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Liquid−Liquid Equilibria of Water + Pentan-1-ol + 2,6,6-Trimethylbicyclo[3.1.1]hep-2-ene or 6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane at (293.15, 303.15, 313.15, and 323.15) K

Xuejun Huang, Yao Chen,* Changwei Wang, and Hui Wang

Department of Chemistry, Jinan University, Guangzhou, 510632, China

ABSTRACT: Mutual solubility data of water + pentan-1-ol and liquid−liquid equilibrium of water + pentan-1-ol +2,6,6-trimethylbicyclo[3.1.1]hep-2-ene (α-pinene) and water + pentan-1-ol + 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene) have been measured experimentally at (293.15, 303.15, 313.15, and 323.15) K under atmospheric pressure. The estimated uncertainty of phase composition and temperature were about (0.0005 and 0.05) K, respectively. The experimental ternary liquid−liquid equilibrium data have been simultaneously predicted and correlated by the extended and modified UNIQUAC models.

■ INTRODUCTION

Pinenes are natural organic substances that are typically presented in wood turpentine. The main constituents of the liquid phase obtained when steam-distillation is applied to the pine rosin are α-pinene, β-pinene, and limonene. α-Pinene, β-pinene, and their derivatives are widely used in detergent, cosmetic, food, and pharmaceutical due to their useful and functional characteristics and solvent properties.[1] Alcoholic extracts of citrus essential oils are popularly used in industry. In the solvent extraction, methanol and ethanol are often used because pinenes can be easily soluble in the alcohols but insoluble in water. A literature survey shows that there are some works on liquid−liquid equilibria (LLE) data for systems containing pinenes, water, and some alcohols or acetone.[1−4] In order to examine multicomponent phase equilibrium behaviors of α-pinene and β-pinene in the (water + pentan-1-ol) mixtures and influence of temperature on the distribution of pentan-1-ol between aqueous and organic phases, we measured the tie-line compositions for the ternary systems of (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) mixtures at (293.15, 303.15, 313.15, and 323.15) K. The experimental LLE results were correlated by means of the extended and modified UNIQUAC models[5,6] including both binary and ternary parameters coming from multicomponent intermolecular interactions. The vapor−liquid equilibria (VLE) data for the binary systems of (pentan-1-ol + α-pinene or β-pinene) and mutual solubility data for the binary systems of (water + α-pinene or + β-pinene) have been available from the literatures.[7,2] Mutual solubility data for the binary system of (water + pentan-1-ol) were measured in this work.

■ EXPERIMENTAL SECTION

Materials. α-Pinene, β-pinene, and pentan-1-ol were obtained from Aladdin Company, with minimum mass fraction of 0.980, 0.980, and 0.990, respectively. Bidistilled water was used. Gas chromatography analysis gave mass fractions of 0.9910 for α-pinene, 0.9900 for β-pinene, 0.9954 for pentan-1-ol, and 0.9999 for water.

Apparatus and Procedures. Liquid−liquid equilibria measurements for the ternary systems (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) mixtures were carried out at (293.15, 303.15, 313.15, and 323.15) K. The temperature uncertainty was ± 0.05 K. A solution of volume from (55 to 100) cm^3 was loaded into the glass equilibrium cell placed in the thermostatted water bath at an expected temperature. The mixture was then stirred vigorously by magnetic stirrer for 5 h and then allowed to settle for 5 h, which was sufficient to separate into two liquid phases. The aqueous and organic phases were analyzed by a gas chromatograph (GC-14C) equipped with a thermal conductivity detector. The temperatures of the injection system and detector were set at 513.15 K, respectively. The initial and final temperatures of the oven were kept at (378.15 and 503.15) K, respectively. The hydrogen flow rates for both the separation and the reference columns were set at $1\ cm^3\cdot s^{-1}$. Good separation of the three components was obtained on a 3 m in length stainless steel column packed with Porapak Q. The peak areas of the components, detected with a chromatopac (N2000), were calibrated by gravimetrically weighed mixtures. Three analyses at least for each sample were made to obtain a mean value. The estimated uncertainty of the mole fraction was about 0.0005.

