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

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ABSTRACT: Liquid−liquid and three-liquid-phase equilibria of a ternary system: water + tetradecane + propylene glycol *n*-propyl ether were measured at (298.15, 308.15, and 318.15) K under atmospheric pressure. The system exhibits one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in the triangle phase diagram at these three temperatures. The experimental data were further correlated with the nonrandom two-liquid (NRTL) model, and the average deviation of compositions was 0.0157 mass fraction.

INTRODUCTION

Propylene glycol *n*-propyl ether (C_3P_1) is widely used in household and industrial cleaning formulations, such as glass and all purpose cleaners. The symbol C_iP_j is the abbreviation of a propylene glycol ether $CH_3(CH_2)_{i-1}(OCH_2CH(CH_3))_jOH$. In binary water + C_iP_j systems, the lower critical solution temperature decreases with the increasing number of propylene oxide groups *j* under the condition of a fixed chain length *i*. The tendency of the lower critical solution temperature change in binary water + C_iP_j systems is opposite to that of the water + ethylene glycol ether systems.[1] The interaction between water and C_iP_j is obviously different from that between water and ethylene glycol ether. In our laboratory, we have investigated the phase behavior of several ternary water + oil + ethylene glycol ether systems[2−7] and the water + hexadecane + C_3P_1 system.[8] Many glycol ethers have attracted increasing interest as relatively benign alternatives to certain conventional solvents due to their biodegradability and low aquatic and mammalian toxicity.[9−11]

In this study, liquid−liquid equilibrium measurements of the ternary system water + tetradecane + C_3P_1 were performed at (298.15, 308.15, and 318.15) K under atmospheric pressure. The experimental data were correlated with the NRTL (nonrandom two-liquid) model[12] to estimate six effective binary interaction parameters at different temperatures by using the commercial simulator (Aspen Plus).

EXPERIMENTAL SECTION

Tetradecane ($C_{14}H_{30}$) was purchased from Tokyo Chemical Industry Co. with a purity of 0.990 and was used as received. The propylene glycol *n*-propyl ether (C_3P_1) was a Dow Chemical product and was fractionally distilled under a reduced pressure until a purity of > 99.5 % was obtained, as determined by gas chromatography. 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.

All samples were placed in a homemade computer-controlled water thermostat,[5] whose temperature was controlled within ± 0.005 K, and left at least 12 h for equilibration. The temperature was measured by using a quartz thermometer (2804A, Quartz Thermometer, Hewlett-Packard), and the uncertainty of temperature was 0.01 K. After equilibrium was reached, all of the liquid phases were transparent with sharp and mirror-like interfaces. Following equilibration, each of the liquid phases was carefully sampled by syringe (Hamilton) for further experiments on the determination of composition by gas chromatography (GC-8A, Shimadzu Co., Japan) equipped with a thermal conductivity detector. The area fraction of each peak was calculated and recorded by the computer equipped with a data acquisition interface card (Scientific Information Service Co., Taiwan). The temperatures of 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} to flow through a 2 m long steel column packed with Poropak P 80/100 mesh.

To calibrate the gas chromatography in the composition range of interest, single-phase binary mixtures of C_3P_1 + water and C_3P_1 + tetradecane with known compositions were used. Three samples were prepared in the same prescribed mass fraction for each tie triangle and each tie line. 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 + tetradecane + C_3P_1 at (298.15, 308.15, and 318.15) K are given in Tables 1, 2, and 3, respectively. There are one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in the triangle phase diagram at these three temperatures, as shown in Figures 1, 2, and 3. It should be noted that there is no three-liquid-phase-coexisting tie triangle in the water + hexadecane + C_3P_1 system at 298.15 K.[8] Therefore, the lower critical solution temperature of the water + tetradecane + C_3P_1 system is lower than that of the

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

experimental data						calculated results					
tetradecane-rich phase		C_3P_1-rich phase		water-rich phase		tetradecane-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											
0.0046	0.1782	0.2970	0.6678	0.7407	0.2586	0.0056	0.1775	0.2711	0.6958	0.7412	0.2580
Two-Liquid-Phase-Coexisting Region on Tetradecane/C_3P_1 Side											
0.0041	0.1767	0.2738	0.6834			[a]	[a]	[a]	[a]		
0.0061	0.2059	0.1797	0.7358			0.0115	0.2410	0.1844	0.7397		
0.0094	0.2555	0.1255	0.7327			0.0212	0.3271	0.1335	0.7365		
0.0142	0.3074	0.0987	0.7051			0.0280	0.3857	0.1083	0.7175		
Two-Liquid-Phase-Coexisting Region on Water/Tetradecane Side											
0.0034	0.1639			0.7706	0.2282	0.0044	0.1611			0.7642	0.2351
0.0016	0.1183			0.8231	0.1744	0.0021	0.1205			0.8223	0.1773
0.0005	0.0659			0.8681	0.1285	0.0008	0.0808			0.8818	0.1179
0.0001	0.0272			0.9277	0.0690	0.0002	0.0412			0.9413	0.0584
Two-Liquid-Phase-Coexisting Region on Water/C_3P_1 Side											
		0.3769	0.6106	0.6937	0.3053			0.2962	0.6863	0.7327	0.2667
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						0.0042	0.0274	0.0258	0.0248	0.0123	0.0117

