Temperature Dependence on Mutual Solubility Data of the Binary (Methanol + α-Pinene or β-Pinene) Systems and Ternary Liquid−Liquid Equilibria for the (Methanol + Ethanol + α-Pinene or β-Pinene) Systems

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Mutual solubility data of the binary systems (methanol + α-pinene or β-pinene) at temperatures ranging from 288.15 K close to upper critical solution temperatures, and ternary liquid−liquid equilibria and tie-lines of the mixtures (methanol + ethanol + α-pinene or β-pinene) at temperatures 288.15 K, 298.15 K, and 308.15 K have been measured. The experimental binary and ternary liquid−liquid equilibrium data have been correlated by the original, extended, and modified UNIQUAC models. Good agreement between the experimental and correlated values was obtained using the extended and modified UNIQUAC models. The temperature dependence of the binary and ternary liquid−liquid phase equilibria (methanol + α-pinene or β-pinene) mixtures with ethanol was demonstrated experimentally and represented by the extended and modified UNIQUAC models.

Introduction

As environmentally friendly organic solvents, chemical compounds obtained from natural products have been increasing recently in use. Pinene, having two structural isomers of α-pinene (CAS number 80-56-8) and β-pinene (CAS number 127-91-3), is a main constituent of pine resin and found in pine conifers. Pinene is widely used as synthetic starting meterials in medicine and additives to fragrance and flavor goods. In the purification of pinene extracted from pine resins and blending of pinene into aqueous alcohol, the phase equilibria of pinene mixtures are essential for the process design developments. The solubilities of the ternary mixtures of pinene with water, methanol, ethanol, 1-propanol, and 1-butanol have been examined earlier.[1−3]

The miscibility of pinene mixtures with hydrocarbons, alcohol, and water depends on their different affinities as well as temperature of the mixtures. In this work, we measured the mutual solubility data of the binary systems (methanol + α-pinene or β-pinene) at the temperatures ranging from 288.15 K to close to upper critical temperature and liquid−liquid equilibria (tie-lines) for the ternary (methanol + ethanol + α-pinene or β-pinene) mixtures at the temperatures 288.15 K, 298.15 K, and 308.15 K. Two-phase mixtures with methanol-rich and pinene-rich phases were formed. Furthermore, we studied the temperature dependence on mutual solubility data of (methanol + α-pinene or β-pinene) mixtures and ternary LLEs of (methanol + ethanol + α-pinene or β-pinene) mixtures using the original UNIQUAC,[4] the extended UNIQUAC,[5] and the modified UNIQUAC[6] models.

Experimental Section

Materials. Purities of the chemicals used in this work were as follows: (−)-α-pinene (abbreviated hereafter as α-pinene, Fluka), > 99 %; (−)-β-pinene (β-pinene, Fluka), > 99 %; methanol (Wako Pure Chemicals), > 99.7 %; and ethanol (Wako Pure Chemicals), > 99.5 % in mass percent. Densities of chemicals were measured with an Anton Paar (DMA58) densimeter at 298.15 K and compared with the literature[7] as shown in Table 1. All chemicals were used without further purification.

Table 1. Densities of Pure Components at $T = 298.15$ K

component	$\rho^{\text{exp}}/\text{kg}\cdot\text{m}^{-3}$	$\rho^{\text{lit}}/\text{kg}\cdot\text{m}^{-3}$
α-pinene	853.88	853.90
β-pinene	866.84	866.70
methanol	786.62	786.37
ethanol	785.24	784.93

