

Liquid–Liquid Phase Behaviors of Geraniol in Aqueous Alcohol Mixtures

Hengde Li,^{*,†} Tianfei Zhang,[†] Weiqin Fu,[†] and Kazuhiro Tamura^{*,‡}

[†]Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

[‡]Department of Chemistry and Chemical Engineering, Division of Material Engineering and Material Sciences, Graduate School of Natural Science & Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

ABSTRACT: Liquid–liquid equilibrium (LLE) data of the binodal curves and tie-line compositions were examined for ternary mixtures of (water + methanol + geraniol) and (water + ethanol + geraniol) at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$. The immiscible area of the (water + methanol + geraniol) system is wider than that for the ethanol system at the same temperature. The experimental liquid–liquid equilibrium data have been represented by using the original UNIQUAC, extended UNIQUAC, and modified UNIQUAC models.

INTRODUCTION

Monoterpenoids have acyclic, monocyclic, and bicyclic structures and exist in nature as volatile hydrocarbons, alcohols, ketones, aldehydes, ethers, and other.¹ Geraniol ($\text{C}_{10}\text{H}_{18}\text{O}$) is an acyclic monoterpene alcohol as show in Figure 1 and one the of important fragrance terpenoid. It is the primary component of rose oil, palmarosa oil, and citronella oil and many other essential oils. Geraniol (44.6 %) and linalool (28.61 %) were the main components of the essential oil from plants grown wild in Croatia.² It is well-known that various beers also contain many flavor compounds (such as geraniol) derived from barley malts, hops, yeast fermentation, and other raw materials.³ It has a rose-like odor and is commonly used in perfumes, flavors, and cosmetics. Despite many studies^{4–8} on flavor, food, and biochemistry for volatile compositions (such geraniol) all reported, there are few data on the physical and thermodynamic properties such as vapor pressure, liquid–liquid distribution, and so on. It is therefore necessary to obtain the fundamental properties in the extraction, separation, and purification processing design and control for these monoterpenoids. In view of a possible future food, cosmetic, or pharmaceutical application of the extract, it is necessary to use solvents such ethanol or water.⁹

Geraniol is insoluble in water but soluble in most common organic solvents where monoterpenes ($\text{C}_{10}\text{H}_{16}$) are partially soluble in methanol and almost insoluble in water at ambient temperatures.¹⁰ In this work, we focus on the liquid–liquid phase equilibrium properties of systems containing oxygenated monoterpenoids, geraniol in aqueous alcohol solutions. Similar researches LLE data of the system containing terpene or monoterpene and solvent (alcohol), ternary (limonene + ethanol + water) from (293.15 to 323.15) K,⁹ (linalool + ethanol + water),¹¹ (limonene + linalool + diethylene glycol),¹² and (limonene + linalool + 1,2-propanediol or 1,3-propanediol)¹³ and (water + ethanol + citral) and (water + ethanol + limonene) systems at 293 K,¹⁴ are available in the literature. On the other hand, ternary (water + methanol + terpene),¹⁰ (water + ethanol + α -pinene, or β -pinene or limonene),¹⁵ and (water + terpene + 1-propanol or 1-butanol) systems at 293 K;¹⁶ binary (methanol + α -pinene or β -pinene) and

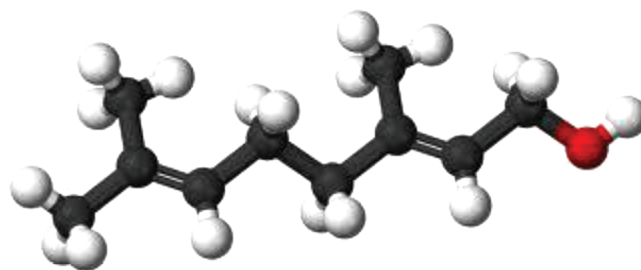


Figure 1. Chemical structure of geraniol.

ternary (methanol + ethanol + α -pinene or β -pinene);¹⁷ and binary (methanol + limonene) and ternary (methanol + ethanol + limonene) systems¹⁸ have been reported previously.

In the present paper, to examine the multicomponent phase equilibrium behaviors of geraniol in the (water + methanol) or (water + ethanol) mixture and the distribution ratios of alcohols between organic and aqueous phases, we measured the mutual solubilities of geraniol dissolved in water and their LLE and tie-line data of ternary mixtures at (283.15, 298.15, and 313.15) K.

