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Mutual Solubilities of Terpene in Methanol and Water and Their Multicomponent Liquid−Liquid Equilibria

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Multicomponent liquid−liquid equilibria measured at $T = 298.15$ K have been reported for the ternary (water + methanol + α-pinene or + β-pinene or + limonene) and (water or methanol + α-pinene + limonene) systems and the quaternary (water + methanol + α-pinene + limonene) systems. The mutual solubilities of terpenes (α-pinene, β-pinene, and limonene) in methanol and water have been measured at $T = 298.15$ K. The experimental multicomponent liquid−liquid equilibrium data have been satisfactorily represented by using the extended UNIQUAC and modified UNIQUAC models.

Introduction

Terpentine oil extracted from pine resin is a mixture of numerous terpenoid compounds and volatile terpenes. The main components [2-pinene (α-pinene), 1-pinene (β-pinene), 3-carene (Δ-3-carene), and dipentene ((±)-limonene)] have a common chemical formula $C_{10}H_{16}$ but different structures as shown in Figure 1. Pinenes and limonene are potentially useful and functional substances that are widely used in detergent, perfume, food, and medicine intermediates due to their favorable odor characteristics and solvent properties. From an environmental viewpoint, limonene is used as a benign solvent for the reuse and volume reduction of foam polystyrene in place of hydrocarbons. Recently these natural substances have been able to consider being more advantages to conventional petroleum solvents.

In a process design of the operative separation of terpenes from terpentine oil as well as the purification of terpenes, the phase equilibria for these muticomponent mixtures have an important role. So far, the experimental vapor−liquid equilibrium data for binary terpene systems,[1−3] (terpene + hydrocarbon) systems,[4] and (terpene + 1-butanol or 1-pentanol) systems[5] have been reported previously. For the liquid−liquid equilibrium data containing terpene components, the ternary (pinene + Δ_3-carene + acetonitrile, nitromethane, or dimethylformamide) systems at 298.15 K,[6] (water + ethanol + citral or limonene) systems at 293 K,[7] and (limonene + ethanol + H_2O) systems from 293.15 K to 323.15 K[8] have been found in the literature.

We further study that the solubilities of terpenes (α-pinene, β-pinene, or limonene) in aqueous methanol solutions where the terpenes are readily soluble in alcohols except for methanol, but partially soluble in methanol, and almost insoluble in water at ambient temperatures. In the present paper, to understand the multicomponent phase equilibrium behaviors of the terpenes in the (water + methanol) mixtures and the distribution of methanol between terpene and water phases, we measured the mutual solubilities of the terpenes dissolved in water or methanol and their multicomponent liquid−liquid equilibria (LLE) and tie-lines of ternary and quaternary mixtures at 298.15 K.

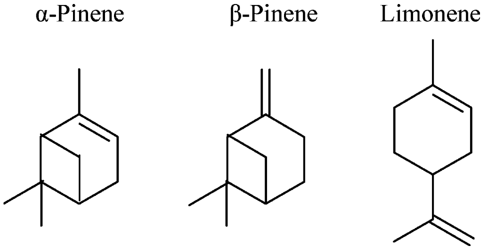

Figure 1. Structures of α-pinene, β-pinene, and limonene.

Table 1. Densities ρ of Pure Components at 298.15 K

	ρ/(g·cm^{-3})			ρ/(g·cm^{-3})	
component	measd	lit[9]	component	measd	lit[9]
water	0.99692	0.99705	(−)-α-pinene	0.85388	0.8539
methanol	0.78662	0.78637	(−)-β-pinene	0.86684	0.8667
dodecane	0.74541	0.74518	(+)-limonene	0.83731	0.8384
toluene	0.86235	0.86219			

Experimental Section

Materials. (−)-α-Pinene (abbreviated hereafter as α-pinene), (−)-β-pinene (β-pinene), and *R*(+)-limonene (limonene) were supplied by Fluka Chemika (Sigma-Aldrich Chemie GmbH) with minimum purities of 99 %, 99 %, and 98 % as stated by a GC assay. Methanol, water, dodecane, and toluene were obtained from Wako Pure Chemical, whose purities in mass were 99.8 %, 99.99 %, 99.0 %, and 99.8 %. All chemicals were used without further purification. Densities of the chemicals used for the experimental work, measured with an Anton Paar (DMA58) densimeter at 298.15 K, agree well with the literature values[9] as shown in Table 1.