Procedure and Experimental Results. Liquid−liquid equilibrium (LLE) measurements for the ternary (methanol + ethanol + α-pinene or β-pinene) mixtures were carried out at the temperatures 288.15 K, 298.15 K, and 308.15 K within ± 0.01 K, and the binary (methanol + α-pinene or β-pinene) systems were measured at temperatures ranging from 288.15 K to close to upper critical solution temperatures and at atmospheric pressure. A detailed procedure and explanation of the LLE measurements was described earlier, so a brief outline of the measurements is given here. The mixtures with a volume of approximately 80 cm^3 loaded in an equilibrium cell were stirred vigorously by using a magnetic stirrer for 5 h and settled for 5 h, enough to separate the two phases. The headspace of the cell was filled with dry nitrogen gas to keep off contamination of moisture. After phase equilibrium has been reached, samples of the two layers were withdrawn with a precision Hamiltion syringe, and their compositions were analyzed by a GLC (Shimadzu, GC-8A) equipped with a thermal conductivity detector. The temperatures of the injection port and detector were set at 513 K, and the oven temperature was increased from (403 to 513) K at a rate of 32 $\text{K}\cdot\text{min}^{-1}$. The helium flow rates for both the separation and reference columns were set at 50 $\text{mL}\cdot\text{min}^{-1}$. A stainless steel column packed with Porapak Q 2 m in length was used to separate every component. The peak

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Table 2. Liquid−Liquid Equilibrium Data of Binary Systems at Different Temperatures

T/K	methanol-rich phase x_1	pinene-rich phase x_1
	Methanol (1) + α-Pinene (2)	
288.15	0.9241	0.1288
293.04	0.9179	0.1373
298.15	0.9129	0.1574
304.93	0.9012	0.1850
308.15	0.8912	0.2177
313.28	0.8821	0.2567
318.17	0.8678	0.2989
323.16	0.8403	0.3486
328.09	0.8019	0.4394
	Methanol (1) + β-Pinene (2)	
288.15	0.9043	0.1909
293.22	0.8926	0.2085
298.15	0.8893	0.2357
304.87	0.8625	0.2902
308.15	0.8463	0.3254
313.28	0.8169	0.3954
316.22	0.7817	0.4549
318.03	0.7652	0.5176

Table 3. Liquid−Liquid Equilibrium Data of Methanol (1) + Ethanol (2) + α-Pinene (3) at T = (288.15, 298.15, and 308.15) K

methanol-rich phase		α-pinene-rich phase	
x_1	x_2	x_1	x_2
	288.15 K		
0.8023	0.0959	0.1484	0.0207
0.7134	0.1528	0.1850	0.0472
0.6125	0.2080	0.2101	0.0797
0.5271	0.2309	0.2632	0.1240
0.4397	0.2469	0.3245	0.1860
	298.15 K		
0.7944	0.0887	0.1931	0.0271
0.6913	0.1409	0.2411	0.0576
0.6167	0.1691	0.2834	0.0864
0.5670	0.1865	0.3153	0.1180
	308.15 K		
0.8526	0.0261	0.2220	0.0064
0.8177	0.0499	0.2466	0.0160
0.7678	0.0776	0.2659	0.0317
0.7001	0.1092	0.3469	0.0636

area of the components, detected to analyze with a chromatopac (Shimadzu, C-R6A), was calibrated by gravimetrically weighed mixtures. For each sample solution, three analyses were made to obtain a mean value. The accuracy of the tie-line measurements was estimated within ± 0.001 in mole fraction.

Tables 2 to 4 summarize the experimental mutual solubility data of (methanol + α-pinene) and (methanol + β-pinene) mixtures and ternary LLE tie-line compositions for (methanol + ethanol + α-pinene) and (methanol + ethanol + β-pinene) mixtures.

Calculated Results and Discussion

Calculation Procedure. Liquid−liquid equilibrium (LLE) calculations were carried out by solving the thermodynamic criteria and mass balance equation.