[a] This experimental total composition falls in the calculated three-liquid-phase-coexisting tie triangle.

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

experimental data						calculated results					
tetradecane-rich phase		C_3P_1-rich phase		water-rich phase		tetradecane-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											
0.0088	0.2514	0.1962	0.7180	0.8140	0.1854	0.0115	0.2627	0.1692	0.7290	0.8124	0.1870
Two-Liquid-Phase-Coexisting Region on Tetradecane/C_3P_1 Side											
0.0094	0.2581	0.1827	0.7229			[a]	[a]	[a]	[a]		
0.0182	0.3416	0.1108	0.7030			0.0205	0.3443	0.1175	0.7071		
0.0315	0.4315	0.0793	0.6273			0.0285	0.4071	0.0930	0.6739		
Two-Liquid-Phase-Coexisting Region on Water/Tetradecane Side											
0.0031	0.1635			0.8452	0.1511	0.0038	0.1692			0.8494	0.1501
0.0012	0.1087			0.8685	0.1289	0.0018	0.1224			0.8824	0.1172
0.0004	0.0633			0.9028	0.0949	0.0007	0.0800			0.9198	0.0798
0.0001	0.0271			0.9467	0.0510	0.0002	0.0396			0.9595	0.0402
Two-Liquid-Phase-Coexisting Region on Water/C_3P_1 Side											
		0.2017	0.7216	0.7993	0.2004			0.1884	0.7393	0.8088	0.1907
		0.2510	0.7141	0.7969	0.2031			0.2171	0.7466	0.8015	0.1981
		0.3861	0.6139	0.7490	0.2510			0.2557	0.7443	0.7887	0.2113
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						0.0014	0.0124	0.0390	0.0404	0.0129	0.0118

[a] This experimental total composition falls in the calculated three-liquid-phase-coexisting tie triangle.

water + hexadecane + C_3P_1 system.[8] Consequently, the lower critical solution temperature of the ternary water + alkane + C_3P_1 system decreases with the increasing carbon chain length of the alkane.

For the three-liquid-phase-coexisting tie triangle at 298.15 K, the C_3P_1 mass fraction of the tetradecane-rich phase is less than that of the water-rich phase, as shown in Table 1. As the temperature increases, the composition of the middle C_3P_1-rich

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

experimental data						calculated results					
tetradecane-rich phase		C_3P_1-rich phase		water-rich phase		tetradecane-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											
0.0268	0.4026	0.1204	0.6808	0.8673	0.1322	0.0318	0.4247	0.1064	0.6810	0.8657	0.1338
Two-Liquid-Phase-Coexisting Region on Tetraadecane/C_3P_1 Side											
0.0424	0.4732	0.0977	0.6492			*a*	*a*	*a*	*a*		
Two-Liquid-Phase-Coexisting Region on Water/Tetradecane Side											
0.0163	0.3327			0.8671	0.1318	0.0184	0.3368			0.8705	0.1290
0.0082	0.2564			0.8688	0.1292	0.0105	0.2662			0.8792	0.1204
0.0036	0.1777			0.8783	0.1196	0.0048	0.1930			0.8964	0.1032
0.0011	0.1048			0.9070	0.0902	0.0018	0.1240			0.9242	0.0754
0.0003	0.0438			0.9505	0.0485	0.0005	0.0590			0.9610	0.0387
Two-Liquid-Phase-Coexisting Region on Water/C_3P_1 Side											
		0.1470	0.7154	0.8654	0.1341			0.1342	0.7261	0.8633	0.1362
		0.1846	0.7409	0.8611	0.1386			0.1646	0.7583	0.8585	0.1411
		0.3007	0.6993	0.8345	0.1655			0.2163	0.7837	0.8459	0.1541
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						0.0019	0.0143	0.0156	0.0094	0.0091	0.0084

[a] This experimental total composition falls in the calculated three-liquid-phase-coexisting tie triangle.