Procedure and Experimental Data. Binary, ternary, and quaternary LLE for the (water + methanol + α-pinene or β-pinene or limonene) systems were measured at the temperature 298.15 K. The mutual solubility measurement on terpene in water was carried out using the extraction method[10] because the solubilities of terpene in water are quite low, generally on the order of parts per million by

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Table 2. Mutual Solubilities (x) in Mole Fraction of Binary Systems at 298.15 K

no.	binary system	(1) in (2) x_1	(2) in (1) x_2	lit[11]
1	water (1) + α-pinene (2)	0.0040	6.96×10^{-7}	
2	water (1) + β-pinene (2)	0.0058	1.68×10^{-6}	
3	water (1) + limonene (2)	0.0052	1.63×10^{-6}	1.82×10^{-6}
4	methanol (1) + α-pinene (2)	0.1683	0.0861	
5	methanol (1) + β-pinene (2)	0.2373	0.1165	
6	methanol (1) + limonene (2)	0.2872	0.1200	

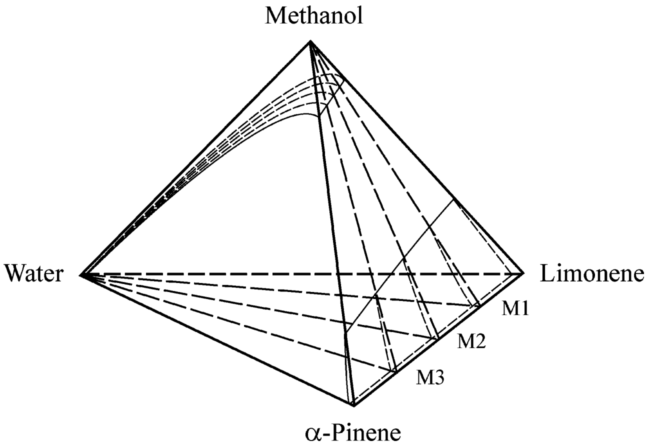

Figure 2. Schematic representation of liquid−liquid equilibrium to the quaternary system (water + methanol + α-pinene + limonene).

Table 3. Liquid−Liquid Equilibrium Tie-Line Data of Ternary Systems at 298.15 K

phase I x_1	phase I x_2	phase I x_3	phase II x_1	phase II x_2	phase II x_3
Water (1) + Methanol (2) + α-Pinene (3)					
0.8992	0.1008	0.0000	0.0040	0.0011	0.9949
0.7445	0.2555	0.0000	0.0041	0.0036	0.9923
0.6324	0.3675	0.0001	0.0040	0.0069	0.9891
0.5432	0.4563	0.0005	0.0041	0.0097	0.9862
0.4319	0.5668	0.0013	0.0042	0.0130	0.9828
0.3859	0.6120	0.0021	0.0043	0.0160	0.9797
0.3362	0.6602	0.0036	0.0044	0.0202	0.9754
0.2715	0.7223	0.0062	0.0045	0.0252	0.9703
0.2187	0.7725	0.0088	0.0045	0.0373	0.9582
0.1232	0.8543	0.0225	0.0045	0.0475	0.9480
0.0504	0.9088	0.0408	0.0045	0.0961	0.8994
Water (1) + Methanol (2) + β-Pinene (3)					
0.8986	0.1014	0.0000	0.0058	0.0033	0.9909
0.8161	0.1839	0.0000	0.0059	0.0067	0.9874
0.6977	0.3022	0.0001	0.0062	0.0115	0.9823
0.5914	0.4081	0.0005	0.0060	0.0168	0.9772
0.4937	0.5051	0.0012	0.0062	0.0211	0.9727
0.3725	0.6243	0.0032	0.0063	0.0337	0.9600
0.2738	0.7183	0.0079	0.0072	0.0449	0.9479
0.1712	0.8105	0.0183	0.0065	0.0731	0.9204
0.1205	0.8487	0.0308	0.0065	0.0961	0.8974
0.0549	0.8899	0.0552	0.0070	0.1599	0.8331
Water (1) + Methanol (2) + Limonene (3)					
0.9024	0.0976	0.0000	0.0052	0.0046	0.9902
0.8180	0.1820	0.0000	0.0052	0.0084	0.9864
0.7057	0.2942	0.0001	0.0056	0.0116	0.9828
0.6053	0.3945	0.0002	0.0055	0.0165	0.9780
0.4881	0.5111	0.0008	0.0052	0.0247	0.9701
0.3873	0.6104	0.0023	0.0056	0.0301	0.9643
0.2995	0.6954	0.0051	0.0061	0.0419	0.9520
0.2037	0.7837	0.0126	0.0055	0.0607	0.9338
0.1493	0.8314	0.0193	0.0054	0.0819	0.9127
0.1071	0.8629	0.0300	0.0055	0.1049	0.8896
0.0352	0.9023	0.0625	0.0052	0.1767	0.8181
Water (1) + α-Pinene (2) + Limonene (3)					
1.0000	5.90×10^{-7}	4.27×10^{-7}	0.0043	0.7471	0.2486
1.0000	3.75×10^{-7}	8.96×10^{-7}	0.0046	0.4975	0.4979
1.0000	1.61×10^{-7}	1.32×10^{-6}	0.0049	0.2485	0.7466
Methanol (1) + α-Pinene (2) + Limonene (3)					
0.9083	0.0788	0.0129	0.1888	0.7018	0.1094
0.9030	0.0688	0.0282	0.2012	0.5739	0.2249
0.8986	0.0578	0.0436	0.2216	0.4486	0.3298
0.8930	0.0452	0.0618	0.2431	0.3219	0.4350
0.8871	0.0315	0.0814	0.2568	0.2094	0.5338
0.8851	0.0164	0.0985	0.2716	0.1018	0.6266