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{1}$$

$$\sum_i x_i^{\mathrm{I}} = \sum_i x_i^{\mathrm{II}} = 1 \tag{2}$$

Table 4. Liquid−Liquid Equilibrium Data of Methanol (1) + Ethanol (2) + β-Pinene (3) at T = (288.15, 298.15, and 308.15) K

methanol-rich phase		β-pinene-rich phase	
x_1	x_2	x_1	x_2
	288.15 K		
0.8084	0.0647	0.2141	0.0207
0.7232	0.1179	0.2537	0.0469
0.6603	0.1512	0.2678	0.0620
0.5920	0.1720	0.3208	0.0947
	298.15 K		
0.8162	0.0423	0.2621	0.0155
0.7574	0.0813	0.2834	0.0341
0.6997	0.1029	0.3228	0.0556
0.6349	0.1302	0.3687	0.0731
	308.15 K		
0.8213	0.0140	0.3339	0.0049
0.7884	0.0254	0.3686	0.0171
0.7527	0.0420	0.3974	0.0297
0.7418	0.0498	0.4609	0.0347
0.6881	0.0562	0.5077	0.0401

Table 5. Structural Parameters for Pure Components

component	r^a	q^a	q'^b	q'^c
α-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
β-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
methanol	1.430	1.430	1.000	1.482
ethanol	2.110	1.972	1.000	1.404

[a] Refs 10 and 11. [b] Ref 5. [c] Ref 6.

where I and II represent the equilibrium phases; x is the liquid-phase mole fraction; and γ is the activity coefficient. In the calculation of binary LLE, the adjustable binary energy parameters for binary (methanol + α-pinene or β-pinene) systems were obtained from the experimental mutual solubilities by solving eqs 1 and 2 simultaneously. In the computation of ternary LLE correlations, the following objective function was used to minimize using the simplex method.[8]

$$F = 100\left\{\sum_k^n \sum_i^3 \sum_j^2 (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2/6n\right\}^{0.5} \tag{3}$$

where n denotes tie-lines k =1 to n, phases j = 1 and 2, and components i = 1, 2, and 3.

To represent the experimental binary and ternary LLE results, we used three kinds of activity coefficient models: the original UNIQUAC,[4] the extended UNIQUAC,[5] and the modified UNIQUAC.[6] In the extended and modified UNIQUAC models, the interaction correction factor of pure component q' was used to improve the phase equilibrium representation. The segment fraction ϕ_i, the corrected segment fraction ϕ_i', and the surface fraction θ_i in a ternary system are given by

$$\phi_i = \frac{x_i r_i}{\sum_j^3 x_j r_j}, \quad \phi_i' = \frac{x_i r_i^{3/4}}{\sum_j^3 x_j r_j^{3/4}}, \quad \theta_i = \frac{x_i q_i}{\sum_j^3 x_j q_j} \tag{4}$$

where r_i and q_i are the molecular-geometric volume and surface parameters of pure components, which depend on the molecular size and shape of pure components and can be estimated from Bondii's method.[9] The pure-component molecular parameters, r_i and q_i, and the correlation factor q'_i, taken from the refs 5, 6, 10, and 11 were listed in Table 5.

The adjustable binary parameter τ_{ij} is defined by the binary energy parameter a_{ij}

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{CT}\right) \tag{5}$$

where the third parameter C, introduced by Maurer and Prausnitz,[12] was set to 1.0 in the original UNIQUAC and the extended UNIQUAC model and 0.65 in the modified UNIQUAC model.

Table 6. Calculated Results of Binary Phase Equilibrium Data Reduction[b]

system (1 + 2)	T/K	N	model	a_{12}/K	a_{21}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$	ref
methanol + ethanol	298.15	11	I	−141.75	169.45	0.18			0.7	10[a]
			II	262.72	−118.69	0.56	0.01	0.3	3.0	10
			III	292.63	−132.64	0.57	0.01	0.3	3.0	10
methanol + α-pinene	288.15	MS	I	−2.1825	655.64	this work				
			II	340.23	1258.1					
			III	63.418	1187.9					
	298.15	MS	I	−4.7110	650.29					
			II	337.92	1256.0					
			III	57.028	1187.2					
	308.15	MS	I	−7.5136	624.87					
			II	328.27	1220.3					
			III	46.442	1151.6					
methanol + β-pinene	288.15	MS	I	−4.6000	599.09	this work				
			II	316.43	1162.0					
			III	49.294	1092.3					
	298.15	MS	I	−5.9056	589.82					
			II	314.86	1152.2					
			III	43.611	1080.2					
	308.15	MS	I	−11.504	572.01					
			II	298.87	1130.7					
			III	29.718	1076.2					

