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Ternary Liquid-liquid Equillibria for (Water + Methanol + β-Citronellol) at 283.15 and 313.15 K

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Abstract. Liquid-liquid equilibrium tie-line data are reported for ternary mixture of (water + methanol + β -citronellol) at 283.15 and 313.15 K. The miscibility for the ternary (water + methanol + β-citronellol) LLE was increasing as the the temperature increased. The experimental liquid–liquid equilibrium data have been satisfactorily represented by using an extended UNIQUAC model.

Introduction

Citronellol ($C_{10}H_{20}O$) is a natural acyclic monoterpenoid (monoterpene alcohol) and one the of important fragrance terpenoid. Citronellol is found in citronella oils (50%), oils of rose (18-55%) [1], and is commonly used in perfumes, flavors, synthesis and biotransformation. So far, many studies on flavor, food and biochemistry for citronellol have been reported [2-4]. Phase equilibrium studies supply essential information for the design and optimisation of separation processes. However, the solvent extraction technique is limited by the lack of liquid-liquid equilibrium data for systems containing terpenes (monoterpenoids) at several temperatures.

In this work, we focus on the liquid-liquid phase equilibrium properties of system containing citronellol in aqueous methanol solution. Similar researches such as ternary (water + ethanol + citral) system at 293 K [5], ternary (water + methanol + terpene) [6], binary (methanol + limonene) and ternary (methanol + ethanol + limonene) systems [7] have been reported previously. In the present paper, to examine the multicomponent phase equilibrium behaviors of β-citronellol in mixture (water + methanol) and the distribution ratios of methanol between organic and aqueous phases, we measured the mutual solubilities of β-citronellol dissolved in water, and their LLE and tie-line data of ternary mixture at 283.15 and 313.15 K.

Experimental

Materials. (±)-β-citronellol(CAS No.106-22-9, 3,7-dimethyl-6-octen-1-ol) and methanol were supplied by Aladdin Company, with minimum purities of 98% and 99.9% as stated by a GC assay. Bidistilled water was used. All chemicals were used without further purification.

Procedure and Experimental Data. Ternary liquid-liquid equilibria for the (water + methanol + β-citronellol) system were measured with a tie-line method at 283.15 and 313.15 K within 0.01 K. The experimental procedure was described in detail previously [8]. The mixture 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 precision Hamiltion syringes and the quantitative analysis of their compositions were performed by a gas chromatography (Agilent 7820A). Table 1 summarizes the experimental ternary LLE tie-line compositions (accuracy within ±0.001 in mole fraction) for the ternary system at 283.15 and 313.15 K. Fig. 1 and 2 show the experimental tie-line data and distribution ratios for methanol of the system, respectively.

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Table 1. Liquid–liquid Equilibrium Tie-line Data (mole fraction) of Ternary Water (1) + Methanol (2) + β-Citronellol (3) System at 283.15 and 313.15 K.

water rich phase				β-citronellol rich phase		
x_1	x_2	x_3		x_1	x_2	x_3
			283.15K			
0.9998	0.0000	0.0002		0.1970	0.0000	0.8030
0.9350	0.0648	0.0002		0.2095	0.0832	0.7073
0.8700	0.1297	0.0003		0.2177	0.1703	0.6120
0.8125	0.1872	0.0003		0.2268	0.2478	0.5254
0.7455	0.2535	0.0010		0.2323	0.3180	0.4497
0.6895	0.3091	0.0014		0.2591	0.3799	0.3610
0.6078	0.3887	0.0035		0.3018	0.4532	0.2450
0.5086	0.4637	0.0277		0.4162	0.4932	0.0906
			313.15K			
0.9999	0.0000	0.0001		0.2333	0.0000	0.7667
0.9347	0.0650	0.0003		0.2478	0.0998	0.6524
0.8779	0.1218	0.0003		0.2549	0.1855	0.5596
0.8120	0.1876	0.0004		0.2779	0.2707	0.4514
0.7575	0.2415	0.0010		0.2851	0.3275	0.3874
0.6873	0.3102	0.0025		0.3217	0.3940	0.2843
0.6192	0.3712	0.0096		0.3712	0.4455	0.1833
0.5605	0.4175	0.0220		0.4542	0.4452	0.1006

