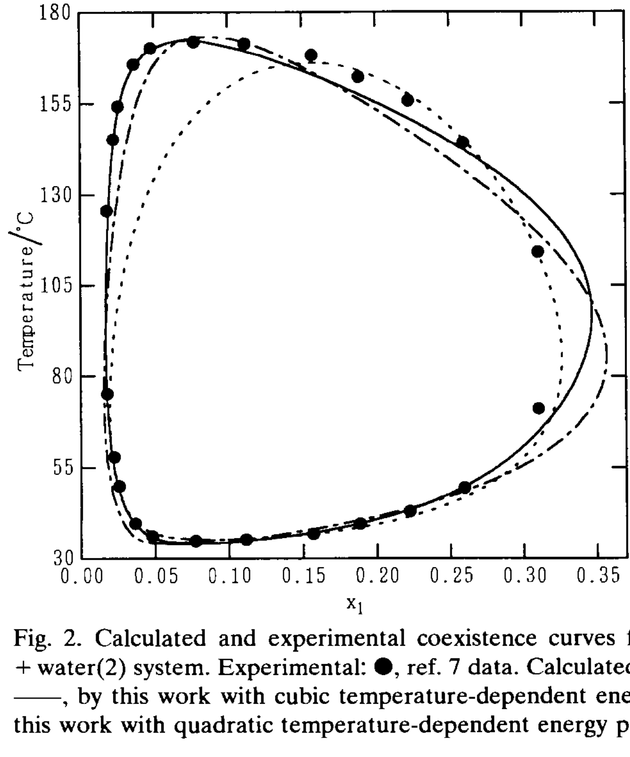

Fig. 2. Calculated and experimental coexistence curves for the 1-propoxy-2-propanol(1) + water(2) system. Experimental: ●, ref. 7 data. Calculated: – – –, by Yu and Nishiumi [1]; ——, by this work with cubic temperature-dependent energy parameter; ·······, by this work with quadratic temperature-dependent energy parameter.

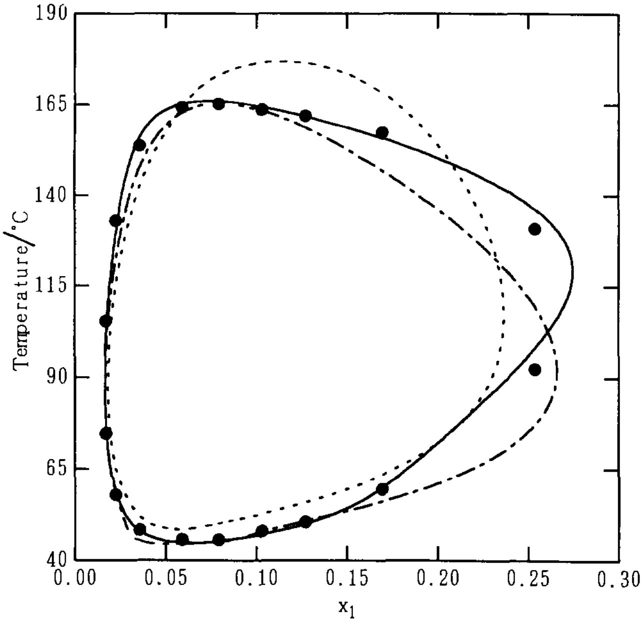

Fig. 3. Calculated and experimental coexistence curves for the 2,6-dimethylpyridine(1) + water(2) system. Experimental: ●, ref. 8 data. Calculated: – – –, by Yu and Nishiumi [1]; ——, by this work with cubic temperature-dependent energy parameter; ·········, by this work with quadratic temperature-dependent energy parameter.

Figures 1–3 show the experimental mutual coexistence data points, and the calculated curves obtained from the method of Yu and Nishiumi and those obtained from the present work. The method of Yu and Nishiumi reproduces only the experimental data in the lower critical regions and could not correlate well the experimental data in the upper critical regions. In contrast, our method is able to represent all experimental data with good accuracy: the cubic temperature dependence of the energy parameters yields a more improved agreement than the quadratic dependence. These results suggest that the temperature-dependent energy parameters play an important role in the correlation of the experimental data of a liquid–liquid equilibrium with a UCST and an LCST over a wide temperature range.

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REFERENCES

1 M. Yu and H. Nishiumi, J. Phys. Chem., 96 (1992) 842–845.
2 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135–144.
3 I. Nagata and T. Yamada, Ind. Eng. Chem. Process Des. Dev., 11 (1972) 575–578.
4 J.M. Sørensen and W. Arlt, Liquid–Liquid Equilibrium Data Collection, Binary Systems,

DECHEMA Chemistry Data Ser., Vol. V, Part 1, DECHEMA, Frankfurt am Main, Germany, 1979.
5 H.L. Cox and L.H. Cretchner, J. Am. Chem. Soc., 48 (1926) 451–453.
6 De Forest P. Rudd and B. Wisdom, J. Chem. Phys., 33 (1960) 1816–1819.
7 H.L. Cox, W.L. Nelson and L.H. Cretchner, J. Am. Chem. Soc., 49 (1927) 1080–1083.
8 O. Flaschner, J. Chem. Soc., 95 (1909) 668–685.