[a] Binary energy parameters and deviations were taken from ref 10. [b] N, no. of data points; MS, mutual solubility; I, UNIQUAC; II, Extended UNIQUAC; III, Modified UNIQUAC.

The binary energy parameters of the miscible mixture (methanol + ethanol)[10] can be obtained from binary experimental vapor−liquid equilibria (VLE) using the thermodynamic equations

$$Py_i\Phi_i = x_i\gamma_i P_i^{\mathrm{s}}\Phi_i^{\mathrm{s}} \exp\{V_i^{\mathrm{L}}(P - P_i^{\mathrm{s}})/RT\} \tag{6}$$

$$\ln \Phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})P/RT \tag{7}$$

where P, y, and Φ are the total pressure, the vapor-phase mole fraction, and the fugacity coefficient, respectively. The pure component vapor pressure P^{s} was calculated by using the Antoine equation with coefficients taken from the literature.[10] The liquid molar volume V^{L} was obtained by a modified Racket equation.[13] The pure and cross second virial ratios B_{ij} in eq 7 were estimated by the method of Hayden and O'Connell.[14] An optimum set of the binary energy parameters a_{ij} was obtained using a maximum likelihood principle,[15] where standard deviations in the measured quantities were set as σ_p = 133 Pa for pressure; σ_T = 0.05 K for temperature; σ_x = 0.001 for liquid mole fraction; and σ_y = 0.003 for vapor mole fraction. Since no experimental binary vapor-phase data of (ethanol + pinene) have been found in the literature, the binary energy parameters of the miscible mixtures for the (ethanol + pinene) were obtained from the ternary LLE correlation. Table 6 summarizes the binary parameters and calculated results for constituent binary systems.

Calculated Results for Binary Systems. Table 2 shows the experimental tie-line compositions for the binary (methanol + α-pinene) and (methanol + β-pinene) systems from 288.15 K to upper critical solution temperatures. The binary energy parameters a_{ij} were obtained from the experimental mutual solubilities at every temperature by solving eqs 1 and 2. We assumed that the energy parameters are given by a quadratic function of temperature to obtain quantitative agreement with experimental data.[6]

$$a_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2 \tag{8}$$

The coefficients A_{ij}, B_{ij}, and C_{ij} of the energy parameter a_{ij} were obtained by a least-squares minimization method and listed in Table 7. Figures 1 and 2 show the experimental and calculated mutual solubilities for (methanol + α-pinene) and (methanol + β-pinene) systems by the modified UNIQUAC model. As shown in Figures 1 and 2, the binary LLE systems have an upper critical solution temperature, and the mutual solubilities increase as system temperature goes up. The coexistence curves could be satisfactorily described by the modified UNIQUAC model. Figures 3 and 4 show the binary parameters for (methanol + α-pinene) and (methanol + β-pinene) systems estimated at each temperature using the modified UNIQUAC model and calculated results of the fitting of a_{ij} into eq 8 with the modified UNIQUAC model. The coexistence curves calculated using the temperature dependence of the binary energy parameters given by eq 8 were in good agreement with the estimated values over an upper critical solution temperature.

Table 7. Constants A_{ji}, B_{ji}, and C_{ji} of Binary Parameter a_{ji} Used in the Modified UNIQUAC Model[a]

system (1 + 2)	A_{12} A_{21}	B_{12}/K B_{21}/K	$10^{-3}C_{12}$/K^2 $10^{-3}C_{21}$/K^2
methanol + α-pinene	−1554.89	11.6616	−20.98
	−1378.36	102.239	−174.5
methanol + β-pinene	−3313.63	23.4993	−41.05
	−7064.31	56.8337	−8.700

[a] $a_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2$.