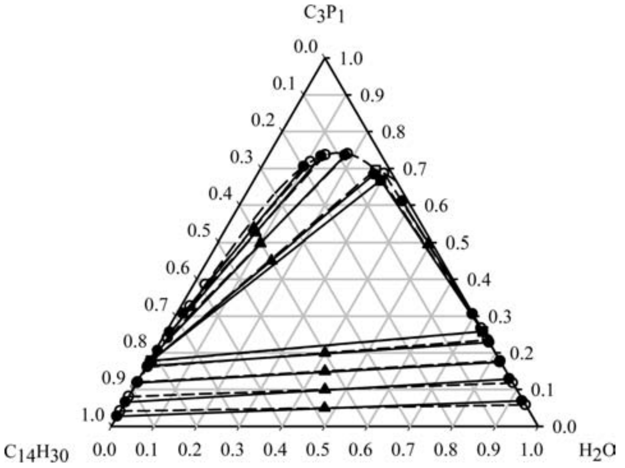

Figure 1. Ternary liquid–liquid equilibria (mass fraction) for the system water + tetradecane + C_3P_1 at 298.15 K: experimental tie lines (●, solid lines), calculated binodal curves (dashed curves), tie lines (○ dashed lines), and total compositions (▲); experimental three-liquid-phase-coexisting tie triangle (■, solid lines); calculated three-liquid-phase-coexisting tie triangle (□, dashed lines).

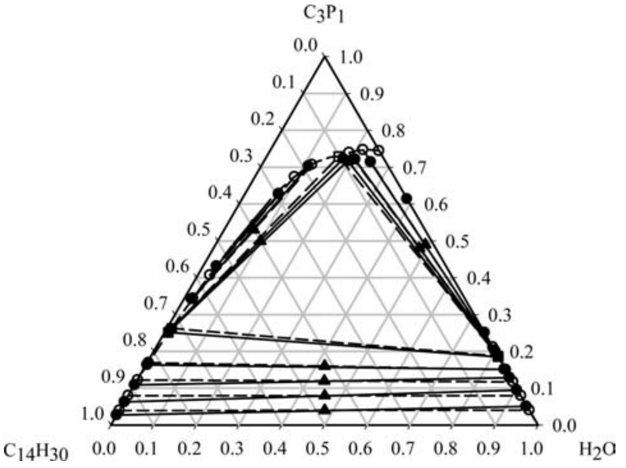

Figure 2. Ternary liquid–liquid equilibria (mass fraction) for the system water + tetradecane + C_3P_1 at 308.15 K: experimental tie lines (●, solid lines), calculated binodal curves (dashed curves), tie lines (○ dashed lines), and total compositions (▲); experimental three-liquid-phase-coexisting tie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

phase approaches the composition of upper tetradecane-rich phase, and the C_3P_1 mass fraction of the tetradecane-rich phase becomes larger than that of the water-rich phase at 318.15 K, as shown in Table 3. This variation indicates that glycol ether C_3P_1 moves continuously from the water-rich phase to the oil-rich phase with an increase in temperature, consistent with the observation in the water + hexadecane + C_3P_1 system[8] and in the water + oil + ethylene glycol ether systems.[2−7]

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

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

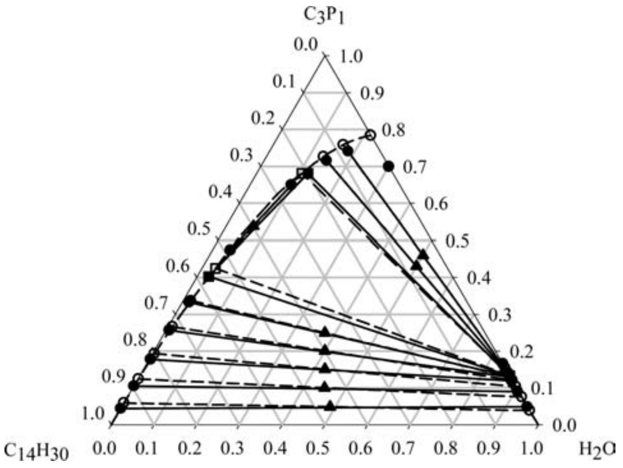

Figure 3. Ternary liquid−liquid equilibria (mass fraction) for the system water + tetradecane + C_3P_1 at 318.15 K: experimental tie lines (●, solid lines), calculated binodal curves (dashed curves), tie lines (○ dashed line), and total compositions (▲); experimental three-liquid-phase-coexisting tie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

Table 4. Effective NRTL Interaction Parameters for the System Water (1) + Tetradecane (2) + C_3P_1 (3)

T/K	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	τ_{32}
298.15	9.2889	6.5005	4.0670	−0.8955	−0.2452	1.8216
308.15	8.8754	6.0590	4.0711	−0.7146	−0.1615	1.5467
318.15	8.6583	5.6043	4.2154	−0.6249	−0.2818	1.5268

where R is the gas constant and g_{ij} is the NRTL energy parameter between molecules i and j. For a pair of substances, it requires two effective binary interaction parameters. Thus, there should be six binary interaction parameters for a ternary system. We used defaults in all algorithm options and determined six effective binary interaction parameters 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 4.

