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Liquid−Liquid Equilibria for the Ternary System Water + Hexadecane + Propylene Glycol *n*-Propyl Ether

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ABSTRACT: Liquid−liquid equilibria of a ternary system, water + hexadecane + propylene glycol *n*-propyl ether, were measured at temperatures ranging from (298.15 to 333.15) K under atmospheric pressure. At 298.15 K, the system exhibits only one two-liquid- phase-coexisting envelope in the triangle phase diagram. The system exhibits one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in the triangle phase diagram for the temperature ranging from (308.15 to 333.15) K. The experimental data were successfully correlated with the NRTL model.

INTRODUCTION

Precise liquid−liquid equilibrium data of mixtures of the type water + oil + glycol ether are needed in several industrial applications, for example, herbicides, tertiary oil recovery, and the production of drugs.[1,2] In addition, the phase behavior of these mixtures is also important in fundamental research of critical phenomena, phase conductivity, and wetting transitions.[3−9] In our laboratory, we have performed liquid−liquid equilibrium measurements of several ternary water + oil + C_iE_j systems.[10−15] The symbol C_iE_j is the abbreviation of an ethylene glycol ether $CH_3(CH_2)_i(OCH_2CH(CH_3))_jOH$. It is well understood that the lower critical solution temperature of a binary water + C_iE_j system increases as the number of ethylene oxide groups j increases under the condition of a fixed chain length i.[16] On the other hand, the opposite effect is observed in the water + C_iP_j system, where the symbol C_iP_j is the abbreviation of a propylene glycol ether $CH_3(CH_2)_i(OCH_2CH(CH_3))_jOH$. That is, the lower critical solution temperature of a binary water + C_iP_j system decreases as the number of propylene oxide groups j increases under the condition of a fixed chain length i. It is obvious that the interaction between water and C_iE_j is different from that between water and C_iP_j. It triggers our interest to investigate the phase behavior of the ternary water + oil + C_iP_j system.

In this study, liquid−liquid equilibrium measurements of the ternary system water + hexadecane + propylene glycol *n*-propyl ether (C_3P_1) were performed at 298.15 K, 308.15 K, 318.15 K, 328.15 K, and 333.15 K under atmospheric pressure. The experimental data were correlated with the NRTL (nonrandom, two-liquid) model[17] to estimate six effective binary interaction parameters at different temperatures by using the commercial simulator (Aspen Plus).

EXPERIMENTAL SECTION

Hexadecane ($C_{16}H_{34}$) oil was obtained from Merck with a purity of 99 % and was used as received. The propylene glycol *n*-propyl ether (C_3P_1) was a Dow Chemical product and was fractionally distilled under reduced pressure until a purity of > 99.5 % was obtained, as determined by gas chromatography. C_3P_1 is mainly used in household and industrial cleaning formulations, such as glass and all-purpose cleaners. A standard toxicity study[18] shows that C_3P_1 has a lack of genotoxic, developmental, and reproductive hazards. Water was purified by double-distillation and then followed by a PURELAB Maxima Series (ELGA Labwater) purification system with the resistivity always better than 18.2 MΩ·cm.

Three samples were prepared in the same prescribed mass fraction and placed in a computer-controlled water thermostat, whose temperature was controlled within ± 0.005 K and left at least 12 h for equilibration. After equilibrium was reached, each phase was analyzed with a gas chromatograph (China Chromatography 9800, China Chromatography Co.) equipped with a thermal conductivity detector, and area fraction was recorded by the computer equipped with a data acquisition interface card (Scientific Information Service Co., Taiwan). The temperatures of the injector port and thermal conductive detector were both held at 563.15 K, and the oven temperature was held at 513.15 K. The flow rate of the carrier gas, helium, was maintained at 30 mL·min^{-1}. The sample was isothermally separated in a 2 m long steel column packed with Poropak P 80/100 mesh. Each run took about 18 min.

Single-phase binary mixtures of C_3P_1 + water and C_3P_1 + hexadecane with known compositions were used to calibrate the instrument in the composition range of interest. At least three measurements were performed for each phase in every sample. The experimental uncertainty of the gas chromatography was within ± 0.0009 mass fraction.