EXPERIMENTAL SECTION

Materials. 3,7-Dimethylocta-2,6-diene-1-ol (geraniol, CAS No.106-24-1), methanol, and ethanol were supplied by Aladdin Company, with minimum purities of 0.980, 0.999, and 0.998 by mass fraction, respectively. Water (bidistilled water) with a purity higher than 0.9999 by mass fraction was used. All chemicals were used without further purification.

Procedure and Experimental Data. Ternary liquid–liquid equilibria for the (water + methanol + geraniol) and (water + ethanol + geraniol) systems were measured with a tie-line method at the temperatures (283.15, 298.15, and 313.15) K

Received: August 25, 2011

Accepted: October 29, 2011

Published: November 22, 2011

Table 1. Experimental Liquid–Liquid Equilibrium Mole Fractions x (Tie-Line Data) for the System Water (1) + Methanol (2) + Geraniol (3) at Temperature $T = (283.15, 298.15, \text{ and } 313.15)$ K and Pressure $P = 101.3 \text{ kPa}$ ^a

water rich phase (I)			geraniol rich phase (II)		
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
$T = 293.15 \text{ K}$					
0.9997	0.0000	0.0003	0.2228	0.0000	0.7772
0.9472	0.0522	0.0006	0.2309	0.0702	0.6989
0.8767	0.1228	0.0005	0.2376	0.1670	0.5954
0.8190	0.1804	0.0006	0.2575	0.2549	0.4876
0.7578	0.2403	0.0019	0.2745	0.3164	0.4091
0.7051	0.2929	0.0020	0.3004	0.3779	0.3217
0.6585	0.3382	0.0033	0.3352	0.4181	0.2467
0.5568	0.4183	0.0249	0.4535	0.4526	0.0939
$T = 298.15 \text{ K}$					
0.9999	0.0000	0.0001	0.2339	0.0000	0.7661
0.9481	0.0517	0.0002	0.2389	0.0768	0.6843
0.9110	0.0888	0.0002	0.2483	0.1398	0.6119
0.8683	0.1314	0.0003	0.2538	0.1955	0.5507
0.8043	0.1947	0.0010	0.2857	0.2814	0.4329
0.7513	0.2475	0.0012	0.3066	0.3383	0.3551
0.6851	0.3113	0.0036	0.3631	0.4032	0.2337
0.6285	0.3625	0.0090	0.4100	0.4239	0.1661
0.5855	0.3893	0.0252	0.4617	0.4262	0.1121
$T = 313.15 \text{ K}$					
0.9998	0.0000	0.0002	0.2385	0.0000	0.7615
0.9539	0.0452	0.0009	0.2493	0.0768	0.6739
0.8909	0.1089	0.0002	0.2779	0.1749	0.5472
0.8261	0.1732	0.0007	0.2823	0.2655	0.4522
0.7782	0.2205	0.0013	0.3189	0.3142	0.3669
0.7218	0.2754	0.0028	0.3518	0.3738	0.2744
0.6679	0.3245	0.0076	0.3971	0.4102	0.1927
0.6224	0.3579	0.0197	0.4896	0.3992	0.1112

^a Standard uncertainties u are $u(T) = 0.01 \text{ K}$ and $u(x) = 0.0005$.

within $\pm 0.01 \text{ K}$. The experimental procedure was described in detail previously.¹⁹ The mixtures with a volume of approximately 80 cm^3 loaded in the equilibrium cell were stirred vigorously by using a magnetic stirrer for 5 h and settled for 5 h at the constant temperature enough to separate 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 two layers were withdrawn with a precision Hamilton syringe and their compositions were analyzed by gas chromatography (Agilent 7820A) equipped with both a thermal conductivity detector (TCD) and flame ionization detector (FID) and a 16-sample automatic liquid sampler. The temperatures of injection port and TCD detector were set at 523.15 K and the oven temperatures were increased from (323 to 503) K at a rate of 0.67 K s^{-1} . The hydrogen flow rate for the separation column was set at $0.0125 \text{ cm}^3 \text{ s}^{-1}$ (split ratio 100:1). A GC capillary column (DB-624, $30 \text{ m} \times 0.25 \text{ mm}$) was used to separate every component. The peak area of the components, detected to analyze with EzChrom Elite Compact software, was calibrated by gravimetrically weighed mixtures. For each sample solution, three analyses were made to