Calculated Results and Discussion

Correlation of experimental data. To represent the experimental ternary LLE data, we used the extended UNIQUAC proposed by Nagata [9]. In the model, the binary energy parameters a_{ij} can be obtained from binary experimental phase equilibrium data. The binary energy parameters a_{ij} for the miscible mixture were obtained from vapor-liquid equilibrium data reduction using the following thermodynamic equations:

$$Py_i\Phi_i = x_i\gamma_i P_i^s\Phi_i^s \exp\{V_i^L(P-P_i^s)/RT\}. \quad (1)$$

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

where P, x, y, and γ are the total pressure, the liquid-phase mole fraction, the vapor-phase mole fraction, and the activity coefficient. A set of the energy parameters a_{ij} for the immiscible mixture was obtained from the mutual solubilities by solving Eq 3 and 4 with a Newton-Raphson iterative method.

$$(\gamma_i x_i)^I = (\gamma_i x_i)^{II}. \quad (3)$$

$$\sum_i x_i^I = \sum_i x_i^{II} = 1. \quad (4)$$

where I and II represent equilibrium phases. The binary parameters obtained by the extended UNIQUAC model are listed in Table 2. In this work, the binary parameters a_{23} and a_{32} can be obtained fitting the model to experimental ternary LLE by minimizing the objective function,

$$F = 100\left\{\sum_k^n\sum_i^3\sum_j^2\left(x_{ijk}^{exp} - x_{ijk}^{cal}\right)^2 / 6n\right\}^{0.5}. \quad (5)$$

where phases j = 1 and 2, tie-lines k = 1 to n, components i = 1, 2, to 3. The deviation between experimental and calculated values was expressed by the root mean square deviation (RMS %), which can be defined by Eq 5.

Results and discussion. Table 2 shows the RMS deviations between experimental and correlated results along with the binary parameters for the (water + alcohol + β-citronellol) systems.

Table 2. Calculated Results for Ternary Water (1) + Methanol (2) + β-Citronellol (3) Liquid-liquid Equilibria at 283.15 and 313.15 K.

Temperature	RMS [%]	Parameters [a]		Parameters [b]		Parameters [c]	
		a_{12}[K]	a_{21}[K]	a_{13}[K]	a_{31}[K]	a_{23}[K]	a_{32}[K]
283.15K	1.18	-194.68	279.50	607.88	604.38	13.55	242.93
313.15K	0.93	-194.68	279.50	843.46	590.69	-69.27	285.57

Parameters [a] - Ref. [10]

Parameters [b] - This work

Parameters [c] - Estimated parameters

The RMS deviations obtained from the two ternary systems were 1.18 % and 0.93 %. Fig. 1 illustrates good agreement of the experimental ternary results with those correlated of the ternary LLE system.