weight. The solubility of terpene in water was obtained by the following procedure. Approximately 50 mL of terpene and 250 mL of pure water loaded in an equilibrium glass flask were placed in a temperature-controlled water bath at $T = (298.15 \pm 0.01)$ K, stirred vigorously by using a magnetic stirrer for 24 h, and then settled in the bath for 72 h to ensure the separation of two layers. A sample about 75 mL in volume was taken from the separated water layer. The sample mixture weighted was added to approximately 2 mL of dodecane solution containing a known amount of toluene. The sample mixture was mixed enough in a flask by using a magnetic stirrer for 3 h. After the water and dodecane layers were separated, 5 μL sample of the dodecane layer was used to analyze the concentration of terpene in water by a GLC (Shimadzu, GC-8A) equipped with a thermal conductivity detector. The oven temperatures of injection port and detector were set at 513 K and were increased from 403 K to 513 K at a rate of 32 °C/min. The helium flow rates for both separation and reference columns were set at 50 mL/min. A stainless steel column packed with Porapak Q with 3 mm i.d. and 2 m in length was used to separate every component. The peak area of the components, detected to analyze with a chromatopac (Shimadzu, C-R6A), was calibrated by gravimetrically weighed mixtures. The mutual solubilities of limonene in water were in good agreement with the literature within experimental uncertainties.[11]

Multicomponent LLE measurements except for the mutual solubility of terpene in water were carried out as follows. About 80 mL of the mixture was loaded in the equilibrium cell, stirred vigorously by using a magnetic stirrer for 5 h, and settled for 5 h enough to ensure phase separation. 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 two layers were withdrawn with a precision Hamiltion syringe, and their compositions were analyzed by the GLC. 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.

Figure 2 represents schematically a tetrahedron to show the quaternary LLE surface for the (water + methanol + α-pinene + limonene) system. Following Sørensen, the quaternary envelope is classified by type 4, which is made of four ternary LLE by type 2 on the tetrahedron surface. The quaternary mixtures for the tie-line measurements were prepared by mixing the binary miscible mixtures (α-pinene + limonene) whose compositions are M_1, M_2, and M_3 with water and then methanol stepwise to cover the two-phase envelope. The three quaternary planes are called by

Table 4. Liquid−Liquid Equilibrium Tie-Line Data of Water (1) + Methanol (2) + α-Pinene (3) + Limonene (4) System at 298.15 K