RESULTS AND DISCUSSION

The experimental equilibrium compositions of the ternary system water + hexadecane + C_3P_1 at 298.15 K, 308.15 K, and 318.15 K are given in Tables 1, 2, and 3, respectively. At 298.15 K, the system exhibits only one two-liquid-phase-coexisting region in the triangle phase diagram, as shown in Figure 1. Note that the C_3P_1 mainly partitions into the lower aqueous phase, and the

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Table 1. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water + Hexadecane + C_3P_1 at 298.15 K

experimental data				calculated results			
hexadecane-rich phase		water-rich phase		hexadecane-rich phase		water-rich phase	
H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1
0.0001	0.0246	0.9261	0.0739	0.0002	0.0355	0.9344	0.0640
0.0004	0.0599	0.8625	0.1375	0.0005	0.0682	0.8688	0.1293
0.0013	0.1005	0.7978	0.1990	0.0011	0.0971	0.8010	0.1965
0.0019	0.1218	0.7302	0.2664	0.0018	0.1195	0.7306	0.2662
0.0021	0.1259	0.5813	0.4135	0.0022	0.1320	0.5823	0.4113
0.0021	0.1260	0.4926	0.4982	0.0020	0.1255	0.4945	0.4954
0.0021	0.1263	0.4098	0.5776	0.0018	0.1193	0.4073	0.5762
0.0021	0.1282	0.3231	0.6558	0.0018	0.1187	0.3213	0.6509
0.0023	0.1359	0.2426	0.7244	0.0021	0.1293	0.2377	0.7137
0.0031	0.1560	0.1739	0.7673	0.0031	0.1554	0.1707	0.7486
0.0086	0.2556	0.0884	0.7551	0.0080	0.2522	0.0910	0.7379
Average error: $\Sigma_{i=1}^{N}(\lvert W_i^{\mathrm{expt}} - W_i^{\mathrm{calc}}\rvert)/N$, where N is the number of tie lines				0.0002	0.0053	0.0033	0.0072

Table 2. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water + Hexadecane + C_3P_1 at 308.15 K

experimental data						calculated results					
hexadecane-rich phase		C_3P_1-rich phase		water-rich phase		hexadecane-rich phase		C_3P_1-rich phase		water-rich phase	
H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1
Three-Liquid-Phase-Coexisting											
0.0037	0.1681	0.2632	0.7034	0.8004	0.1982	0.0039	0.1614	0.2485	0.7171	0.7984	0.2002
Two-Liquid-Phase-Coexisting Region on the Hexadecane/C_3P_1 Side											
0.0043	0.1852	0.1849	0.7547			0.0056	0.1908	0.1888	0.7569		
0.0084	0.2539	0.1155	0.7585			0.0102	0.2619	0.1260	0.7801		
0.0223	0.4050	0.0661	0.6703			0.0152	0.3413	0.0879	0.7715		
Two-Liquid-Phase-Coexisting Region on the Water/Hexadecane Side											
0.0023	0.1440			0.8217	0.1752	0.0028	0.1422			0.8244	0.1743
0.0012	0.1018			0.8546	0.1400	0.0014	0.1085			0.8677	0.1312
0.0004	0.0592			0.8966	0.0979	0.0006	0.0732			0.9123	0.0867
0.0002	0.0268			0.9463	0.0483	0.0002	0.0371			0.9565	0.0426
Two-Liquid-Phase-Coexisting Region on the Water/C_3P_1 Side											
		0.2689	0.7072	0.7925	0.2075			0.2564	0.7179	0.7962	0.2026
		0.2883	0.6949	0.7906	0.2094			0.2649	0.7183	0.7937	0.2055
		0.3861	0.6139	0.7490	0.2510			0.2816	0.7184	0.7879	0.2121
Average error: $\Sigma_{i=1}^{N}(\lvert W_i^{\mathrm{expt}} - W_i^{\mathrm{calc}}\rvert)/N$, where N is the number of tie lines						0.0014	0.0146	0.0273	0.0396	0.0112	0.0095

composition of C_3P_1 is relatively small in the upper oil-rich phase.

As the system temperature was increased to 308.15 K, a three-liquid-phase-coexisting region was detected in the triangle phase diagram (Figure 2). It indicates that the lower critical solution temperature, a transition between two-liquid-phase-coexisting and three-liquid-phase-coexisting, of the water + hexadecane + C_3P_1 system is somewhere between (298.15 and 308.15) K. Both systems at 308.15 K and at 318.15 K exhibit one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes, as shown in Figures 2 and 3, respectively. Note that the water + C_3P_1 binary system exhibits partially immiscible behavior at (308.15 and 318.15) K, as shown in Figures 2 and 3, respectively. In addition, the experimental results of this binary system are also listed in the last column of Tables 2 and 3. The equilibrium compositions of the three-liquid-phase-coexisting tie triangle were also determined at (328.15 and 333.15) K as reported in Table 4. This implies that the upper critical solution temperature of this system is above 333.15 K.