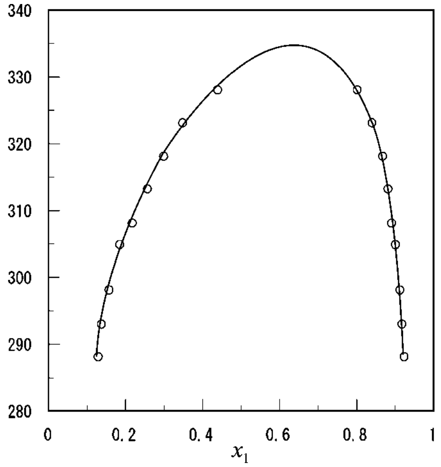

Figure 1. Experimental and calculated mutual solubility for the binary system (methanol + α-pinene). ○, experimental data and x_1 denotes mole fraction of methanol; and −, correlated by the modified UNIQUAC model.

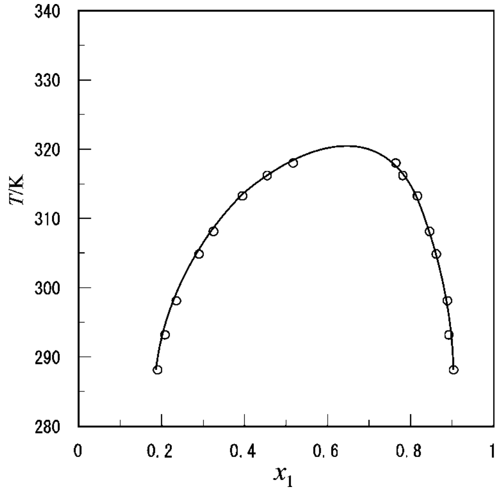

Figure 2. Experimental and calculated mutual solubility for the binary system (methanol + β-pinene). ○, experimental data and x_1 denotes mole fraction of methanol; and −, correlated by the modified UNIQUAC model.

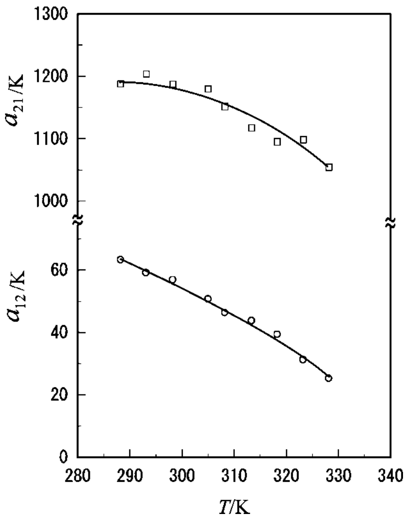

Figure 3. Temperature dependence of binary energy parameters for the binary system (methanol + α-pinene). ○, □, binary energy parameters of the modified UNIQUAC model; and −, correlated by eq 8.

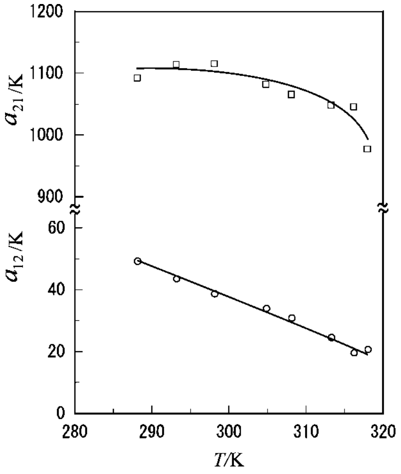

Figure 4. Temperature dependence of binary energy parameters for the binary system (methanol + β-pinene). ○, □, binary energy parameters of the modified UNIQUAC model; and −, correlated by eq 8.