Table 2. Experimental Liquid–Liquid Equilibrium Mole Fractions x (Tie-Line Data) for the System Water (1) + Ethanol (2) + Geraniol (3) at Temperature $T = (283.15, 298.15, \text{ and } 313.15)$ K and Pressure $P = 101.3 \text{ kPa}$ ^a

water rich phase (I)			geraniol rich phase (II)		
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}
$T = 293.15 \text{ K}$					
0.9997	0.0000	0.0003	0.2228	0.0000	0.7772
0.9783	0.0212	0.0005	0.2342	0.0600	0.7058
0.9572	0.0423	0.0005	0.2365	0.1127	0.6508
0.9250	0.0747	0.0003	0.2657	0.1982	0.5361
0.9153	0.0844	0.0003	0.2783	0.2284	0.4933
0.8904	0.1090	0.0006	0.3121	0.2894	0.3985
0.8695	0.1299	0.0006	0.3586	0.3321	0.3093
0.8458	0.1524	0.0018	0.4009	0.3540	0.2451
0.8336	0.1645	0.0019	0.4414	0.3654	0.1932
0.8268	0.1710	0.0022	0.4704	0.3613	0.1683
0.8028	0.1939	0.0033	0.5028	0.3608	0.1364
$T = 298.15 \text{ K}$					
0.9999	0.0000	0.0001	0.2339	0.0000	0.7661
0.9799	0.0199	0.0002	0.2483	0.0687	0.6830
0.9605	0.0392	0.0003	0.2711	0.1274	0.6015
0.9410	0.0587	0.0003	0.2915	0.1881	0.5204
0.9237	0.0760	0.0003	0.3098	0.2294	0.4608
0.9010	0.0985	0.0005	0.3361	0.2817	0.3822
0.8888	0.1105	0.0007	0.3634	0.3067	0.3299
0.8713	0.1279	0.0008	0.4080	0.3288	0.2632
0.8530	0.1443	0.0027	0.4455	0.3389	0.2156
0.8419	0.1556	0.0025	0.4817	0.3402	0.1781
0.7603	0.2192	0.0205	0.6597	0.2824	0.0579
$T = 313.15 \text{ K}$					
0.9998	0.0000	0.0002	0.2385	0.0000	0.7615
0.9811	0.0188	0.0001	0.2574	0.0772	0.6654
0.9632	0.0366	0.0002	0.2752	0.1397	0.5851
0.9422	0.0575	0.0003	0.3123	0.2037	0.4840
0.9316	0.0681	0.0003	0.3353	0.2468	0.4179
0.8974	0.1019	0.0007	0.3668	0.3065	0.3267
0.8839	0.1152	0.0009	0.4119	0.3242	0.2639
0.8768	0.1220	0.0012	0.4403	0.3230	0.2367
0.6634	0.2698	0.0668	0.7908	0.1929	0.0163

^a Standard uncertainties u are $u(T) = 0.01 \text{ K}$ and $u(x) = 0.0005$.

obtain a mean value. The accuracy of the tie-line measurements was estimated less than ± 0.001 in mole fraction.

Tables 1 and 2 summarize the experimental ternary LLE tie-line compositions for the both water (1) + methanol (2) + geraniol (3) and water (1) + ethanol (2) + geraniol (3) systems at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$. Figure 2 shows the experimental tie-line data for the systems containing methanol and ethanol at 298.15 K, and Figure 3 shows the experimental distribution ratios of methanol and ethanol for the systems.

■ CALCULATED RESULTS AND DISCUSSION

Activity-Coefficient Models. To represent the experimental ternary LLE data, we used the original UNIQUAC,²⁰ and two

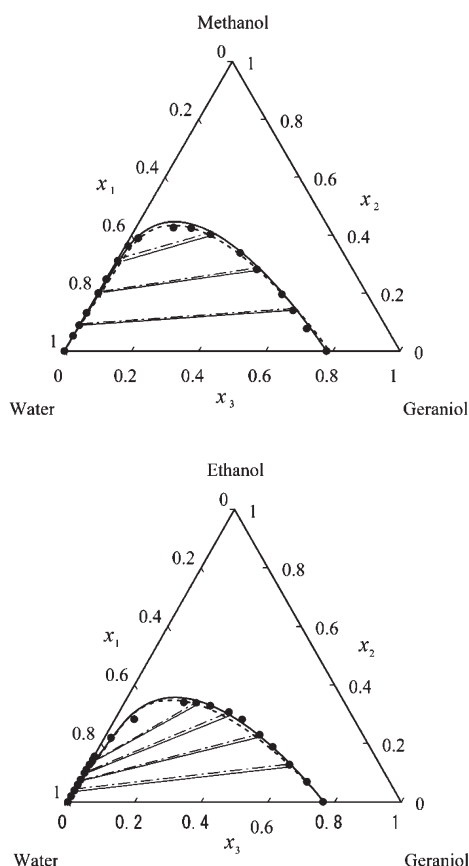


Figure 2. Liquid–liquid equilibria for ternary (water + methanol + geraniol) and (water + ethanol + geraniol) systems at 298.15 K. Experimental tie-line (●—●—●); correlation A (----); correlation B (—), by extended UNIQUAC with binary parameters from Tables 4 and 5; correlation B (—), by extended UNIQUAC with binary and ternary parameters from Tables 4 and 5.