In the temperature window ranging from (308.15 to 333.15) K, the effect of the temperature on the composition of the three-liquid-phase-coexisting region was examined, as shown in Figure 4. It is easily observed in Figure 4 that the apex of the three-liquid-phase-coexisting tie triangle, that is, the C_3P_1-rich phase, shifts

Table 3. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water + Hexadecane + C_3P_1 at 318.15 K

experimental data						calculated results					
hexadecane-rich phase		C_3P_1-rich phase		water-rich phase		hexadecane-rich phase		C_3P_1-rich phase		water-rich phase	
H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1
Three-Liquid-Phase-Coexisting											
0.0072	0.2321	0.1936	0.7383	0.8472	0.1520	0.0076	0.2250	0.1797	0.7499	0.8464	0.1528
Two-Liquid-Phase-Coexisting Region on the Hexadecane/C_3P_1 Side											
0.0105	0.2889	0.1289	0.7489			0.0110	0.2719	0.1345	0.7573		
0.0189	0.3682	0.0938	0.7095			0.0152	0.3250	0.1044	0.7463		
Two-Liquid-Phase-Coexisting Region on the Water/Hexadecane Side											
0.0027	0.1604			0.8653	0.1329	0.0039	0.1702			0.8713	0.1279
0.0010	0.0985			0.8951	0.1026	0.0014	0.1108			0.9092	0.0901
0.0004	0.0421			0.9416	0.0574	0.0003	0.0540			0.9539	0.0455
Two-Liquid-Phase-Coexisting Region on the Water/C_3P_1 Side											
		0.2209	0.7438	0.8497	0.1503			0.2017	0.7632	0.8419	0.1576
		0.3007	0.6993	0.8345	0.1655			0.2269	0.7731	0.8353	0.1647
Average error: $\Sigma_{i=1}^{N}(\lvert W_i^{\text{expt}} - W_i^{\text{calc}}\rvert)/N$, where N is the number of tie lines						0.0010	0.0169	0.0246	0.0300	0.0070	0.0065

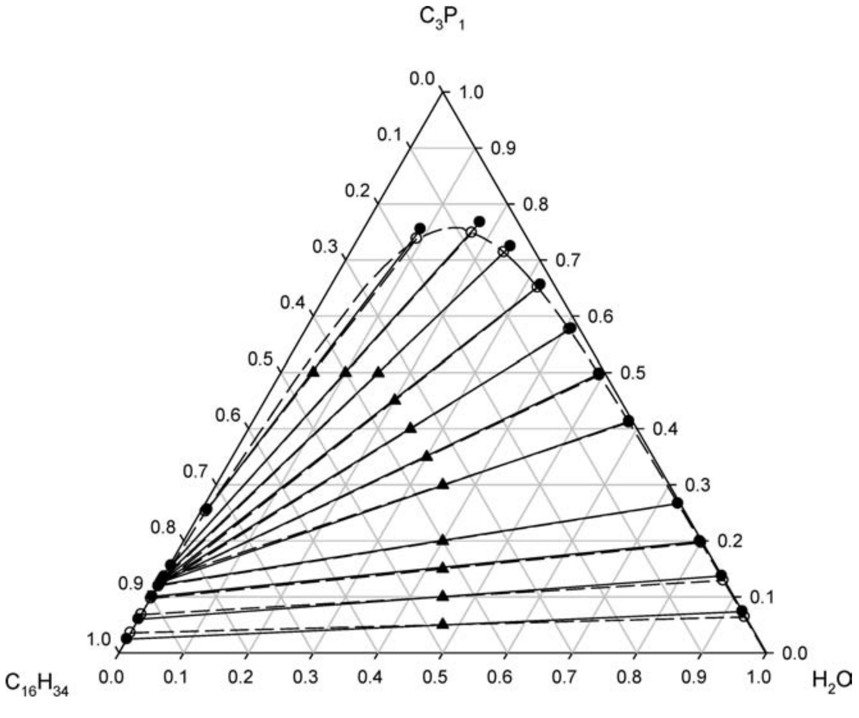

Figure 1. Ternary liquid−liquid equilibria (mass fraction) for the system water + hexadecane + C_3P_1 at 298.15 K: experimental tie lines (●, solid lines); calculated binodal curve (dashed curve) and tie lines (○, dashed lines); and total compositions (▲).

