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Liquid−Liquid Equilibria for the Binary Systems (Water + Di-*n*-butyl Phthalate), (Water + Di-ethyl Phthalate), and (Water + Di-isobutyl Hexahydrophthalate) from (298.2 to 348.2) K

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Liquid−liquid equilibrium data for the binary systems water + di-*n*-butyl phthalate, water + di-ethyl phthalate, and water + di-isobutyl hexahydrophthalate in the temperature range of (298.2 to 348.2) K at normal pressure were determined. The organic compound concentrations in the aqueous phase were measured by the high-performance liquid chromatograph, while the water concentrations in the organic phase were measured by the Karl Fischer equipment. The NRTL and UNIQUAC models, of which the interaction parameters were expressed as a function of the temperature from (298.2 to 348.2) K, were used to correlate the obtained liquid−liquid equilibrium data. The results show that the correlation accuracy of the UNIQUAC model is better than the NRTL model at the studied temperatures.

Introduction

Di-*n*-butyl phthalate (DBP), di-ethyl phthalate (DEP), and di-isobutyl hexahydrophthalate (DIBE) are very useful chemicals in industrial production because of their low volatility. DEP and DBP are mainly used as plasticizer [1] to improve the performance of the industrial products. DBP and DIBE can be used as organic solvent to recover maleic anhydride in the production of maleic anhydride, while DEP is a potential solvent. The design and optimization of organic solvent recovery process require the liquid−liquid equilibrium (LLE) data for the water with DBP or DEP or DIBE at about 343.2 K. Moreover, their widespread application might lead to great environmental contamination that might have effects on humans[2] or damage to the environment. Knowing these data will help us to deal with them. However, the LLE data of water + DIBE are not available in the literature, and the LLE data of water + DBP and water + DEP have been reported[3] only up to 323.2 K as well as the published solubility data[3−6] of DBP or DEP in water at 298.2 K were different from each other. So it is necessary to measure the mutual solubility of the water with DBP, DEP, or DIBE from (298.2 to 348.2) K.

In addition, it is needed to select appropriate analytical method to ensure the measurement accuracy because the mutual solubilities of the water with DBP, DEP, or DIBE are very low in the temperature range of (298.2 to 348.2) K at normal pressure. In the literature,[7] the high-performance liquid chromatograph and the gas chromatograph are considered to be the best choices to determine the low contents of DBP or DEP in aqueous solution although there are some electrophoretic methods that also can be used to determine these data. For compounds that cannot be volatilized readily, the high-performance liquid chromatograph (HPLC), which is not limited by the volatility or stability of the sample compound,[8] can be used instead of the gas chromatograph. Therefore, the HPLC is used to analyze the contents of DBP, DEP, and DIBE in the present systems because the boiling points of DBP and DEP are about 613 K and 568 K, respectively, and DIBE is easy to decompose at its boiling point.

Table 1. Comparison between Measured Results and Known Values

	aqueous solution		organic solution
compound	x_2 (DBP)	x_2 (DEP)	x_1 (water)
measured	8.883×10^{-5}	2.108×10^{-4}	0.03527
known	8.909×10^{-5}	2.109×10^{-4}	0.03533
absolute deviation	-2.6×10^{-7}	1×10^{-7}	6×10^{-5}

In this paper, LLE data for the three binary systems (water + DBP, water + DEP, and water + DIBE) were obtained by using HPLC and the Karl Fischer equipment. These data were correlated by the NRTL and UNIQUAC models,[9] of which the interaction parameters were expressed as a function of the temperature from (298.2 to 348.2) K. The average absolute deviations (AAD) for the UNIQUAC model are less than that for the NRTL model.

Experimental Section

Chemicals. Industrial DIBE, supplied by the Shengli Oil Field in China, was further purified by three times distillation at a low pressure. The purity of DIBE was checked by HPLC and was found to be higher than 99.5 %. Analytical-grade DBP, DEP, dimethyl phthalate, and 4-chloroguaiacol (purity 99.5 %) supplied by Tianjin Solvent Factory in China were used as received without further purification. Chromatographic-grade methanol (purity 99.8 %) was used throughout all experiments. Water was prepared from distilled water purified by ion-exchange resins.