The LLE data for the ternary systems of (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) mixtures at (293.15, 303.15, 313.15, and 323.15) K and atmospheric pressure are presented in Tables 1 and 2. All concentrations

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Table 1. Equilibrium Phase Compositions for Ternary Mixtures of Water(1) + Pentan-1-ol(2) + α-Pinene(3) at (293.15, 303.15, 313.15, and 323.15) K, x_1^{I}, x_2^{I}, x_3^{I}, x_1^{II}, x_2^{II}, and x_3^{II}

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
T = 293.15 K					
0.0069	0.2198	0.7733	0.9983	0.0017	0.0000
0.0407	0.3581	0.6012	0.9982	0.0018	0.0000
0.0586	0.4745	0.4669	0.9981	0.0019	0.0000
0.1003	0.5245	0.3752	0.9980	0.0020	0.0000
0.1182	0.5649	0.3169	0.9979	0.0021	0.0000
0.1821	0.5973	0.2206	0.9978	0.0022	0.0000
0.2193	0.6306	0.1501	0.9976	0.0024	0.0000
0.2553	0.6349	0.1098	0.9975	0.0025	0.0000
T = 303.15 K					
0.0153	0.2386	0.7461	0.9985	0.0015	0.0000
0.0312	0.3104	0.6584	0.9984	0.0016	0.0000
0.0325	0.3897	0.5778	0.9983	0.0017	0.0000
0.0791	0.5107	0.4102	0.9982	0.0018	0.0000
0.0982	0.5449	0.3569	0.9981	0.0019	0.0000
0.1960	0.5937	0.2103	0.9980	0.0020	0.0000
0.2878	0.6237	0.0885	0.9978	0.0022	0.0000
T = 313.15 K					
0.0540	0.2107	0.7353	0.9987	0.0013	0.0000
0.0957	0.3553	0.5490	0.9986	0.0014	0.0000
0.1118	0.4449	0.4433	0.9985	0.0015	0.0000
0.1566	0.5284	0.3150	0.9984	0.0016	0.0000
0.2150	0.5802	0.2048	0.9983	0.0017	0.0000
0.2671	0.6084	0.1245	0.9982	0.0018	0.0000
T = 323.15 K					
0.0287	0.2179	0.7534	0.9990	0.0010	0.0000
0.0519	0.3676	0.5805	0.9989	0.0011	0.0000
0.1188	0.4538	0.4274	0.9987	0.0013	0.0000
0.1466	0.4787	0.3747	0.9986	0.0014	0.0000
0.1668	0.5255	0.3077	0.9985	0.0015	0.0000
0.2186	0.5606	0.2208	0.9984	0.0016	0.0000
0.2486	0.5909	0.1605	0.9982	0.0018	0.0000

are expressed in mole fractions. The results are also graphically presented in Figures 1 and 2. In these figures, the experimental tie-lines are shown for all temperatures studied as points joined by broken lines. As can be observed, temperature has little effect on the LLE of the systems.

RESULTS AND DISCUSSION

The binary energy parameters a_{ji} of the models for the miscible mixtures were obtained from the VLE data reduction according to the following thermodynamic equations by using a computer program described by Prausnitz et al.[8]

$$P y_i \varphi_i = x_i \gamma_i P_i^{\mathrm{s}} \varphi_i^{\mathrm{s}} \exp\left\{\frac{V_i^{\mathrm{L}}(P - x_i \gamma_i P_i^{\mathrm{s}})}{RT}\right\} \qquad (1)$$

Table 2. Equilibrium Phase Compositions for Ternary Mixtures of Water(1) + Pentan-1-ol(2) + β-Pinene(3) at (293.15, 303.15, 313.15, and 323.15) K, x_1^{I}, x_2^{I}, x_3^{I}, x_1^{II}, x_2^{II}, and x_3^{II}