A flash calculation was applied to predict the equilibrium composition of each tie line by using the regression results of six effective binary interaction parameters, and the experimental total compositions were assigned as input data. The calculated results for each tie line are given in Tables 1 to 3. The calculated binodal curves are also presented by dashed curves in Figures 1 to 3.

Note that the lower critical solution temperature of binary water + C_3P_1 system is 305.15 K.[1] Thus, the binary water + C_3P_1 system exhibits partially immiscible behavior at (308.15 and 318.15) K, and the experimental results are listed in the last row of Tables 2 and 3. At 298.15 K, the binary water + C_3P_1 system is completely miscible and there is a close two-liquid-phase-coexisting envelope on the water/C_3P_1 side. In our regression result, however, the two-liquid-phase-coexisting envelope on the water/C_3P_1 side is open. The phase behavior of the system water + tetradecane + C_3P_1 can be fairly well-described by the NRTL model.

■ CONCLUSION

The liquid−liquid equilibria of the ternary water + tetradecane + C_3P_1 system were measured at (298.15, 308.15, and 318.15) K under atmospheric pressure. The system exhibits one three-liquid-phase-coexisting tie triangle, and three two-liquid-phase-coexisting envelopes appeared in the triangle phase diagram of the water + tetradecane + C_3P_1 system at these temperatures. The lower critical solution temperature of the water + alkane + C_3P_1 system increases as the chain length of alkane decreases. The effect of the temperature on the phase behavior of the water + tetradecane + C_3P_1 system is qualitatively consistent with that of the water + hexadecane + C_3P_1 system.[8] The liquid−liquid equilibrium data were used to fit the effective binary interaction parameters at each temperature. The NRTL model can well describe the phase behavior of this ternary system with the average deviation of compositions of 0.0157 mass fraction.

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■ REFERENCES

(1) Christensen, S. P.; Donate, F. A.; Frank, T. C.; LaTulip, R. J.; Wilson, L. C. Mutual Solubility and Lower Critical Solution Temperature for Water + Glycol Ether Systems. *J. Chem. Eng. Data* **2005**, *50*, 869–877.

(2) Hu, H.; Chiu, C. D.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + *n*-Dodecane + 2-(2-*n*-Hexyloxyethoxy)-ethanol. *Fluid Phase Equilib.* **1999**, *164*, 187–194.

(3) Hu, H.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + *n*-Tetradecane + 2-(2-*n*-Hexyloxyethoxy)ethanol at 293.15 and 303.15 K. *J. Chem. Eng. Data* **2000**, *45*, 304–307.

(4) Liu, Y. L.; Chiou, D. R.; Chen, L. J. Liquid-Liquid Equilibrium for the Ternary System Water + Octane + Diethylene Glycol Monobutyl Ether. *J. Chem. Eng. Data* **2002**, *47*, 310–312.

(5) Lin, B. J.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + Dodecane + 2-Butyloxtethanol in the Temperature Range from 25 to 65 °C. *J. Chem. Eng. Data* **2002**, *47*, 992–996.

(6) Liu, Y. L.; Lin, B. J.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + Decane + Diethylene Glycol Monobutyl Ether at 20 °C, 30 °C, and 40 °C. *J. Chem. Eng. Data* **2003**, *48*, 332–336.

(7) Lin, B. J.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + Tetradecane + 2-Butyloxtethanol. *Fluid Phase Equilib.* **2004**, *216*, 13–20.

(8) Su, C. H.; Chen, L. J. Liquid-Liquid Equilibria for the Ternary System Water + Hexadecane + Propylene Glycol *n*-Propyl Ether. *J. Chem. Eng. Data* **2011**, *56*, 589–594.

(9) Spencer, P. J. New Toxicity Data for the Propylene Glycol Ethers − A Commitment to Public Health and Safety. *Toxicol. Lett.* **2005**, *156*, 181–188.

(10) Cowan, R. M.; Kwon, J. Aerobic Biodegradation of Ethylene Glycol Ethers. *Hazard. Ind. Wastes* **1999**, *31*, 273–282.

(11) Staples, C. A.; Boatman, R. J.; Cano, M. L. Ethylene Glycol Ethers: An Environmental Risk Assessment. *Chemosphere* **1998**, *36*, 1585–1613.

(12) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.