Apparatus and Procedure. A HPLC (model L-7100) made in Japan with an analytical column (C18), and UV spectrophotometric detector (254 nm) was used to determine the organic compound content in the aqueous phase. The mobile phase was a mixture of methanol and distilled water (76:24, v/v). The flow rate was 1 mL/min at room temperature. A Karl Fischer

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Table 2. LLE Experimental Data for the Three Binary Systems Water (1) + DBP (2), Water (1) + DEP (2), and Water (1) + DIBE (2) and the Absolute Deviations between the Calculated Values Using NRTL or UNIQUAC Model and the Experimental Values

	aqueous phase			organic phase		
		Δx_2[a]			Δx_1	
T/K	$x_{2,e}$	NRTL	UNIQUAC	$x_{1,e}$	NRTL	UNIQUAC
			Water (1) + DBP (2)			
298.2	3.92×10^{-6}	-1.56×10^{-6}	-0.06×10^{-6}	0.0584	−0.0015	−0.0015
318.2	6.03×10^{-6}	-2.33×10^{-6}	0.16×10^{-6}	0.0610	0.0024	0.0026
333.2	8.61×10^{-6}	-3.63×10^{-6}	-0.12×10^{-6}	0.0672	0.0011	0.0014
343.2	1.04×10^{-5}	-4.40×10^{-6}	-0.07×10^{-6}	0.0748	−0.0032	−0.0027
AAD		2.98×10^{-6}	0.10×10^{-6}		0.0021	0.0021
			Water (1) + DEP (2)			
298.2	2.01×10^{-4}	-0.85×10^{-4}	-0.04×10^{-4}	0.0962	−0.0014	−0.0022
318.2	2.44×10^{-4}	-1.00×10^{-4}	0.06×10^{-4}	0.1140	0.0032	0.0042
333.2	2.94×10^{-4}	-1.27×10^{-4}	0.01×10^{-4}	0.1356	0.0008	0.0022
343.2	3.35×10^{-4}	-1.53×10^{-4}	-0.07×10^{-4}	0.1563	−0.0055	−0.0048
AAD		1.16×10^{-4}	0.045×10^{-4}		0.0027	0.0034
			Water (1) + DIBE (2)			
298.2	3.42×10^{-6}	-0.84×10^{-6}	0.72×10^{-6}	0.0659	−0.0023	0.0015
318.2	7.67×10^{-6}	-4.13×10^{-6}	-1.39×10^{-6}	0.0813	−0.0025	0.0004
333.2	8.56×10^{-6}	-4.20×10^{-6}	-0.22×10^{-6}	0.0964	−0.0055	−0.0033
348.2	9.06×10^{-6}	-3.80×10^{-6}	1.74×10^{-6}	0.1043	−0.0007	0.0006
AAD		3.24×10^{-6}	1.02×10^{-6}		0.0028	0.0015

[a] $\Delta x_2 = x_{2,c} - x_{2,e}$.

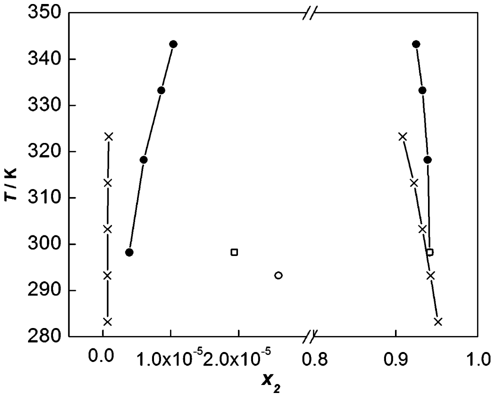

Figure 1. LLE data for water (1) + DBP (2): ●, this work; ×, Rehak et al.[3]; ○, Frohoff-Hulsmann et al.;[4] □, Chen.[5]