activity-coefficient models with binary and ternary parameters: the extended UNIQUAC proposed by Nagata²¹ and the modified UNIQUAC proposed by Tamura.¹⁹

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 unlike components. The segment fraction ϕ_i and surface fraction θ_i of component i are expressed as

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

where r_i is the molecular-geometric volume parameter of pure component, q_i is the molecular-geometric surface parameter of pure component that can be estimated from the Bondi'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 ,^{22–24} and the correlation factor q' fixed in the model are listed in Table 3.

The modified UNIQUAC model couples with the combinatorial correction term of Gmehling et al.²⁵ and the residual term of the extended UNIQUAC model²⁶ involving a universal value of the third

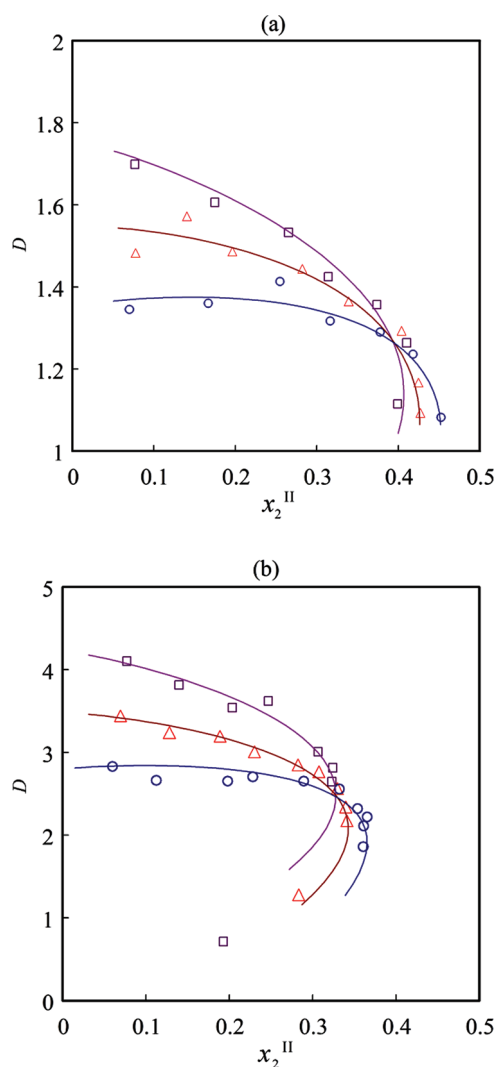


Figure 3. Comparison of experimental and calculated distribution ratios of alcohol for (a): (water + methanol + geraniol) and (b): (water + ethanol + geraniol) systems at $T = (283.15, 298.15$ and $313.15)$ K: ○, 283.15 K; △, 298.15 K; and □, 313.15 K. correlation B (—), by extended UNIQUAC with binary and ternary parameters from Tables 4 and 5.

Table 3. UNIQUAC Structural Parameters for Pure Components

component	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
ethanol	2.110	1.972	0.920	1.404
geraniol	7.034 ^d	6.100 ^d	$q^{0.2}$	$q^{0.75}$

^a UNIQUAC. ^b Extended UNIQUAC. ^c Modified UNIQUAC. ^d Calculated from Bondi's method.

parameter C as derived by Maurer and Prausnitz.²⁷ In the modified UNIQUAC model, the corrected segment fraction ϕ'_i is given by

$$\phi'_i = \frac{x_i r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \quad (2)$$

Table 4. Calculated Results of Binary Phase Equilibrium Data Reduction

system (1 + 2)	T		model ^a	a ₁₂	a ₂₁	σ(P)	σ(T)	10 ³ σ(x)	10 ³ σ(y)	ref
	K	N ^b		K	K	kPa	K			
water + methanol	298.15	10	I	-350.44	419.59	0.13	0.0	1.2	7.3	22
			II	-194.68	279.50	0.11	0.0	1.0	4.0	
			III	-306.97	292.13	1.06	0.1	1.5	14.7	
water + ethanol	298.15	12	I	-17.09	258.64	0.05	0.0	1.1	5.6	23
			II	40.36	154.29	0.13	0.0	0.9	4.8	
			III	-29.61	195.65	0.13	0.0	1.0	5.2	
water + geraniol	283.15	MS	I	124.57	298.74					this work
			II	607.55	569.56					
			III	127.84	493.12					
water + geraniol	298.15	MS	I	209.56	246.99					this work
			II	871.96	577.10					
			III	293.17	409.20					
water + geraniol	313.15	MS	I	173.61	286.28					this work
			II	765.95	606.03					
			III	209.77	468.23					