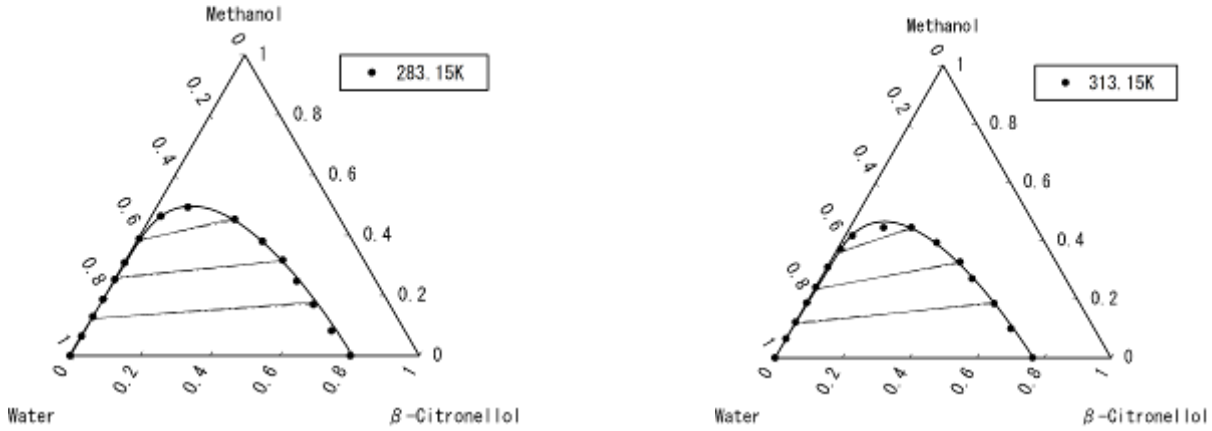

Fig. 1. Liquid-liquid equilibria for ternary (water + methanol + β-citronellol) system at at 283.15 and 313.15 K. Experimental tie-line (●−·−●); Correlated (——), by the extended UNIQUAC with binary parameters from Table 2.

In order to examine the liquid-liquid distribution ratio of methanol in (water + β-citronellol) mixture, the distribution ratio of methanol (component 2) in the ternary LLE mixtures was defined by

$$D_2 = x_2^{organicphase} / x_2^{aqueousphase}. \quad (6)$$

Fig.2 compares the tendencies and differences of experimental distribution ratios of methanol in the ternary (water + methanol + β-citronellol) at 283.15 and 313.15 K. The distribution ratio of methanol for the mixture at 313.15 K was higher than that at 283.15 K at a concentration of methanol. On the other hand, the distribution ratio of methanol at a system temperature was decreasing as the concentration of methanol in the mixture increased. The result for the distribution ratios of methanol correlated (——) by the extended UNIQUAC model was in a fair agreement with the experimental values.

Fig.3 illustrates the comparison of immiscible regions for ternary (water + methanol + β-citronellol) LLE at T = 283.15 and 313.15K. It was observed that the miscibility for the ternary (water + methanol + β-citronellol) LLE was increasing as the the temperature increased.

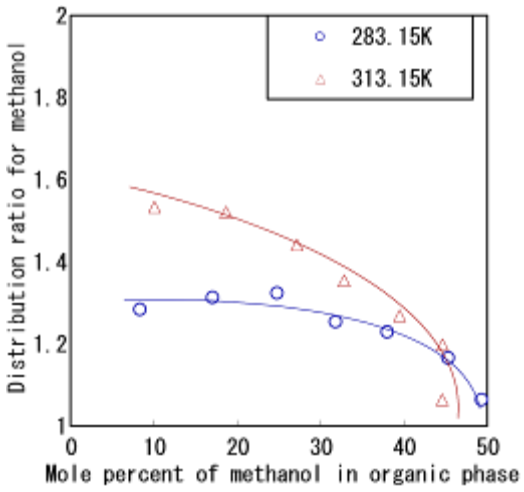

Fig. 2 Comparison of distribution ratios

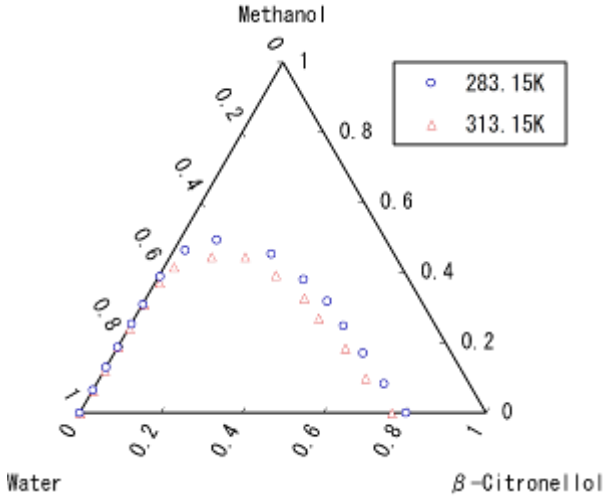

Fig. 3 Comparison of immiscible region

Conclusions

Liquid-liquid equilibrium data of tie-line compositions were presented for the ternary mixture of (water + methanol + β-citronellol) at 283.15 and 313.15 K. The distribution ratio of methanol for the mixture was increasing as the system temperature increased, and was decreasing as the concentration of methanol in the mixture increased in a constant temperature. The miscibility for the ternary (water + methanol + β-citronellol) LLE was increasing as the the system temperature increased. The experimental liquid-liquid equilibrium data have been satisfactorily represented by using extended UNIQUAC.

Acknowledgements

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