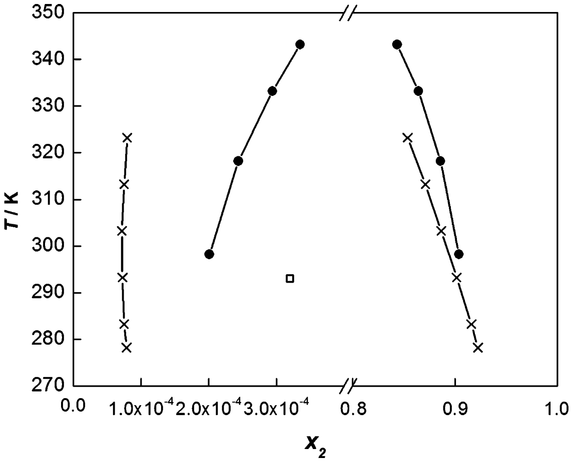

Figure 2. LLE data for water (1) + DEP (2): ●, this work; × , Rehak et al.[3]; □, Dramur and Tatli.[6]

equipment (KFR-C01) made in China was used for the measurement of the water content in the organic phase for the binary systems.

A certain volume of water and organic compound was put into a glass equilibrium still.[10] The still was provided with an external jacket in which water was circulated at constant temperature using a thermostat (made in China). The temperature was maintained with an uncertainty of ± 0.1 K. After the samples were stirred with a magnetic agitator for about 1 day, the sampel was settled for about 2 days to ensure that LLE was established. The top phase was sampled using a microsyringe first, with care being taken to leave a layer of material at least 0.5 cm thick above the interface. The bottom phase was taken out using a microsyringe with a long needle. To prevent contamination of one phase by the other, a tiny bubble of air was retained in the needle tip and expelled once in the bottom phase. All the samples were diluted with known weight methanol to prevent phase separation at room temperature. The compositions of aqueous phase and organic phase were respectively analyzed by HPLC and Karl Fischer equipment. Each sample was analyzed three times.

Table 3. Structure Parameters of UNIQUAC Model

	R	Q
H_2O	0.920	1.400
DBP	10.708	8.536
DEP	8.7666	7.016
DIBE	12.1904	9.944

Precision of Analytical Methods. To examine the precision of the analytical methods, three liquid mixtures of DBP or DEP in aqueous phase and water in DBP solution of known composition by weighing were respectively analyzed by HPLC and Karl Fischer equipment. The known values and the measured results are listed in Table 1. In Table 1, the absolute errors in the measured DBP or DEP concentrations in water and water concentration in DBP are 2.6×10^{-7}, 1.0×10^{-7}, and 6×10^{-5} mol fraction, respectively, which are at least 1 order of magnitude less than that of present experimental data in Table 2. They mean the precision of the analytical methods.

Results and Discussion

LLE data obtained for the binary systems water + DBP and water + DEP from (298.2 to 343.2) K and water + DIBE from (298.2 to 348.2) K are shown in Table 2, where the index refers to the component (1 = water, 2 = organic compound) and e represents the experimental results. The results in the Table 2 indicate that all the mutual solubilities of water and the organic

Table 4. NRTL Parameters for the Three Binary Systems Water (1) + DBP (2), Water (1) + DEP (2), and Water (1) + DIBE (2)

	$a_{12} = 0.30$				
	$g_{12} - g_{22} = a_1 + b_1 \times T$		$g_{21} - g_{11} = a_2 + b_2 \times T$		
systems	a_1/J·mol^{-1}	b_1/J·mol^{-1}·K^{-1}	a_2/J·mol^{-1}	b_2/J·mol^{-1}·K^{-1}	F
H_2O (1) + DBP (2) (298.2∼343.2 K)	18871.92	38.97	12089.89	32.91	0.013
H_2O (1) + DEP (2) (298.2∼343.2 K)	10627.66	34.84	21119.29	−3.76	0.011
H_2O (1) + DIBE (2) (298.2∼348.2 K)	15723.76	49.35	27916.44	−23.29	0.397

Table 5. UNIQUAC Parameters for the Three Binary Systems Water (1) + DBP (2), Water (1) + DEP (2), and Water (1) + DIBE (2)

	$u_{12} - u_{22} = c_1 + d_1 \times T$		$u_{21} - u_{11} = c_2 + d_2 \times T$		
systems	c_1/J·mol^{-1}	d_1/J·mol^{-1}·K^{-1}	c_2/J·mol^{-1}	d_2/J·mol^{-1}·K^{-1}	F
H_2O (1) + DBP (2) (298.2∼343.2 K)	2106.03	−5.34	924.52	15.54	0.0038
H_2O (1) + DEP (2) (298.2∼343.2 K)	777.95	−3.22	5051.22	0.72	0.0027
H_2O (1) + DIBE (2) (298.2∼348.2 K)	1333.91	−3.68	3790.27	7.04	0.0927

compounds (DBP, DEP, or DIBE) increase with the rise in the temperature.