counterclockwise with the increasing temperature, consistent with the observation in the water + oil + C_iE_j system.[15,19] Note that C_3P_1 moves continuously from the water-rich phase to the hexadecane-rich phase with the increase of temperature, as shown in Table 4, also consistent with the observation in the water + oil + C_iE_j system.[15,19]

The NRTL model of Renon and Prausnitz[15] was used to correlate the experimental data by using data regression of the commercial simulator Aspen Plus. The nonrandomness parameters, α_{ij}, for the NRTL model were fixed at $\alpha_{12} = 0.2$, $\alpha_{13} = 0.3$, and $\alpha_{23} = 0.3$ for the water (1) + hexadecane (2) + C_3P_1 (3) system. All algorithm options were used as defaults to obtain the effective binary interaction parameter, τ_{ij}, defined by

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \quad (1)$$

where R is the gas constant and g_{ij} is the NRTL energy parameter between molecules i and j.

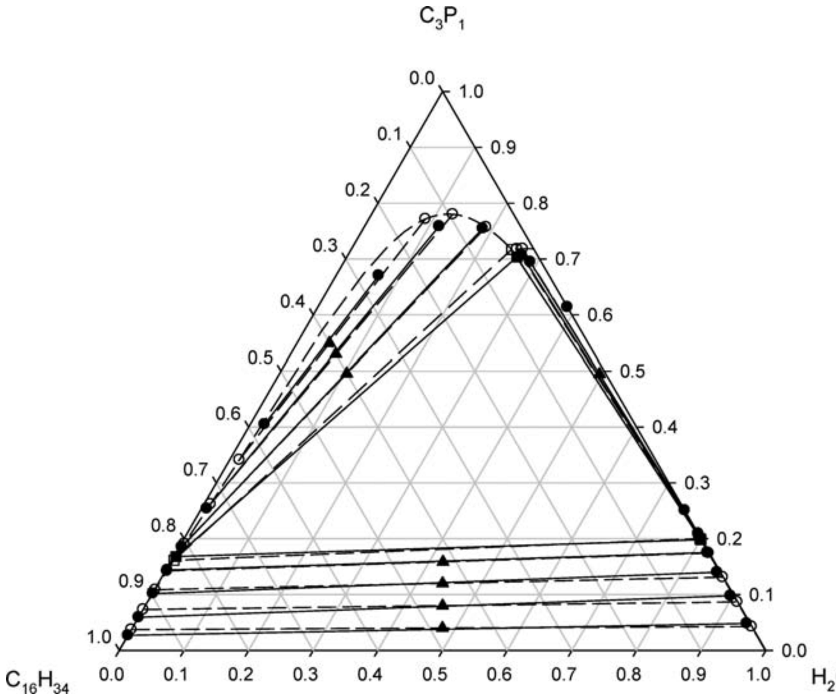

Figure 2. Ternary liquid−liquid equilibria (mass fraction) for the system water + hexadecane + C_3P_1 at 308.15 K: experimental tie lines (●, solid lines), calculated binodal curves (dashed curves) and tie lines (○, dashed lines), and total compositions (▲); experimental three-liquid-phase-coexisting tie triangle (■, solid lines); calculated three-liquid-phase-coexisting tie triangle (□, dashed lines).

