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Liquid−Liquid Equilibrium for the System Water + 1,4-Dioxane + 2,6-Dimethyloct-7-en-2-ol over the Temperature Range of (343.2 to 358.2) K

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Liquid−liquid equilibrium (LLE) data for the ternary system water + 1,4-dioxane + 2,6-dimethyloct-7-en-2-ol (DHM−OH) were determined at atmospheric pressure over the temperature range of (343.2 to 358.2) K. The reliability of the experimental tie-line was determined through the Othmer−Tobias correlation. The experimental data were also compared with the values correlated by the NRTL and improved UNIQUAC models. Good quantitative agreement was obtained with these models.

Introduction

Terpene alcohols and esters are two important groups of fine chemicals used in flavors and perfumes.[1] Among them, 2,6-dimethyloct-7-en-2-ol (DHM−OH) is extensively used, due to its excellent stability and powerful limelike aroma. The simplest pathway for the synthesis of this flavor is the direct hydration of 3,7-dimethylocta-1,6-diene (DHM).[2] According to the synthesis of α-terpineol,[3] 1,4-dioxane is chosen as the solvent for the synthesis of 2,6-dimethyloct-7-en-2-ol, and we have found that 1,4-dioxane is a good solvent for the synthesis of 2,6-dimethyloct-7-en-2-ol in our research. However, information related to liquid−liquid equilibrium (LLE) involving water, 1,4-dioxane, and 2,6-dimethyloct-7-en-2-ol is scarce in the literature. In this work, we present liquid−liquid equilibrium measurements of water + 1,4-dioxane + 2,6-dimethyloct-7-en-2-ol over the temperature range of (343.2 to 358.2) K under atmospheric pressure. The experimental data were employed to determine the binary interaction parameters in the NRTL and improved UNIQUAC models. The models and parameters provide a basis for the synthesis of the dihydromyrcenol.

Experimental Section

Chemicals. 1,4-Dioxane ($w > 0.995$, analytical grade) was purchased from SINO PHARM. 2,6-Dimethyloct-7-en-2-ol ($w > 0.995$, analytical grade) was supplied by Xiamen. The purity of these materials was checked by gas chromatography and used without further purification. Distilled water was prepared in our laboratory. The densities of all chemicals were measured using a liquid densimeter (model YM 1, Beijing, China). The uncertainty of this densimeter is better than 0.01 $\text{g}\cdot\text{cm}^{-3}$. Refractive indices ($n_D$) of the pure components were also determined with the help of a digital refractometer (model WYS-2S, Sichuan, China). The uncertainty of this refractometer is ± 0.0001. The density and refractive index of the substances are listed in Table 1.

Table 1. Densities and Refractive Indices of Pure Components

	density $d_{25}\cdot 10^{-3}/\text{kg}\cdot\text{m}^{-3}$		refractive index n_D^{20}	
component	experimental	literature	experimental	literature
water	0.997	0.997[4]	1.3330	1.33299[4]
1,4-dioxane	1.0259	1.02795[5]	1.4220	1.4224[5]
2,6-dimethyloct-7-en-2-ol	0.8318	0.8300 to 0.8360[4]	1.4408	1.4390 to 1.4430[4]

Apparatus and Procedure. Liquid−liquid equilibrium data for the ternary system were measured by an apparatus including a jacketed glass cell, a magnetic agitator, and a thermometer. In the jacketed equilibrium glass cell (internal volume of about 30 cm^3), the temperature was measured with a mercury-in-glass thermometer with a precision of better than 0.1 K. The temperature was kept constant by circulating water from a water bath (501 type, Shanghai, China), which was equipped with a temperature controller capable of maintaining the temperature at a fixed value within ± 0.1 K. The prepared mixtures were introduced into the equilibrium cell and were agitated vigorously for at least 7 h to sufficiently mix the compounds and then settled to at least 12 h for complete phase separation. The samples were taken by a syringe from both the upper (organic phase) and lower layers (aqueous phase).To prevent the samples from splitting into two phases when removed from the equilibrium cell, the sampling operation was quick enough, and the sucked samples were diluted quantitatively by ethanol immediately. A series of LLE measurements were made by changing either the temperature or the composition of the mixture.