^a I, UNIQUAC; II, extended UNIQUAC; III, modified UNIQUAC. ^b N, number of experimental data MS, mutual solubility σ, deviation.

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

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

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

Calculation. The binary energy parameters a_{ij} for the miscible mixtures were obtained from vapor–liquid equilibrium data reduction using the following thermodynamic equations:

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

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

where P , x , y , and γ are the total pressure, the liquid-phase mole fraction, the vapor-phase mole fraction, and the activity coefficient. The pure component vapor pressure P^s was calculated by using the Antoine equation with coefficients taken from the literature.^{22,23} The liquid molar volume V^L was obtained by a modified Rackett equation.²⁸ 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.²⁹ An optimum set of the binary energy parameter a_{ij} was obtained using a maximum-likelihood principle,³⁰ where standard deviations in the measured quantities were set as $\sigma(P) = 133.3$ Pa for pressure; $\sigma(T) = 0.05$ K for temperature; $\sigma(x) = 0.001$ for liquid mole fraction; $\sigma(y) = 0.003$ for vapor mole fraction.

A set of the energy parameters for the immiscible mixtures was obtained from the mutual solubilities by solving eqs 6 and 7 with a Newton–Raphson iterative method.

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

$$\sum_i x_i^I = \sum_i x_i^{II} = 1 \quad (7)$$

where I and II represent equilibrium phases. The binary parameters obtained by the original UNIQUAC, extended and modified UNIQUAC models are listed in Table 4.

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

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

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 $M = 6n$ for a ternary system. The deviation between experimental and calculated values was expressed by the root-mean-square deviation rms (%), which can be defined by eq 8.

Results and Discussion. The LLE phase behavior of the ternary mixtures measured show a type I for the (water + methanol or ethanol + geraniol) systems according to the classification of Sorensen and Arlt. The ternary LLEs of the (water + methanol or ethanol + geraniol) systems consist of two miscible systems (water + methanol or ethanol) and (methanol or ethanol + geraniol) and one immiscible system (water + geraniol). To correlate the experimental LLE data using the original UNIQUAC, extended and modified UNIQUAC models, we used the methods of correlation A and B (for the extended and modified UNIQUAC models). In correlation A, the binary parameters of the extended and modified UNIQUAC models were determined from the binary phase equilibrium data. However, the binary vapor–liquid equilibria for (methanol + geraniol) and (ethanol + geraniol) have not been reported. In the present work, a set of the binary parameters for miscible pair alcohol (2) + geraniol (3) can be determined from the experimental ternary LLEs of the water (1) + alcohol (2) + geraniol (3) systems by minimizing the objective function of eq 8 using the binary parameters of water (1) + alcohol (2) and water (1) + geraniol (3) systems given in Table 4. Table 5 lists the root-mean-square deviations (rms) between the experimental and calculated results by the method of the correlation A and the

Table 5. Calculated Results for Ternary Liquid–Liquid Equilibria at Temperature $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}^a$

system (1 + 2 + 3)	T		model ^b	correlation A			correlation B			
				rms	a_{23}	a_{32}	rms	τ_{231}	τ_{132}	τ_{123}
	K	N		%	K	K	%			
water + methanol + geraniol	283.15	8	I	1.08	−81.48	166.53				
			II	1.16	−6.65	215.44	1.12	0.0090	0.0105	0.0113
			III	1.34	−199.86	233.62	1.02	0.0013	0.1187	−0.1398
	298.15	9	I	0.93	−104.33	261.18				
			II	0.97	−83.94	262.42	0.44	−0.7058	2.1204	−1.1426
			III	1.21	−254.43	370.17	0.57	1.6833	−1.9419	−1.7530
	313.15	8	I	0.96	−127.26	290.97				
			II	1.03	−130.74	287.41	0.54	−0.7583	2.2857	−1.3214
			III	1.35	−291.94	407.65	0.62	2.0316	−2.1595	−2.2149
water + ethanol + geraniol	283.15	11	I	1.72	−125.26	537.56				
			II	1.21	−103.85	336.04	0.45	−0.9411	2.7132	−1.6642
			III	1.56	−182.13	686.99	0.37	0.2632	−1.2186	1.8737
	298.15	11	I	2.19	−162.57	719.22				
			II	1.39	−207.71	452.66	0.74	−0.2857	0.4191	0.0163
			III	1.87	−258.59	1487.00	0.73	0.0037	−1.2282	2.8134
	313.15	9	I	2.89	−131.43	344.07				
			II	2.69	77.50	127.50	0.67	0.0010	0.5000	0.5000
			III	3.01	−252.13	1091.00	1.32	0.0108	0.0011	0.1033
average			I	1.63						
			II	1.41			0.66			
			III	1.72			0.77			