The comparison between the present experimental data with the corresponding literature values[3−6] for the binary systems water + DBP and water + DEP are illustrated in Figures 1 and 2, where x_2 represents the molar fraction of organic compound in aqueous phase and organic phase. As seen in Figures 1 and 2, the measured solubilities of water in organic phase at about 300 K, obtained by Karl-Fisher, are in agreement with the literature values[3] although there are slight differences between them when the temperature is over 300 K. The measured solubilities of DBP or DEP in water are between the published data[3−6] whose values differ greatly from each other. The solubilities of DBP (about 10^{-5}−10^{-6} mol fraction) in aqueous phase are about 1 to 2 orders of magnitude larger than the values (about 10^{-7} mol fraction) of literature,[3] while DEP's solubilities (about 10^{-4} mol fraction) are in the same magnitude with the literature values.[3,6] This indicates that the lower the solubilities of organic compound in aqueous phase are, the larger differences between the present and the published data are, which conforms to the general rule of very low concentration causing large relative deviation in the measurement. In addition, the wide divergence may be a reflection of the impact on determination of such variables as the component purity, equilibrium time, sampling way, and analysis method. To further examine present experimental procedure, the solubilities of dimethyl phthalate and 4-chloroguaiacol, respectively, in water at 293.2 K and 288.2 K were measured according to the experimental method mentioned above. The measured results, 4.95×10^{-4} and 5.12×10^{-4} mole fraction, respectively, are consistent with the reported values, 4.00×10^{-4} and 5.16×10^{-4} mole fraction, in the literature.[3,11]

The NRTL and UNIQUAC models were used to correlate the experimental dada for the three binary systems water + DBP, water + DEP, and water + DIBE. The interaction parameters of the NRTL and UNIQUAC models were expressed as a function of the temperature in the range of experimental temperatures. The structure parameters used in the UNIQUAC model, which were from the CHEMCAD software, are listed in the Table 3. The objective function (F) in the correlation was

$$F = \sum_{j=1}^{4} \sum_{i=1}^{2} (x_{i,\mathrm{w}}\gamma_{i,\mathrm{w}} - x_{i,\mathrm{o}}\gamma_{i,\mathrm{o}})_j^2$$

where x and γ are the molar fraction and the activity coefficient; i represents the component (1 = water, 2 = organic compound); and j represents the four temperatures.

The nonrandom parameter α_{12} of the NRTL model was selected to be 0.30 by minimizing the value of the objective function. The obtained parameters of the NRTL and UNIQUAC models, along with the values of objective function, are summarized in Tables 4 and 5. The values of objective function suggest that the UNIQUAC model is more suitable to the correlation of the low mutual solubilities for present three binary systems than the NRTL model when the interaction parameters of the two models are expressed as a function of the temperature from (298.2 to 348.2) K.

The parameters in Tables 4 and 5 were used to calculate the LLE data of the three binary systems at experimental temperatures. The absolute deviations (Δx) between the calculated and the experimental values are also listed in Table 2. The LLE data calculated using the UNIQAUC models are in relatively better agreement with the experimental data than that obtained using the NRTL model (see Table 2). The average absolute deviations (AAD) for the two models are also listed in Table 2. The average absolute deviations (AAD) for the UNIQUAC model, representing model's correlation accuracy, are 1 to 2 orders of magnitude less than that of the measured data in Table 2.

Conclusions

LLE data for water with DBP or DEP from (298.2 to 343.2) K and for water with DIBE from (298.2 to 348.2) K were determined. These LLE data were correlated by using the NRTL and UNIQUAC models, respectively. The results show that the UNIQUAC model is more suitable to the correlation of LLE for present three binary systems than the NRTL model when the interaction parameters of the two models are expressed as a function of the temperature from (298.2 to 348.2) K. The correlation accuracy of the UNIQUAC model is satisfactory because the average absolute deviations (AAD) for the UNIQUAC model are 1 to 2 orders of magnitude less than that of the measured data in Table 2.

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