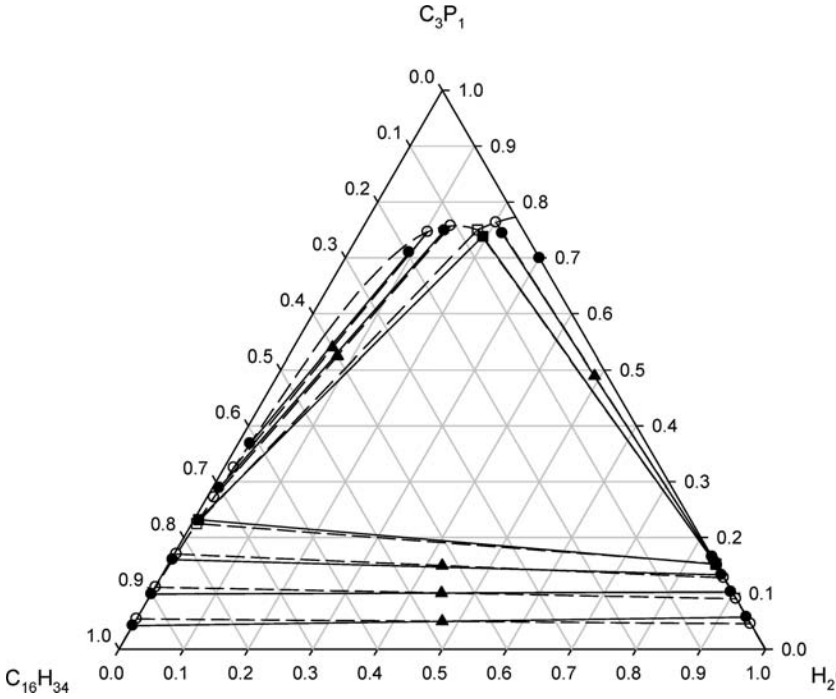

Figure 3. Ternary liquid−liquid equilibria (mass fraction) for the system water + hexadecane + C_3P_1 at 318.15 K: experimental tie lines (●, solid lines), calculated binodal curves (dashed curves) and tie lines (○ dashed line), and total compositions (▲); experimental three-liquid-phase-coexisting tie triangle (■, solid lines); calculated three-liquid-phase-coexisting tie triangle (□, dashed lines).

There are two effective binary interaction parameters for a pair of substances, and thus six binary interaction parameters are required for a ternary system. For the system at 298.15 K, there is only one two-liquid-phase-coexisting region. These six effective binary interaction parameters were determined by numerically minimizing the following objective function

$$F_w = \sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(\frac{w_{ijk}^{\text{expt}} - w_{ijk}^{\text{calc}}}{w_{ijk}^{\text{expt}}} \right)^2 \tag{2}$$

Table 4. Experimental Mass Fractions of Equilibrium Liquid Phases of a Three-Liquid-Phase-Coexisting Tie Triangle for the Ternary System Water + Hexadecane + C_3P_1 from (308.15 to 333.15) K

	experimental data						calculated value					
	hexadecane-rich phase		C_3P_1-rich phase		water-rich phase		hexadecane-rich phase		C_3P_1-rich phase		water-rich phase	
T (K)	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1	H_2O	C_3P_1
308.15	0.0037	0.1681	0.2632	0.7034	0.8004	0.1982	0.0039	0.1614	0.2485	0.7171	0.7984	0.2002
318.15	0.0072	0.2321	0.1936	0.7383	0.8472	0.1520	0.0076	0.2250	0.1797	0.7499	0.8464	0.1528
328.15	0.0146	0.3157	0.1526	0.7401	0.8753	0.1230	0.0146	0.3157	0.1526	0.7401	0.8753	0.1230
333.15	0.0240	0.4005	0.1209	0.7095	0.8774	0.1207	0.0241	0.4014	0.1204	0.7093	0.8774	0.1207
Average error: $\Sigma_{i=1}^{N}(\|W_i^{\text{expt}} - W_i^{\text{calc}}\|)/N$, where *N* is the number of tie lines							0.0002	0.0037	0.0073	0.0064	0.0007	0.0007