^a N , number of experimental data rms, root mean square deviation a_{ij} , estimated binary parameter. τ_{ijk} , ternary parameter correlation A with binary parameters correlation B with binary and ternary parameters. ^b I, UNIQUAC; II, extended UNIQUAC; III, modified UNIQUAC.

binary parameters of the alcohol (2) + geraniol (3) system obtained fitting the models to the experimental ternary LLEs. The mean deviations (rms) obtained for the all ternary systems measured at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$ were 1.63 %, 1.41 %, and 1.72 % by the original UNIQUAC, the extended and modified UNIQUAC models, respectively.

In a further accurate representation of the ternary LLEs as referred by the correction B, the ternary parameters τ_{ijk} was used. As the binary parameters of the water (1) + geraniol (3) and water (1) + alcohol (2) system given in Table 4 and those of alcohol (2) + geraniol (3) systems given in Table 5 were determined, the ternary parameters in the models can be obtained fitting the models to the experimental ternary LLEs by minimizing the objective function defined by eq 8. Table 5 shows the rms deviations between experimental and correlated results along with the ternary parameters for the (water + alcohol + geraniol) system. The mean deviations obtained from the six ternary systems were 0.66 % and 0.77 % by the extended and modified UNIQUAC models. The correlated results using the ternary parameters obtained by the two models were improved remarkably, and the extended UNIQUAC model could reproduced accurately the experimental results in comparison with the modified UNIQUAC model. Figure 2 displays the calculated results (correlation A and B) along with experimental LLE tie-line data at 298.15 K for (water + methanol + geraniol) and (water + ethanol + geraniol) systems. Figure 2 illustrates good agreement of the experimental ternary results with those correlated by including the ternary parameters of the ternary LLE systems.

To examine the liquid–liquid distribution ratios of alcohol (methanol or ethanol) in (water + geraniol) mixture, the distribution ratio of alcohol (component 2) in the ternary LLE mixtures was defined by

$$D = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \quad (9)$$

Figure 3 compares the tendencies and differences of value of experimental distribution ratios of methanol and ethanol in the ternary (water + alcohol + geraniol) at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$. For the ternary systems, the distribution ratio of alcohols was increasing as the system temperature increased. On the other hand, the distribution ratio of alcohol at a system temperature was decreasing as the concentration of alcohol in the mixture increased. The results for the distribution ratios of alcohols calculated by the extended and modified UNIQUAC models were in a fair agreement with the experimental values.

Figure 4 shows the temperature dependence of the ternary LLE envelope with tie-lines for (water + methanol + geraniol) and (water + ethanol + geraniol) systems at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$, where the immiscible regions decrease as temperature increases, could be represented successfully by the extended UNIQUAC model as shown in Figure 2. Figure 5 illustrates the comparison of immiscible regions for ternary (water + methanol + geraniol) and (water + ethanol + geraniol) LLEs at $T = 283.15 \text{ K}$. It is obvious that the ternary LLE envelope with tie-line data for (water + methanol + geraniol) system was larger than that of (water + ethanol + geraniol) system. In other words,