The 1,4-dioxane and 2,6-dimethyloct-7-en-2-ol components in both the organic phase and the aqueous phase were determined using a Varian CP-3800 gas chromatograph (GC) equipped with a hydrogen flame ionization detector (FID). A 25 m long capillary column (0.32 mm diameter with a 0.25 μm film thickness) was used with a temperature-programmed analysis. Column temperature: 373 K hold 1 min, 6 $\text{K}\cdot\text{min}^{-1}$ heating for 8.33 min, 20 $\text{K}\cdot\text{min}^{-1}$ heating for 3 min, 483 K maintain 1 min; injection mode, split ratio 50/1; injector temperature, 553 K and detector temperature, 523 K; carrier gas, nitrogen 15 $\text{mL}\cdot\text{min}^{-1}$; injected volume of 0.2 μL of liquid sample. The FID's response was calibrated with cyclohexanone as an internal standard. The calibration samples were prepared by weighing with an analytical balance accurate to within ± 0.0001 g. The calibration equations were used to convert the area fraction into mass fraction. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. The accuracy of the measurements was within ± 0.0001 in mass fraction. The water in the organic phase was determined by the Metrohm 756 KF Coulometer (measure

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Table 2. LLE Data for the Ternary System of Water (1) + 1,4-Dioxane (2) + 2,6-Dimethyloct-7-en-2-ol (3) at Atmospheric Pressure

	organic phase (I)			aqueous phase (II)		
T/K	x_1	x_2	x_3	x_1	x_2	x_3
343.2	0.1895	0.0951	0.7154	0.988	0.0123	$1.3 \cdot 10^{-04}$
	0.1975	0.1607	0.6418	0.978	0.0217	$2.1 \cdot 10^{-04}$
	0.2151	0.2685	0.5164	0.954	0.0460	$3.4 \cdot 10^{-04}$
	0.2496	0.3302	0.4202	0.936	0.0630	$6.1 \cdot 10^{-04}$
	0.2714	0.3796	0.3490	0.916	0.0834	$1.1 \cdot 10^{-03}$
	0.2961	0.3926	0.3113	0.903	0.0951	$1.7 \cdot 10^{-03}$
	0.3814	0.4248	0.1938	0.870	0.1270	$3.1 \cdot 10^{-03}$
	0.4602	0.4167	0.1232	0.834	0.1612	$4.4 \cdot 10^{-03}$
348.2	0.1531	0.0174	0.8296	0.998	0.0014	$1.2 \cdot 10^{-04}$
	0.1938	0.1795	0.6266	0.978	0.0223	$2.3 \cdot 10^{-04}$
	0.2097	0.2710	0.5194	0.958	0.0414	$5.2 \cdot 10^{-04}$
	0.2645	0.3834	0.3522	0.921	0.0782	$1.0 \cdot 10^{-03}$
	0.3251	0.4136	0.2613	0.896	0.1026	$1.6 \cdot 10^{-03}$
	0.4074	0.4009	0.1917	0.879	0.1186	$2.3 \cdot 10^{-03}$
353.2	0.2001	0.1118	0.6881	0.987	0.0126	$1.3 \cdot 10^{-04}$
	0.2179	0.2021	0.5799	0.971	0.0287	$2.4 \cdot 10^{-04}$
	0.2537	0.2847	0.4617	0.952	0.0471	$6.1 \cdot 10^{-04}$
	0.2954	0.3348	0.3697	0.942	0.0572	$8.3 \cdot 10^{-04}$
	0.3476	0.3657	0.2868	0.952	0.0471	$6.4 \cdot 10^{-04}$
	0.3982	0.3968	0.2050	0.923	0.0758	$1.4 \cdot 10^{-03}$
	0.5454	0.3672	0.0874	0.888	0.1095	$2.3 \cdot 10^{-03}$
358.2	0.1858	0.1041	0.7102	0.987	0.0126	$2.3 \cdot 10^{-04}$
	0.2248	0.1759	0.5993	0.987	0.0133	$2.4 \cdot 10^{-04}$
	0.2722	0.2709	0.4569	0.958	0.0416	$3.2 \cdot 10^{-04}$
	0.3502	0.3857	0.2642	0.916	0.0832	$1.1 \cdot 10^{-03}$
	0.3959	0.3909	0.2133	0.901	0.0979	$1.7 \cdot 10^{-03}$
	0.4522	0.3827	0.1651	0.878	0.1193	$2.8 \cdot 10^{-03}$
	0.5799	0.3305	0.0896	0.825	0.1666	$8.0 \cdot 10^{-03}$

error ≤ 0.3 %). The water in the aqueous phase was calculated by the fraction summation equation.