organic phase			aqueous phase		
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}
T = 293.15 K					
0.3438	0.6562	0.0000	0.9951	0.0049	0.0000
0.0496	0.2246	0.7258	0.9984	0.0016	0.0000
0.0597	0.3538	0.5865	0.9982	0.0018	0.0000
0.0658	0.4576	0.4766	0.9979	0.0021	0.0000
0.0688	0.5359	0.3953	0.9978	0.0022	0.0000
0.1793	0.5803	0.2404	0.9974	0.0026	0.0000
T = 303.15 K					
0.3516	0.6484	0.000	0.9953	0.0047	0.0000
0.0336	0.2093	0.7571	0.9984	0.0016	0.0000
0.0648	0.4779	0.4573	0.9980	0.0020	0.0000
0.0891	0.5236	0.3873	0.9979	0.0021	0.0000
0.1659	0.5679	0.2662	0.9976	0.0024	0.0000
0.2440	0.5803	0.1757	0.9975	0.0025	0.0000
T = 313.15 K					
0.3592	0.6408	0.0000	0.9956	0.0044	0.0000
0.0758	0.1958	0.7284	0.9985	0.0015	0.0000
0.0880	0.3311	0.5809	0.9984	0.0016	0.0000
0.1258	0.4231	0.4511	0.9981	0.0019	0.0000
0.1988	0.4934	0.3078	0.9980	0.0020	0.0000
0.2130	0.5130	0.2740	0.9979	0.0021	0.0000
T = 323.15 K					
0.3755	0.6245	0.0000	0.9958	0.0042	0.0000
0.0767	0.1864	0.7369	0.9986	0.0014	0.0000
0.0579	0.3615	0.5806	0.9985	0.0015	0.0000
0.0776	0.4567	0.4657	0.9983	0.0017	0.0000
0.1798	0.5393	0.2809	0.9980	0.0020	0.0000
0.2550	0.5506	0.1944	0.9979	0.0021	0.0000

Table 3. Structural Parameters for Pure Components

substance	r	q	q'^{a}	q'^{b}
α-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
β-pinene	6.056	4.760	$q^{0.2}$	$q^{0.75}$
water	0.920	1.400	0.960	1.283
pentan-1-ol	4.130	3.590	0.800	1.376

[a] Extended UNIQUAC model. [b] Modified UNIQUAC model.

$$\ln \varphi_i = \frac{\left(2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij}\right)P}{RT} \qquad (2)$$

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.[7,9] The liquid molar volume V^{L} was obtained by a modified Rackett equation.[10] The fugacity

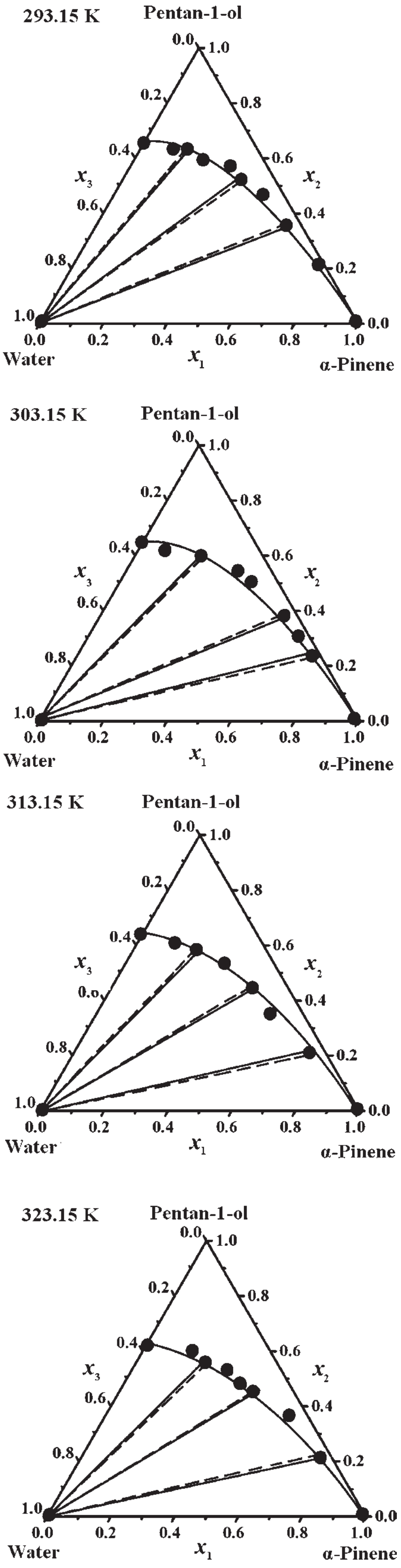

Figure 1. Experimental and calculated LLE for the ternary system of (water + pentan-1-ol + α-pinene) at (298.15, 303.15, 313.15, and 323.15) K. ●, Experimental tie-line data; ---, Predicted results by using binary parameters. ——, Correlated results by using binary and ternary parameters.