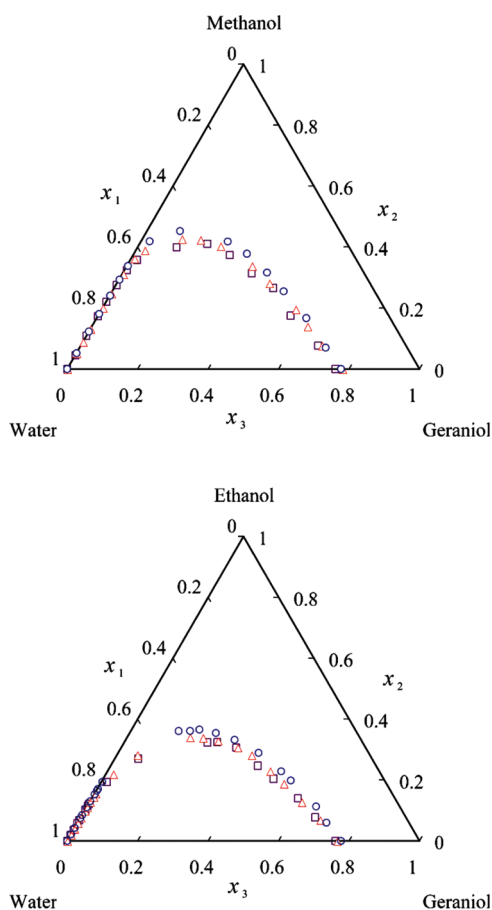


Figure 4. Comparison of experimental ternary (water + methanol + geraniol) and (water + ethanol + geraniol) liquid–liquid equilibria at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$: \circ , 283.15 K; Δ , 298.15 K; and \square , 313.15 K.

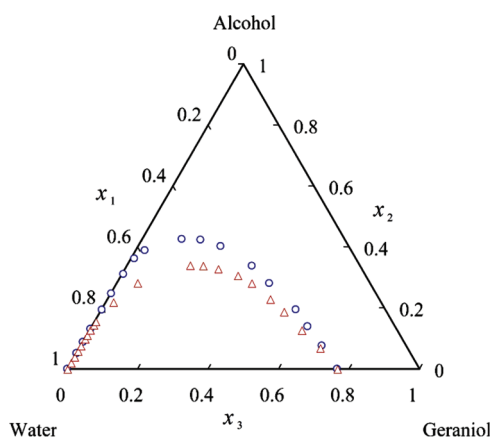


Figure 5. Comparison of immiscible region for experimental ternary LLEs for (water + methanol + geraniol) and (water + ethanol + geraniol) at $T = 283.15 \text{ K}$: \circ , methanol; and Δ , ethanol.

the miscibility for the ternary (water + ethanol + geraniol) LLE was much more than that of (water + methanol + geraniol) LLE. This is explained by a fact that ethanol has a little stronger hydrophobicity because of containing one lipophilic group CH_2 than methanol. In a similar way, the distribution ratio of ethanol

for the (water + ethanol + geraniol) mixture was higher than that of the (water + methanol + geraniol) mixture at a constant temperature and concentration of alcohol.

CONCLUSION

Liquid–liquid equilibrium data of tie-line compositions were presented for the ternary mixtures of (water + methanol or ethanol + geraniol) at $T = (283.15, 298.15, \text{ and } 313.15) \text{ K}$. The immiscible area of (water + methanol + geraniol) system is wider than that for the ethanol system at the constant temperature due to weaker hydrophobicity of methanol than ethanol. The influence on temperature for the ternary LLEs represents that the immiscible regions decrease but the distribution ratios of alcohols increase as temperature increases. The experimental liquid–liquid equilibrium data have been satisfactorily represented by using extended UNIQUAC and modified UNIQUAC by including binary and ternary parameters. The mean deviations obtained from the all six ternary systems were 0.66 % and 0.77 % by the extended and modified UNIQUAC models, respectively.

AUTHOR INFORMATION

Corresponding Author

*(H.L.) Fax: +86-20-3932-2231. E-mail: hd.li@gdut.edu.cn. (K.T.) Fax: +81-76-234-4829. E-mail: tamura@t.kanazawa-u.ac.jp.

Funding Sources

This project was sponsored by the “211” Creative Project of Guangdong Province and SRF for ROCS, SEM, China.