Table 8. Calculated Results for Ternary Systems[a]

				rms	binary parameters	
system (1 + 2 + 3)	T/K	N	model	(%)	a_{23}/K	a_{32}/K
methanol + ethanol + α-pinene	288.15	6	I	2.02	−124.79	300.44
			II	1.28	145.05	986.87
			III	0.43	27.597	1266.4
	298.15	5	I	1.70	−146.91	304.37
			II	0.90	137.42	989.55
			III	0.28	15.107	1190.0
	308.15	5	I	1.31	−156.90	278.34
			II	1.01	138.34	972.65
			III	0.80	2.3016	1100.8
methanol + ethanol + β-pinene	288.15	5	I	1.41	−130.71	308.02
			II	0.65	128.35	993.61
			III	0.37	19.365	1178.9
	298.15	5	I	1.09	−147.62	305.66
			II	0.62	123.57	982.12
			III	0.31	5.5160	1161.2
	308.15	6	I	0.91	−242.99	262.86
			II	0.70	125.76	812.72
			III	0.68	−9.3152	806.22

[a] I, UNIQUAC; II, Extended UNIQUAC; III, Modified UNIQUAC.

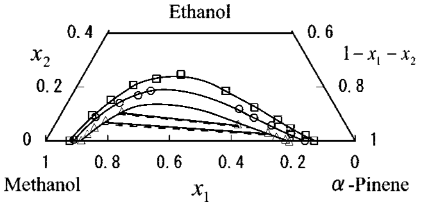

Figure 5. Liquid−liquid equilibrium data of ternary systems (methanol + ethanol +α-pinene) at (288.15, 298.15, and 308.15) K. □, ○, Δ, - - -, experimental tie-line at 288.15 K, 298.15 K, 308.15 K; x_1 and x_2 denote mole fraction of methanol and ethanol; and −, correlated by the modified UNIQUAC model.

Calculated Results for Ternary Systems. The LLE phase behavior for the (methanol + ethanol + α-pinene or β-pinene) systems showed a type I in terms of the classification of Sørensen and Arlt.[16] The ternary LLEs of the (methanol + ethanol + pinene) system consist of two miscible systems (methanol + ethanol) and (ethanol + pinene) and one immiscible system (methanol + pinene). The binary parameters (methanol + ethanol) obtained using eqs 6 and 7 from the binary VLE correlations are given in Table 6. In the representation of the ternary LLE (methanol + ethanol + pinene) systems, since no binary VLE data for the miscible (ethanol + pinene) mixture were available from the literature, the binary parameters for the (ethanol + pinene) system were obtained from the experimental ternary LLEs of the (methanol + ethanol + α-pinene or β-pinene) systems by minimizing the objective function of eq 3. Table 8 lists the correlated binary parameters and root-mean-square deviations (rms) between the experimental and calculated results by three models. The mean deviations correlated for the two sets of ternary systems at (288.15, 298.15, and 308.15) K were 1.41 mol %, 0.86 mol %, and 0.48 mol % for the UNIQUAC model, the extended, and modified UNIQUAC models, respectively. The extended and modified UNIQUAC models could reproduce accurately the experimental results in comparison with the original UNIQUAC model. Figures 5 and 6 compare the experimental tie-line data for the ternary LLE of the (methanol + ethanol + α-pinene) and (methanol + ethanol + β-pinene) systems at (288.15, 298.15, and 308.15) K with the results correlated in terms of the modified UNIQUAC model. The temperature dependence of the ternary LLE envelope with tie-lines, where the immiscible regions decrease as temperature increases, could be represented successfully by the modified UNIQUAC model as shown in Figures 5 and 6.

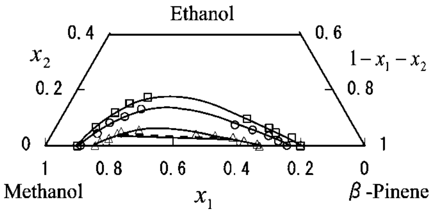

Figure 6. Liquid−liquid equilibrium data of ternary systems (methanol + ethanol + β-pinene) at (288.15, 298.15, and 308.15) K. □, ○, Δ, - - -, experimental tie-line at 288.15 K, 298.15 K, and 308.15 K; x_1 and x_2 denote mole fraction of methanol and ethanol; and −, correlated by modified UNIQUAC model.