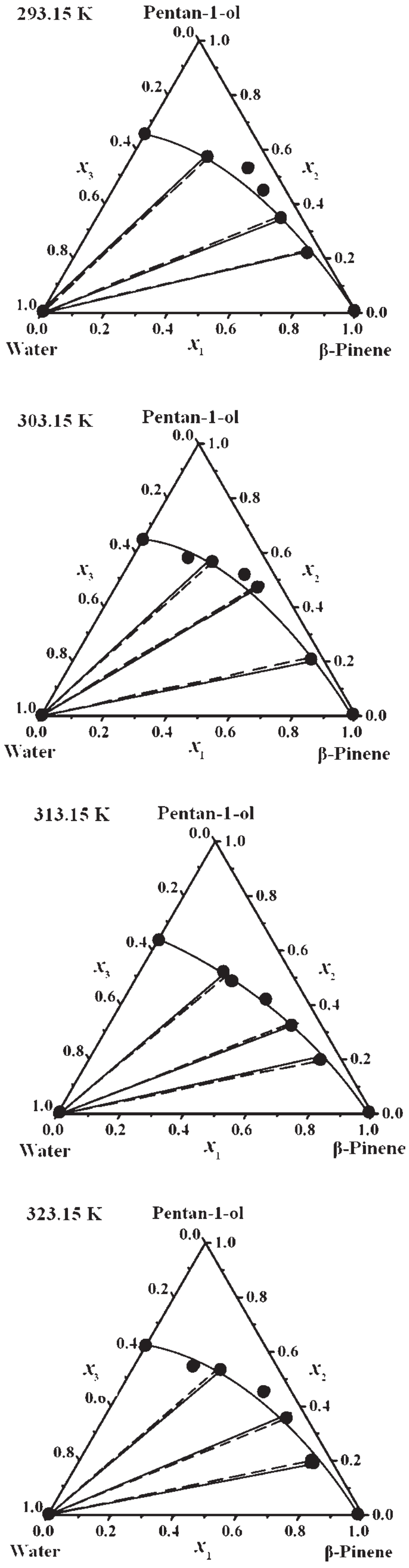

Figure 2. Experimental and calculated LLE for the ternary system of (water + pentan-1-ol + β-pinene) at (298.15, 303.15, 313.15, and 323.15) K. ●, Experimental tie-line data; ---, Predicted results by using binary parameters. ——, Correlated results by using binary and ternary parameters.

Table 4. Calculated Results of Binary Phase Equilibrium Date Reduction

system(1 + 2)	T / K	model	a_{12} / K	a_{21} / K	$\delta(P)$ / kPa	$\delta(T)$	$10^3\delta(x)$	$10^3\delta(y)$
pentan-1-ol + α-pinene	368.15	I[a]	67.56	758.36	2.19	0.04	0.90	6.50
		II[b]	27.24	686.05	2.18	0.04	0.80	6.10
pentan-1-ol + β-pinene	368.15	I	70.14	705.89	2.16	0.03	0.90	7.00
		II	28.84	643.14	2.19	0.03	0.90	7.20
water + pentan-1-ol	293.15	I	523.06	225.74				
		II	493.97	254.60				
	303.15	I	568.50	222.82				
		II	534.73	250.12				
	313.15	I	625.70	219.00				
		II	356.15	161.29				
	323.15	I	690.42	205.68				
		II	395.35	136.76				
water + α-pinene	293.15	I	1300.4	1480.6				
		II	906.45	1713.3				
	303.15	I	1344.v	1531.1				
		II	937.37	1771.8				
	313.15	I	1389.1	1581.6				
		II	968.29	1830.0				
	323.15	I	1433.5	1632.1				
		II	999.21	1888.7				
water + β-pinene	293.15	I	1113.1	1367.0				
		II	783.65	1572.6				
	303.15	I	1151.1	1413.7				
		II	810.38	1626.3				
	313.15	I	1189.1	1460.3				
		II	837.11	1679.9				
	323.15	I	1227.1	1506.9				
		II	863.84	1733.6				

[a] Extended UNIQUAC. [b] Modified UNIQUAC.

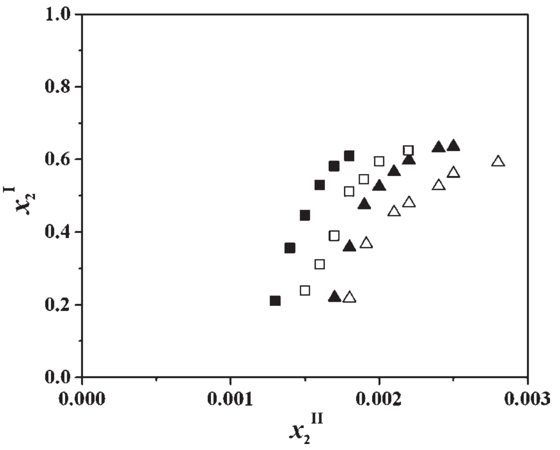

Figure 3. Mole fraction of pentan-1-ol in organic phase in the ternary system of (water + pentan-1-ol + α-pinene), x_2^{I}, mole fraction of pentan-1-ol in aqueous phase, x_2^{II}. Δ, ▲, □, ■, temperatures at (293.15, 303.15, 313.15, and 323.15) K, respectively.