phase I (aqueous)			phase II (organic)		
x_1	x_2	x_3	x_1	x_2	x_3
		M$_1$ (x_3/x_4 = 1/3)			
1.0000	0.0000	0.0000	0.0049	0.0000	0.2479
0.8370	0.1630	0.0000	0.0048	0.0056	0.2463
0.6911	0.3089	0.0000	0.0044	0.0121	0.2458
0.5341	0.4653	0.0001	0.0046	0.0185	0.2433
0.3826	0.6157	0.0004	0.0044	0.0296	0.2406
0.2361	0.7552	0.0020	0.0049	0.0501	0.2345
0.1528	0.8286	0.0044	0.0059	0.0754	0.2296
0.1089	0.8626	0.0068	0.0049	0.0989	0.2224
0.0682	0.8888	0.0103	0.0052	0.1280	0.2161
0.0394	0.8977	0.0158	0.0048	0.1627	0.2070
0.0000	0.8868	0.0281	0.0000	0.2589	0.1860
		M$_2$ (x_3/x_4 = 1/2)			
1.0000	0.0000	0.0000	0.0046	0.0000	0.4975
0.8408	0.1592	0.0000	0.0045	0.0045	0.4954
0.6988	0.3012	0.0000	0.0045	0.0090	0.4945
0.5288	0.4705	0.0003	0.0047	0.0160	0.4891
0.3729	0.6243	0.0014	0.0045	0.0258	0.4845
0.2575	0.7368	0.0028	0.0050	0.0419	0.4764
0.1514	0.8329	0.0079	0.0055	0.0690	0.4615
0.1185	0.8589	0.0115	0.0048	0.0837	0.4546
0.0733	0.8828	0.0213	0.0047	0.1087	0.4435
0.0468	0.8965	0.0279	0.0044	0.1353	0.4307
0.0000	0.8951	0.0528	0.0000	0.2255	0.3868
		M$_3$ (x_3/x_4 = 3)			
1.0000	0.0000	0.0000	0.0043	0.0000	0.7445
0.8685	0.1315	0.0000	0.0041	0.0029	0.7436
0.6955	0.3045	0.0000	0.0045	0.0087	0.7422
0.5454	0.4541	0.0004	0.0045	0.0126	0.7393
0.3975	0.6010	0.0011	0.0048	0.0225	0.7322
0.2673	0.7263	0.0049	0.0047	0.0357	0.7224
0.1674	0.8163	0.0123	0.0048	0.0564	0.7046
0.1291	0.8480	0.0176	0.0045	0.0702	0.6969
0.0844	0.8793	0.0265	0.0047	0.0913	0.6794
0.0415	0.9040	0.0410	0.0046	0.1328	0.6520
0.0000	0.9043	0.0715	0.0000	0.2039	0.6014

M$_1$, M$_2$, and M$_3$. Tables 2 to 4 include the experimental mutual solubilities of the (water + terpene) and (methanol + terpene) systems; ternary liquid−liquid equilibrium tie-line compositions for the (water + methanol + terpene), (methanol + α-pinene + limonene), and (water + α-pinene + limonene) systems; and one quaternary (water + methanol + α-pinene + limonene) system at 298.15 K, respectively.

Calculated Results and Discussion

Extended UNIQUAC and Modified UNIQUAC Models. To represent the experimental quaternary LLE data as well as ternary LLE ones, we use two activity−coefficient models with binary and ternary parameters; the extended UNIQUAC proposed by Nagata[12] and the modified UNIQUAC proposed by Tamura et al.[13]

The excess molar Gibbs energy of the extended UNIQUAC model can be expressed by the sum of the two contributions: the combinatorial term accounts for molecular interactions due to molecular different size and shape, and the residual term accounts for the two-body interaction between unlike binary components and the additional multibody interactions among multicomponent components. The segment fraction (ϕ_i) and surface fraction (θ_i) of component i are expressed as

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{1}$$

Table 5. Structural Parameters for Pure Components

			extended UNIQUAC	modified UNIQUAC
components	r^a	q^a	q'^b	q'^c
water	0.920	1.400	0.960	1.283
methanol	1.430	1.430	1.000	1.482
α-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
β-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
limonene	6.278	5.208	$q^{0.2}$	$q^{0.75}$

[a] Refs 17 and 18. [b] Ref 12. [c] Ref 13.

where r_i is the molecular geometric volume parameter of pure component, and q_i is the molecular geometric surface parameter of pure component that can be estimated from the Bondii's method. In the extended UNIQUAC equation, the interaction correction factor of pure component q_i' was used to improve the phase equilibrium representation. The pure component molecular parameters (r and q) and the correlation factor (q') fixed in the model are listed in Table 5.

The modified UNIQUAC model couples with the combinatorial correction term of Gmehling et al.[14] and the residual term of the extended UNIQUAC model[15] involving a universal value of the third parameter C as derived by Maurer and Prausnitz.[16] In the modified UNIQUAC model, the corrected segment fraction (ϕ_i') is given by

$$\phi_i' = \frac{x_i r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{2}$$

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

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{CT}\right) \tag{3}$$

where a_{ij} can be obtained from binary experimental phase equilibrium data, and C was set to 1 for the extended UNIQUAC and to 0.65 for the modified UNIQUAC. The detailed expressions of activity coefficient of the two models can be reviewed from the literature.[12,13]