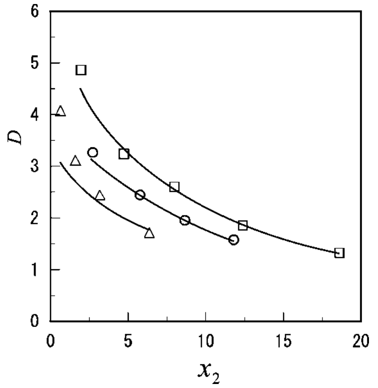

Figure 7. Distribution ratio of ethanol in the α-pinene-rich phase, *D*, at (288.15, 298.15, and 308.15) K as a function of mole fraction of ethanol in the α-pinene-rich phase, x_2. □, ○, Δ, experimental data at 288.15 K, 298.15 K, and 308.15 K; and −, calculated by the modified UNIQUAC model.

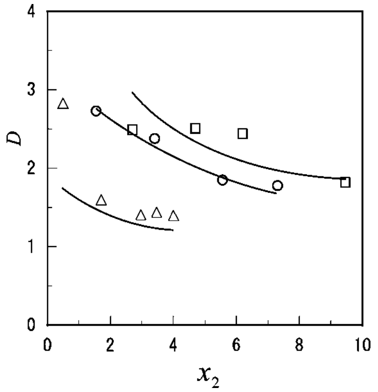

Figure 8. Distribution ratio of ethanol in the β-pinene-rich phase, *D*, at (288.15, 298.15, and 308.15) K as a function of mole fraction of ethanol in the β-pinene rich-phase, x_2. □, ○, Δ, experimental data at 288.15 K, 298.15 K, and 308.15 K; and −, calculated by the modified UNIQUAC model.

The distribution ratio of ethanol (component 2) in the ternary LLE mixtures was defined by

$$D = x_2^{\text{methanol phase}} / x_2^{\text{pinene phase}} \tag{9}$$

Figures 7 and 8 show the experimental and calculated distribution ratio of ethanol for the ternary LLE of (methanol + ethanol + α-pinene) and (methanol + ethanol + β-pinene) systems. The distribution ratio of ethanol for the (methanol + ethanol + pinene) systems using the modified UNIQUAC model showed fair agreement with the experimental values, except for a few points of the scattered experimental results for the (methanol + ethanol + β-pinene) system. The distribution ratio of ethanol for the (methanol + ethanol + α-pinene) mixture was larger than that of the (methanol + ethanol + β-pinene) mixture at same concentration of ethanol. For the ternary systems, the distribution ratio of ethanol was increasing as the system temperature decreased.

Conclusions

Mutual solubility data of the binary systems (methanol + α-pinene or β-pinene) at temperatures ranging from 288.15 K close to upper critical solution temperatures and liquid−liquid equilibria (tie-lines) for the (methanol + ethanol + α-pinene or β-pinene) mixtures at $T = (288.15, 298.15, \text{and } 308.15)$ K were measured. The experimental mutual solubility data and ternary liquid−liquid equilibrium data have been quantitatively represented using the extended and modified UNIQUAC models. The root-mean-square deviations of the (methanol + ethanol + α-pinene) and (methanol + ethanol + β-pinene) systems calculated by the modified UNIQUAC model were 0.50 mol % and 0.45 mol % at $T = (288.15, 298.15, \text{and } 308.15)$ K, respectively. The temperature dependence of the mutual solubility for the (methanol + pinene) systems and the ternary LLEs with tie-lines for the (methanol + ethanol + pinene) systems could be represented successfully by the extended and modified UNIQUAC model.

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