Results and Discussion

The LLE compositions for the water + 1,4-dioxane + 2,6-dimethyloct-7-en-2-ol at 343.2 K, 348.2 K, 353.2 K, and 358.2 K are listed in Table 2, and the experimental data of the ternary system at $T = 343.2$ K are plotted in Figure 1.

From the experimental data, it was easily found that the two-phase region became smaller with increasing temperature. In other words, increasing temperature can improve the solubility of the organic phase and the aqueous phase.

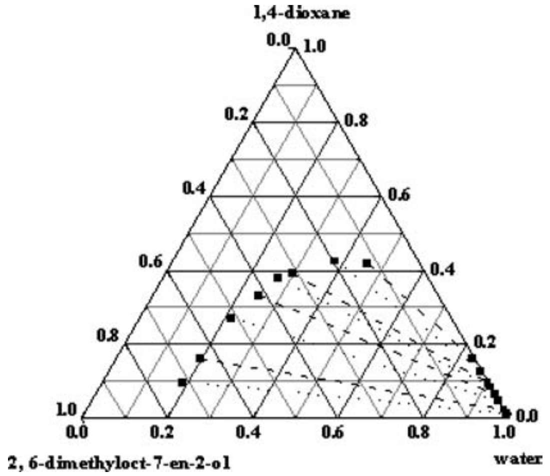

Figure 1. LLE phase diagram for water (1) + 1,4-dioxane (2) + 2,6-dimethyloct-7-en-2-ol (3) at 343.2 K: ■, experimental data in this work; ···, calculated curves by the improved UNIQUAC model; - - -, calculated curves by the NRTL model.

Consistency of Experimental Tie-Line Data. In this study, the Othmer−Tobias correlation (eq 1) was used to ensure the quality of the obtained experimental tie-line data.

$$\ln\left(\frac{1 - w_{32}}{w_{32}}\right) = A + B \ln\left(\frac{1 - w_{11}}{w_{11}}\right) \quad \text{Othmer−Tobias correlation} \quad (1)$$

where w_{11} is the mass fraction of water in the aqueous phase; w_{32} is the mass fraction of 2,6-dimethyloct-7-en-2-ol in the organic-rich phase; and A and B are the parameters of the Othmer−Tobias correlation. The correlation parameters and the correlation coefficient values R^2 are given in Table 3. As can be seen, linear regression yields for all data sets R^2 values better than 0.97.

LLE Calculation. Our experimental data were correlated with the NRTL model of Renon and Prausnitz[6] and improved UNIQUAC.[7] For the NRTL, a value of nonrandomness parameter $\alpha = 0.3$ was used for the water−1,4-dioxane pair,[8] and the rest of α was set to 0.2.[9] For the improved UNIQUAC, the pure component structural parameters (r, q, and q') are listed in Table 4.[10,11]

The LLE experimental data were used to determine the optimum NRTL and improved UNIQUAC binary interaction parameters between water, 1,4-dioxane, and 2,6-dimethyloct-7-en-2-ol. The NRTL and improved UNIQUAC models were fitted to experimental data using an iterative computer program, based on Particle Swarm Optimization, developed by J. Kennedy and R.C. Eberhart.[12,13] The objective function OF[14] used in this case was

$$\mathrm{OF} = \sum_{k=1}^{N}\sum_{i=1}^{3}\left(\frac{K_{ik}^{\mathrm{exp}} - K_{ik}^{\mathrm{cal}}}{K_{ik}^{\mathrm{exp}}}\right)^2 \Big/ 3N = \sum_{k=1}^{N}\sum_{i=1}^{3}\left(\frac{\left(\frac{x_{ik}^{\mathrm{I}}}{x_{ik}^{\mathrm{II}}}\right) - \left(\frac{\gamma_{ik}^{\mathrm{II}}}{\gamma_{ik}^{\mathrm{I}}}\right)}{\left(\frac{x_{ik}^{\mathrm{I}}}{x_{ik}^{\mathrm{II}}}\right)}\right)^2 \Big/ 3N \quad (2)$$

where K_{ik}, γ_{ik}, and x_{ik} are the distribution coefficient, activity coefficient, and mole fraction, respectively. The superscripts I and II denote organic phase and aqueous phase, respectively. The subscripts i and k denote component and tie-line, respectively. N is the number of tie-lines.