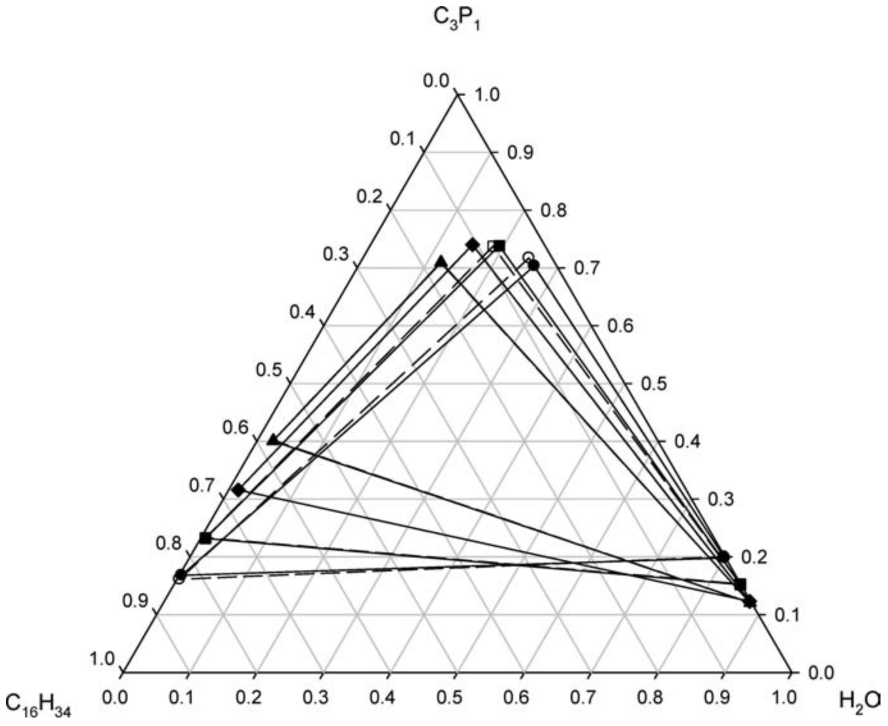

Figure 4. Variation of the liquid−liquid equilibria (mass fraction) of three-liquid-phase-coexisting tie triangle for the system water + hexadecane + C_3P_1 as a function of temperature ranging from (308.15 to 333.15) K: experimental three-liquid-phase-coexisting tie triangles [(●) 308.15 K; (■) 318.15 K; (♦) 328.15 K; (▲) 333.15 K; solid symbols and solid lines]; calculated three-liquid-phase-coexisting tie triangles [(○) 308.15 K; (□) 318.15 K; (◇) 328.15 K; (Δ) 333.15 K; open symbols and dashed lines].

where w_{ijk}^{expt} and w_{ijk}^{calc} are the experimental and calculated, respectively, mass fraction of component *i* in phase *j* along a tie line *k*. The liquid−liquid equilibrium flash calculation was applied to evaluate the compositions of both liquid phases along each tie line by using the experimental total compositions as input data.

On the other hand, for the systems at 308.15 K and higher temperatures, there are one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in each triangle phase diagram, and six binary interaction parameters at each temperature were determined by the numerical regression of only three-liquid-phase-coexisting tie triangle data. The regression results of the effective NRTL binary interaction parameters at each temperature are listed in Table 5.

Once all the six effective binary interaction parameters were determined, the liquid−liquid equilibrium flash calculation was applied to directly predict the compositions of both liquid phases along all tie lines in the two-liquid-phase-coexisting envelopes by using the experimental total compositions as input data. As one can see in Figures 1, 2, and 3, the predicted binodal curves were consistent with the experimental results.

Table 5. Effective NRTL Interaction Parameters for the System Water (1) + Hexadecane (2) + C_3P_1 (3)

T (K)	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	τ_{32}
298.15	7.3636	6.1425	3.9495	−0.8297	−0.1758	1.9134
308.15	7.9891	6.5368	4.1821	−0.8300	−0.4946	2.4736
318.15	8.3341	6.0747	4.2002	−0.6622	−0.4321	2.1365
328.15	7.2903	6.4740	4.2980	−0.6025	−0.7776	2.4578
333.15	7.0167	5.4376	4.2455	−0.5500	−0.8775	2.3135

The calculated results for each tie line are given in Tables 1 to 4. The calculated binodal curves are also presented by dashed curves in Figures 1 to 3. As one can see in Figures 1 to 4, the phase behavior of the system water + hexadecane + C_3P_1 is successfully described by the NRTL model.

CONCLUSION

The liquid−liquid equilibria of the ternary water + hexadecane + C_3P_1 system were measured at (298.15, 308.15, 318.15, 328.15, and 333.15) K under atmospheric pressure. One three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes appeared in the triangle phase diagram of the water + hexadecane + C_3P_1 system at the temperature ranging from (308.15 to 333.15) K. The evolution of phase behavior of the ternary water + hexadecane + C_3P_1 system as a function of temperature is qualitatively consistent with that of the water + oil + C_iE_j system.[15,19] Binary interaction parameters of the NRTL model were determined by directly fitting the liquid−liquid equilibrium data at each temperature. The NRTL model can successfully describe the phase behavior of this ternary system.

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