Calculated Results. The binary energy parameters (a_{ij}) for the miscible mixtures were obtained from vapor−liquid equilibrium data reduction using the following thermodynamic equations:

$$P y_i \Phi_i = x_i \gamma_i P_i^{\mathrm{s}} \Phi_i^{\mathrm{s}} \exp\{V_i^{\mathrm{L}}(P - P_i^{\mathrm{s}})/(RT)\} \tag{4}$$

$$\ln \Phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})P/(RT) \tag{5}$$

where P, x, y, and γ are the total pressure, the liquid-phase mole fraction, the vapor-phase mole fraction, and the activity coefficient, respectively. The pure component vapor pressure (P^{s}) was calculated by using the Antoine equation with coefficients taken from the literature.[17,18] The liquid molar volume (V^{L}) was obtained by a modified Racket equation.[19] The fugacity coefficient (Φ_i) was calculated from eq 5 using the pure and cross second virial coefficients (B_{ij}) estimated by the method of Hayden and O'Connell.[20] An optimum set of the binary energy parameters (a_{ij}) was obtained using a maximum-likelihood principle,[21] where standard deviations in the measured quantities were set as $\sigma_{\mathrm{p}} = 133.3$ Pa for pressure; $\sigma_{\mathrm{T}} = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid mole fraction; $\sigma_y = 0.003$ for vapor mole fraction.

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

no.	system (1 + 2)	T/K	N	model	a_{12}/K	a_{21}/K	δ_P/kPa	δ_T/K	$10^3\delta_x$	$10^3\delta_y$	ref
1	water + methanol	298.15	10	I	−194.68	279.5	0.1	0.0	1.0	4.0	17
				II	−306.97	292.31	1.0	0.1	1.5	14.7	
2	α-pinene + limonene	429.95−448.45	18	I	−88.99	78.78	0.5	0.2	2.2	15.3	2
				II	−71.38	67.33	0.5	0.2	2.2	15.4	
3	water + α-pinene	298.15	MS	I	1758.3	1688.9					this work
				II	921.91	1742.7					
4	water + β-pinene	298.15	MS	I	1567.0	1570.1					this work
				II	797.01	1599.4					
5	water + limonene	298.15	MS	I	1659.3	1722.3					this work
				II	808.98	1773.5					
6	methanol + α-pinene	298.15	MS	I	337.77	1228.5					this work
				II	57.228	1151.1					
7	methanol + β-pinene	298.15	MS	I	309.65	1159.5					this work
				II	40.504	1098.6					
8	methanol + limonene	298.15	MS	I	368.65	1254.1					this work
				II	43.003	1053.7					

[a] N, no. of data points; MS, mutual solubility; I, extended UNIQUAC; II, modified UNIQUAC.

Table 7. Calculated Results for Five Ternary Liquid−Liquid Equilibria at 298.15 K

				RMS[a]	RMS[b]	ternary parameters		
no.	system (1 + 2 + 3)	N	model	(%)	(%)	τ_{231}	τ_{132}	τ_{123}
1	water + methanol + α-pinene	13	I	1.57	0.63	−0.1410	−1.0997	0.4799
			II	1.50	0.64	−0.4668	0.0925	0.1696
2	water + methanol + β-pinene	12	I	1.34	0.43	−0.2047	−0.5487	0.3342
			II	1.15	0.30	−0.4977	−0.0370	0.0223
3	water + methanol + limonene	13	I	1.81	0.26	0.0088	−0.8816	0.1005
			II	2.20	0.86	1.2152	−4.5925	0.0554
4	water + α-pinene + limonene	5	I	0.80	0.79	0.0044	0.0124	0.0128
			II	0.80	0.79	0.0011	0.0010	0.0010
5	methanol + α-pinene + limonene	8	I	0.30	0.25	0.0011	0.0009	0.0011
			II	0.33	0.23	0.0003	0.0014	0.0274
average			I	1.16	0.47			
			II	1.20	0.56			

[a] Predicted with binary parameters. [b] Corrected with binary and ternary parameters.

A set of the energy parameters was obtained from mutual solubilities by solving eqs 6 and 7 with a Newton−Raphson iterative method:

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{6}$$

$$\sum_i x_i^{\mathrm{I}} = \sum_i x_i^{\mathrm{II}} = 1 \tag{7}$$

where I and II represent equilibrium phases. The binary parameters obtained by the extended and modified UNIQUAC models are listed in Table 6.

A ternary parameter that has taken into account three body interactions (τ_{ijk}) was used for the correlation of ternary LLE. The ternary parameters can be obtained fitting the models to experimental ternary LLE by minimizing the objective function:

$$F = 100\{\sum_k^n \sum_i^3 \sum_j^2 (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2/M\}^{0.5} \tag{8}$$

where M denotes the total number of phases $j = 1$ and 2, tie-lines $k = 1$ to n, components $i = 1$, 2, to m, and which is given by $M = 2nm$. The deviation between experimental and calculated values is expressed by the root-mean-square deviation (RMS), which can be defined by eq 8.