The optimization results were judged by calculating the corresponding root-mean-square deviation (rmsd %)[15] values using the following equation

$$\mathrm{rmsd}\ \% = 100\sqrt{\sum_{k=1}^{N}\sum_{j=1}^{2}\sum_{i=1}^{3}\frac{(x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2}{6N}} \quad (3)$$

where the subscript j denotes a different phase.

Table 3. Constants of the Othmer−Tobias Equation

T/K	A	B	R^2
343.2	0.6163	1.0811	0.9800
348.2	0.4601	0.8382	0.9803
353.2	1.4483	1.3780	0.9711
358.2	0.8493	1.0262	0.9734

Table 4. Improved UNIQUAC Structural Parameters of the Pure Component

component	r	q	q'
water	0.92	1.400	1.00
1,4-dioxane	3.1854	2.64	2.64
2,6-dimethyloct-7-en-2-ol	7.7383	6.768	6.768

Table 5. Correlated Results from the NRTL Model for Water (1) + 1,4-Dioxane (2) + 2,6-Dimethyloct-7-en-2-ol (3)

T / K	$i-j$	Δg_{ij} / $J\cdot mol^{-1}$	Δg_{ji} / $J\cdot mol^{-1}$	rmsd %
343.2	1−2	4536.2	1768.8	0.059
	1−3	23705.0	1436.9	
	2−3	37.9	124.0	
348.2	1−2	4804.9	1620.9	0.042
	1−3	24536.7	1657.8	
	2−3	−550.6	421.1	
353.2	1−2	5079.4	1497.4	0.089
	1−3	24898.5	1350.7	
	2−3	−792.6	557. 8	
358.2	1−2	5359.8	1339.9	0.133
	1−3	25507.1	1370.7	
	2−3	−812.6	583.1	

Table 6. Correlated Results from the Improved UNIQUAC Model for Water (1) + 1,4-Dioxane (2) + 2,6-Dimethyloct-7-en-2-ol (3)

T / K	$i-j$	Δu_{ij} / $J\cdot mol^{-1}$	Δu_{ji} / $J\cdot mol^{-1}$	rmsd %
343.2	1−2	−2194.9	5673.5	0.331
	1−3	8476.9	−2988.8	
	2−3	10340.5	−3056.9	
348.2	1−2	−2183.0	5501.9	0.267
	1−3	8614.8	−3019.3	
	2−3	9007.7	−3128.7	
353.2	1−2	−2172.2	5330.5	0.621
	1−3	8900.0	−3116.1	
	2−3	8500.0	−3104.9	
358.2	1−2	−2159.4	5158.9	0.663
	1−3	8910.6	−3133.4	
	2−3	8489.5	−3239.4	

The values of interaction parameters for the NRTL and improved UNIQUAC models at different temperatures are shown in Tables 5 and 6. These parameters are used to calculate LLE tie lines for the present system. Figure 1 also compares the calculated curves from the NRTL and improved UNIQUAC models with the experimental results. As seen from the Tables 5 and 6, good agreements have been obtained for the ternary system.

Conclusions

An experimental investigation of equilibrium behavior of the system composed of water + 1,4-dioxane + 2,6-dimethyloct-7-en-2-ol was carried out at different temperatures of 343.2 K, 348.2 K, 353.2 K, and 358.2 K. The reliability of experimentally measured tie-line data was correlated by Othmer−Tobias. The NRTL and improved UNIQUAC models were used to correlate the experimental LLE data. The optimum NRTL and UNIQUAC parameters were determined using the experimental liquid−liquid data. It was found that both the NRTL and improved UNIQUAC methods fit satisfactorily to the experimental data.

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