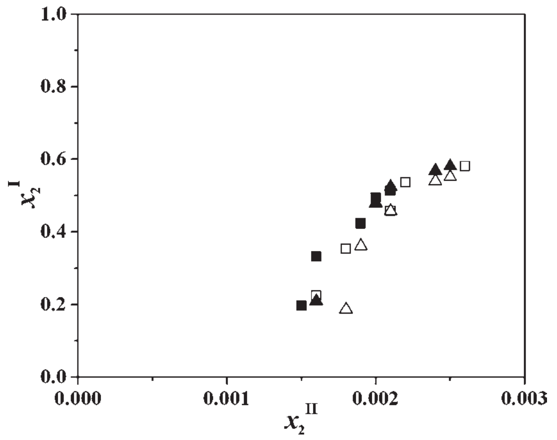

Figure 4. Mole fraction of pentan-1-ol in organic phase in the ternary system of (water + pentan-1-ol + β-pinene), x_2^{I}, mole fraction of pentan-1-ol in aqueous phase, x_2^{II}. Δ, ▲, □, ■, temperatures at (293.15, 303.15, 313.15, and 323.15) K, respectively.

coefficient φ was calculated from eq 2. The cross second virial coefficients B were estimated by the method of Hayden and O'Connell.[11] An optimum set of the binary energy parameters a_{ji} was obtained by using a computer program described by Prausnitz et al.[8] The binary energy parameters for partially

Table 5. Calculated Results of Ternary LLE at Temperatures (293.15, 303.15, 313.15, and 323.15) K

system (1 + 2 + 3)	T K	model	τ_{231}	τ_{132}	τ_{123}	rms[c,d] %	rms[c,e] %
water + pentan-1-ol + α-pinene	293.15	I[a]	1.4492	−7.8483	−0.6537	6.33	1.35
		II[b]	−0.4396	−0.2468	0.5403	2.00	0.45
	303.15	I	−0.4289	−2.2584	−0.9338	6.03	1.40
		II	−0.4076	0.1934	−0.0602	2.33	0.94
	313.15	I	0.8920	−4.6574	−1.1345	5.09	1.49
		II	0.0453	0.3405	−0.0160	0.90	0.77
	323.15	I	−0.1381	−1.8783	−1.1587	5.34	1.55
		II	−0.6703	2.1072	−1.7056	3.43	1.17
water + pentan-1-ol + β-pinene	293.15	I	0.7585	−5.8425	−1.3510	5.92	1.62
		II	−0.3668	0.1943	−0.1581	2.20	1.01
	303.15	I	1.4975	−6.7009	−1.2639	5.96	1.64
		II	−0.4721	0.2726	0.1312	2.03	1.22
	313.15	I	0.6645	−2.8949	−1.4603	4.01	1.73
		II	0.0467	1.8295	−2.4516	2.26	1.35
	323.15	I	2.0819	−6.4109	−1.4564	5.29	1.81
		II	1.6371	−4.1560	−1.2432	3.53	1.72

[a] Extended UNIQUAC. [b] Modified UNIQUAC. [c] Root-mean-square deviation. [d] Predicted results using only binary parameters. [e] Correlated results using binary and ternary parameters.

miscible binary mixtures were obtained from the mutual solubility data by solving the thermodynamic criteria and mass balance equation.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \tag{3}$$

$$\sum_i x_i^{\mathrm{I}} = 1 \text{ and } \sum_i x_i^{\mathrm{II}} = 1 \tag{4}$$

where I and II represent the equilibrium phases. In order to obtain accurate description for the ternary LLE, it is necessary to use ternary parameters. There are two effective binary interaction parameters for a pair of substances. Therefore, six effective binary interaction parameters are required for a ternary system. Ternary parameters τ_{231}, τ_{312}, and τ_{123} were determined from the experimental ternary LLE data using a simplex method[12] by minimizing the objective function:

$$F = 100\cdot\{\sum_k^n \sum_i^3 \sum_j^2 (x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2/6n\}^{0.5} \tag{5}$$

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

Table 3 shows the molecular structural volume and area parameters, r and q, for α-pinene and β-pinene, which were calculated by the method of Bondi,[13] and the others are taken from Prausnitz et al,[8] together with the interaction correction factor q', for which the value for self-associating components was taken from the literature,[5,6] whereas that for nonassociating components was set to $q' = q^{0.75}$ in the modified UNIQUAC model and $q' = q^{0.20}$ in the extended UNIQUAC model.