The results predicted using only binary parameters given in Table 6 are shown in Table 7. The mean RMS deviations between the experimental and predicted results were 1.16 % and 1.20 % in terms of the extended and modified UNIQUAC models. Table 7 summarizes the correlated results for the ternary LLE systems and the values of ternary parameters obtained fitting the models to the experimental ternary LLE systems. The average RMS deviations in the ternary correlations obtained by the extended and modified UNIQUAC models were 0.43 % and 0.56 %, respectively. Figure 3 shows good agreement between the experimental and correlated results for four sets of the ternary systems constituting the quaternary (water + methanol +α-pinene + limonene) system at 298.15 K.

Table 8. Calculated Results for Quaternary Liquid−Liquid Equilibria at 298.15 K

				RMS[a]	RMS[b]
system (1 + 2 + 3 + 4)	type	N	model	(%)	(%)
water + methanol + α-pinene + limonene	IV	33	I	1.12	0.35
			II	1.18	0.59

[a] Predicted with binary parameters. [b] Predicted with binary and ternary parameters

In a representation of the quaternary (water + methanol + α-pinene + limonene) system, two kinds of prediction method were carried out. One is predicted using the extended and modified UNIQUAC models by only the binary parameters, and the other is done by the binary and ternary parameters as shown in Tables 6 and 7. Table 8 shows the predicted results using both models in terms of the two methods. The RMS deviations between the experimental and predicted results with only the binary parameters were 1.12 % and 1.18 %, and those with binary and ternary parameters were 0.35 % and 0.59 % for the extended and modified UNIQUAC models, respectively. Figure 4 compares the experimental and calculated results

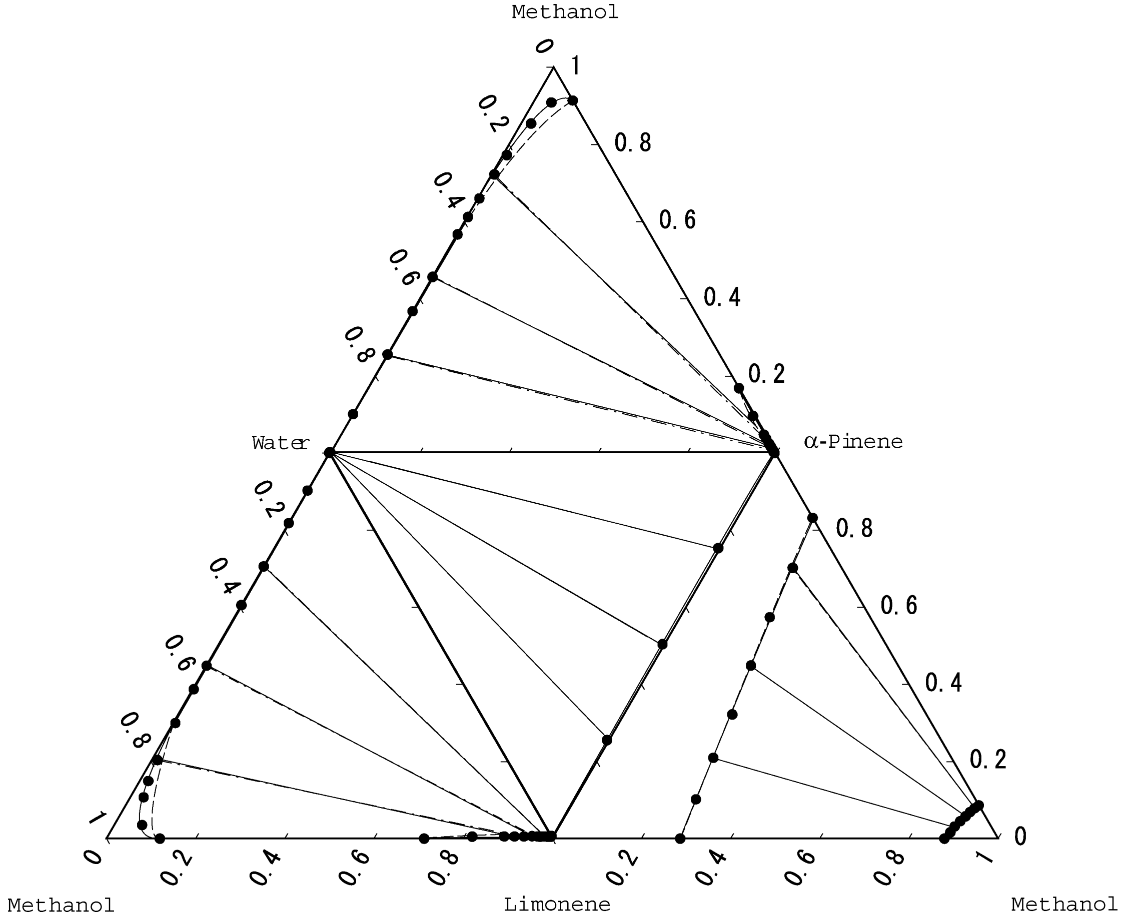

Figure 3. Liquid−liquid equilibria of four ternary mixtures making up (water + methanol + α-pinene + limonene) at 298.15 K. Experimental tie-line (●); predicted (- -) by extended UNIQUAC with binary parameters from Table 6; correlated (—), by extended UNIQUAC with binary and ternary parameters from Tables 6 and 7.