REFERENCES

- (1) Evans, W. C. *Trease and Evans' Pharmacognosy*; W.B. Saunders Company Ltd.: London, 1996.
- (2) Mastelic, J.; Grzunov, K.; Kravar, A. The chemical composition of terpene alcohols and phenols from the essential oil and terpene glycoside isolated from *Thymus pulegioides* L. grown wild in Dalmatia. *Riv. Ital. EPPOS* **1992**, *3*, 19–22.
- (3) Takoi, K.; Koie, K.; Itoga, Y.; Katayama, Y.; Shimase, M.; Nakayama, Y.; Watari, J. Biotransformation of Hop-Derived Monoterpene Alcohols by Lager Yeast and Their Contribution to the Flavor of Hopped Beer. *J. Agric. Food Chem.* **2010**, *58*, 5050–5058.
- (4) Werkhoff, P.; Güntert, M.; Krammer, G.; Sommer, H.; Kaulen, J. Vacuum Headspace Method in Aroma Research: Flavor Chemistry of Yellow Passion Fruits. *J. Agric. Food Chem.* **1998**, *46*, 1076–1093.
- (5) Mockute, D.; Bernotiene, G. The Main Citral-Geraniol and Carvacrol Chemotypes of the Essential Oil of *Thymus pulegioides* L. Growing Wild in Vilnius District (Lithuania). *J. Agric. Food Chem.* **1999**, *47*, 3787–3790.
- (6) Cori, O. Rearrangement of Linalool, Geraniol, and Nerol and Their Derivatives. *J. Org. Chem.* **1986**, *51*, 1310–1316.
- (7) Zhang, X. M.; Archelas, A.; Furstoss, R. Microbiological Transformations. 19. Asymmetric Dihydroxylation of the Remote Double Bond of Geraniol: A Unique Stereochemical Control Allowing Easy Access to Both Enantiomers of Geraniol-6, 7-diol. *J. Org. Chem.* **1991**, *56*, 3814–3817.
- (8) Sung, P. H.; Huang, F. C.; Do, Y. Y.; Huang, P. L. Functional Expression of Geraniol 10-Hydroxylase Reveals Its Dual Function in the Biosynthesis of Terpenoid and Phenylpropanoid. *J. Agric. Food Chem.* **2011**, *59*, 4637–4643.
- (9) Cháfer, A.; Muñoz, R.; Burguet, M. C.; Berna, A. The influence of the temperature on the liquid–liquid equilibria of the mixture limonene + ethanol + H_2O . *Fluid Phase Equilib.* **2004**, *224*, 251–256.

- (10) 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.
- (11) Cháfer, A.; Torre, J.; Muñoz, R.; Burguet, M. C. Liquid-liquid equilibria of the mixture linalool + ethanol + water at different temperatures. *Fluid Phase Equilib.* **2005**, *238*, 72–76.
- (12) Arce, A.; Marchiaro, A.; Rodriguez, O.; Soto, A. Liquid-liquid equilibria of limonene + linalool + diethylene glycol system at different temperatures. *Chem. Eng. J.* **2002**, *89*, 223–227.
- (13) Arce, A.; Marchiaro, A.; Soto, A. Propanediols for separation of citrus oil: liquid-liquid equilibria of limonene + linalool + (1,2-propanediol or 1,3-propanediol). *Fluid Phase Equilib.* **2003**, *211*, 129–140.
- (14) 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.
- (15) 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.
- (16) Li, H.; Tamura, K. Ternary liquid-liquid equilibria for (water + terpene + 1-propanol or 1-butanol) systems at the temperature 298.15 K. *Fluid Phase Equilib.* **2008**, *263*, 223–230.
- (17) Tamura, K.; Li, X.; Li, H. 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. *J. Chem. Eng. Data* **2008**, *53*, 2417–2421.
- (18) Tamura, K.; Li, X.; Li, H. Temperature dependence on mutual solubility of binary (methanol + limonene) mixture and (liquid + liquid) equilibria of ternary (methanol + ethanol + limonene) mixture. *J. Chem. Thermodyn.* **2009**, *41*, 564–568.
- (19) 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.
- (20) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: a New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116–128.
- (21) Nagata, I. Modification of the Extended UNIQUAC Model for Ternary and Quaternary Liquid-Liquid Equilibrium Calculations. *Fluid Phase Equilib.* **1989**, *51*, 53–70.
- (22) Gmehling, J.; Onken, U.; VAPOR-LIQUID EQUILIBRIUM DATA COLLECTION, *Aliphatic Hydrocarbons*; DECHEMA: Frankfurt/Main, 1977; Chemistry Data Series, Vol. I, Part 1.
- (23) Gmehling, J.; Onken, U.; Rearey-Nies, J. R. *Vapor-liquid equilibrium data collection, Aqueous Systems*; DECHEMA: Frankfurt/Main, 1988; Chemistry Data Series, Vol. I, Part 1b.
- (24) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.
- (25) 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.
- (26) Nagata, I. Modification of the Extended UNIQUAC Model for Correlating Liquid-Liquid Quaternary Equilibrium Data. *Fluid Phase Equilib.* **1990**, *54*, 191–206.
- (27) Maurer, G.; Prausnitz, J. M. On the Derivation and Extension of the UNIQUAC Equation. *Fluid Phase Equilib.* **1978**, *2*, 91–99.
- (28) Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514–517.
- (29) 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.
- (30) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multi-component Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.