Table 4 lists the optimized extended and modified UNIQUAC interaction parameters (a_{ij}) in K, together with the root-mean-square deviations between experimental and calculated values: δ_{P} for pressure, δ_{T} for temperature, δ_x for liquid phase mole fraction, and δ_y for vapor phase mole fraction. Table 5 presents the ternary parameters, together with the root-mean-square deviations between the experimental and calculated tie-lines for the ternary LLE. The LLE phase diagrams at (293.15, 303.15, 313.15, and 323.15) K for the ternary systems of (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) were plotted and shown in Figures 1 and 2. Because of the introduction of ternary parameters, the root-mean-square deviations of correlation results are less than ones of prediction results for the ternary systems. Figures 1 and 2 compare the experimental tie-line data for the ternary LLE of the (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) at (293.15, 303.15, 313.15, and 323.15) K with the correlated results of the modified UNIQUAC model. Two-phase regions were observed at all temperatures investigated. The systems exhibit type II phase behavior,[14] having two pairs of partially miscible components (water + pentan-1-ol and water + α-pinene or + β-pinene) and one pair of completely miscible components (pentan-1-ol + α-pinene or + β-pinene), in the temperature range investigated. In Figures 3 and 4, the temperature effect on the distribution of pentan-1-ol between the aqueous phase and the organic phase is visualized: at higher temperature the solubility of pentan-1-ol in the organic phase increases to a larger extent than the solubility in the aqueous phase.

■ CONCLUSIONS

The experimental tie-line compositions for the ternary systems of (water + pentan-1-ol + α-pinene) and (water + pentan-1-ol + β-pinene) mixtures were successfully correlated using the extended and modified UNIQUAC activity coefficient models. The average root-mean-square deviations of correlated results for the measured systems were 1.45 mol % and 1.70 mol % for the extended UNIQUAC model, respectively, and 0.83 mol % and 1.32 mol % for the modified UNIQUAC model, respectively. The modified UNIQUAC model provides a slightly better correlation of the experimental tie-line data than the extended UNIQUAC model.

AUTHOR INFORMATION

Corresponding Author

*Fax: +86-20-85221697. E-mail: tlirq@jnu.edu.cn.

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REFERENCES

(1) Li, H.; Tamura, K. Ternary and quaternary (liquid + liquid) equilibria for (water + ethanol + α-pinene, + β-pinene, or + limonene) and (water + ethanol + α-pinene + limonene) at the temperature 298.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 1036–1041.

(2) Tamura, K.; Li, H. Mutual solubilities of terpene in methanol and water and their multicomponent liquid-liquid equilibria. *J. Chem. Eng. Data* **2005**, *50*, 2013–2018.

(3) Li, X.; Tamura, K. (Ternary liquid + liquid) equilibria for (water + acetone +α-pinene, or β-pinene, or limonene) mixtures. *J. Chem. Thermodyn.* **2010**, *42*, 1400–1405.

(4) Li, H.; Tamura, K. Ternary liquid-liquid equilibria for (water + terpene + 1-propanol or 1-butanol) systems at the temperature 298.15K. *Fluid Phase Equilib.* **2008**, *263*, 223–230.

(5) Nagata, I. Modification of the extended UNIQUAC model for correlating quaternary liquid-liquid equilibria data. *Fluid Phase Equilib.* **1990**, *54*, 191–206.

(6) 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.

(7) 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.

(8) 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.

(9) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection, Aliphatic Hydrocarbons*; DECHEMA: Frankfurt/Main, 1977; Chemistry Data Series, Vol. I, Part 6b.

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

(11) 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.

(12) Nelder, J. A.; Mead, R. A simplex method for minimization. *J. Comput.* **1965**, *7*, 308–313.

(13) Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Gases*; John Wiley & Sons, Inc., New York, 1968.

(14) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection, ternary systems*; DECHEMA: Frankfurt/Main, 1980; Vol. V, Part 2.