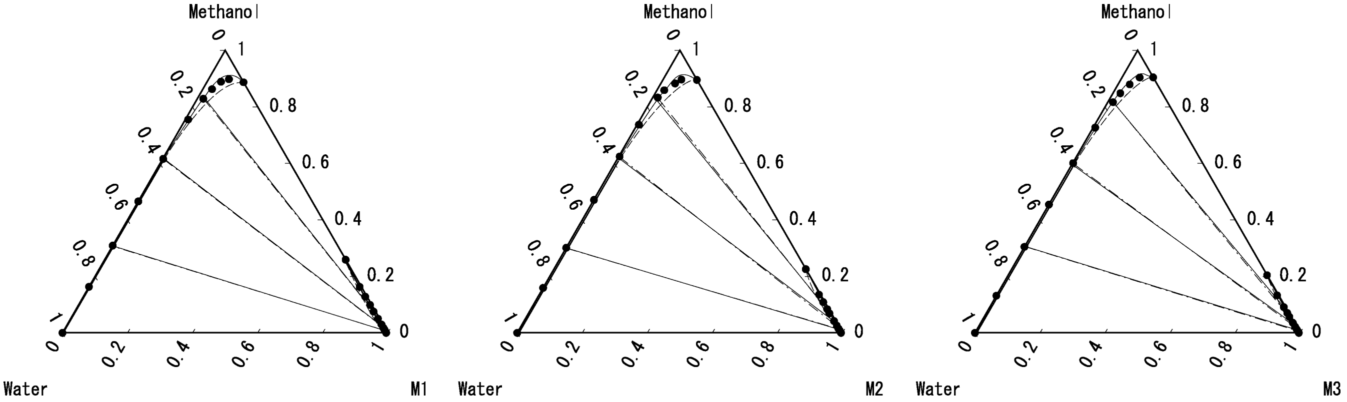

Figure 4. Liquid−liquid equilibria on the planes M1, M2, and M3 of quaternary (water + methanol + α-pinene + limonene) system at 298.15 K. Experimental tie-line (●); predicted (- -) by extended UNIQUAC with binary parameters from Table 6; predicted (—) by extended UNIQUAC with binary and ternary parameters from Tables 6 and 7.

for the quaternary LLE of the (water + methanol + α-pinene + limonene) system, which are plotted on planes M_1, M_2, and M_3 illustrated in Figure 2. Satisfactory results were obtained in the prediction of the quaternary LLE system by means of the binary and ternary parameters in comparison with only the binary parameters. The both models could provide a good representation of the quaternary LLE for the (water + methanol + α-pinene + limonene) system.

Figure 5 compares the experimental and calculated distribution coefficients of methanol in the ternary (water + methanol + terpene) systems, which is define by x_{MeOH} (aqueous phase)/x_{MeOH} (organic phase). The magnitude of the distribution coefficients of methanol decreases in order of α-pinene, β-pinene, and limonene for the ternary (water + methanol + terpene) systems. The results for the distribution coefficients of methanol calculated by the extended and modified UNIQUAC models were in a fair agreement with the experimental values.

Conclusions

Mutual solubilities of terpenes (α-pinene, β-pinene, and limonene) in water and methanol measured at $T = 298.15$ K were presented. Five systems for the ternary LLE including the terpene with water and methanol, and the terpenes with water or methanol, and one quaternary LLE

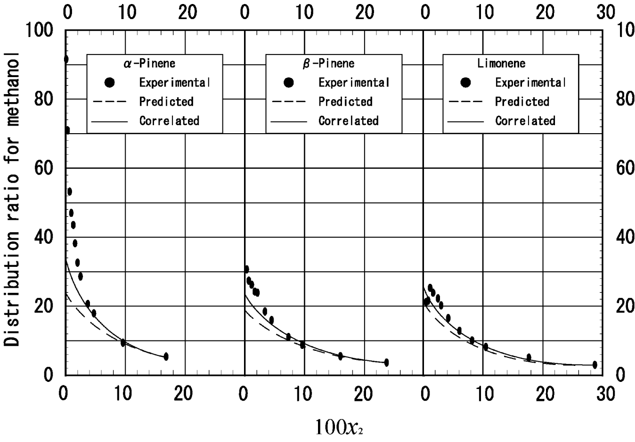

Figure 5. Experimental and calculated (extended UNIQUAC) distribution ratios for methanol (2) of three ternary (water + methanol + terpene) liquid−liquid equilibria at 298.15 K. Distribution coefficient for methanol defined by x_{MeOH} (aqueous phase)/x_{MeOH} (organic phase).

system formed by the binaries and ternaries were measured at T = 298.15 K. The experimental ternary LLE results were well-correlated by using ternary parameters and the experimental quaternary LLE data were satisfactorily predicted using the modified UNIQUAC model as well as the extended UNIQUAC model by including binary and ternary parameters.

Literature Cited

(1) Rodrigues, M. F.; Bernardo-Gil, M. G.vapor−liquid equilibrium of binary mixtures of limonene with α-pinene and β-pinene at reduced pressures. *J. Chem. Eng. Data* **1995**, *40*, 1193−1995.

(2) Bernardo-Gil, M. G.; Ribeito, M. A. Vapor−liquid equilibria of binary systems based on pine resin. *Fluid Phase Equilib.* **1989**, *53*, 15−22.

(3) Bernardo-Gil, M. G.; Albertina Ribeiro, M. Vapor−liquid equilibria of binary mixtures of β-pinene with limonene and *p*-cymene at atmospheric pressure. *Fluid Phase Equilib.* **1993**, *85*, 153−160.

(4) Reich, R.; Sanhueza, V. Vapor−liquid equilibria for α-pinene and β-pinene and for these pinenes with heptane, cyclohexane, 1-octene and cyclohexene. *Fluid Phase Equilib.* **1992**, *77*, 313−325.

(5) Reich, R.; Sanhueza, V. Vapor−liquid equilibria for α-pinene and β-pinene with 1-butanol and 1-pentanol. *Fluid Phase Equilib.* **1992**, *78*, 239−248.

(6) Antosik, M.; Stryjek, R. Liquid−liquid equilibria in ternary α-pinene + Δ_3-carene + polar compound systems. *Fluid Phase Equilib.* **1992**, *71*, 321−331.

(7) Gironi, F.; Gonzalez Farias, I.; Lamberti, L. Liquid−liquid equilibria for the water + ethanol + citral and water + ethanol + limonene systems at 293 K. *J. Chem. Eng. Data* **1995**, *40*, 578−581.

(8) Cháfer, A.; Muñoz, R.; Burguet, M. C.; Berna, A. The influence of the temperature on the mixture limonene + ethanol + H_2O. *Fluid Phase Equilib.* **2004**, *224*, 251−256.

(9) Riddick, J. A.; Bunger, W. B.; Sakano, T. K.; *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986; pp 74, 190, 132, 137, 188, 189, 184.

(10) Polak, J.; Lu, B. C.-Y. Mutual solubilities of hydrocarbons and water at 0 and 25 °C. *Can. J. Chem.* **1973**, *51*, 4018−4023.

(11) Massaldi, H. A.; King, C. J. Simple technique to determine solubilities of sparingly soluble organics: solubility and activity coefficients of D-limonene, *n*-butylbenzene, and *n*-hexyl acetate in water and sucrose solutions. *J. Chem. Eng. Data* **1973**, *18*, 393−397.

(12) Nagata. I. Modification of the extended UNIQUAC model for ternary and quaternary liquid−liquid equilibrium calculations. *Fluid Phase Equilib.* **1989**, *51*, 53−70.

(13) Tamura, K.; Chen, Y.; Tada, K.; Yamada, T.; Nagata. I. Representation of multicomponent liquid−liquid equilibria for aqueous and organic solutions using a modified UNIQUAC model. *J. Solution Chem.* **2000**, *29*, 463−488.

(14) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(15) Nagata. I. Modification of the extended UNIQUAC model for correlating liquid−liquid quaternary equilibrium data. *Fluid Phase Equilib.* **1990**, *54*, 191−206.

(16) Maurer, G.; Prausnitz, J. M. On the derivation and extension of the UNIQUAC equation. *Fluid Phase Equilib.* **1978**, *2*, 91−99.

(17) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection, Vol. I, Part 1, Aliphatic Hydrocarbons*; DECHEMA: Frankfurt/Main, 1977; p 42.

(18) Gmehling, J.; Onken, U.; Arlt, W.; *Vapor−Liquid Equilibrium Data Collection, Vol. I, Part 6b, Aliphatic Hydrocarbons*; DECHEMA: Frankfurt/Main, 1980; pp 491, 362.

(19) Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.

(20) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficient. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

(21) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor−Liquid and Liquid−Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.

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