J. Chem. Thermodynamics 47 (2012) 358–361

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

(Liquid + liquid) equilibria for the ternary system (water + dodecane + propylene glycol *n*-propyl ether)

Cheng-Hao Su, Shih-Yao Lin, Li-Jen Chen *

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 7 November 2011
Accepted 9 November 2011
Available online 18 November 2011

Keywords:
(Liquid + liquid) equilibrium
Phase diagram
NRTL model
Ternary system
Three-liquid-phase-coexisting
Gas chromatography

ABSTRACT

The (liquid + liquid) equilibria of a ternary system (water + dodecane + propylene glycol *n*-propyl ether) were measured at $T = (288.15, 298.15, \text{and } 308.15)$ K under atmospheric pressure. At $T = 298.15$ K, the system exhibits one three-liquid-phase-coexisting tie triangle and three two-liquid-phase-coexisting envelopes in the triangle phase diagram. There is only one two-liquid-phase-coexisting envelope in the triangle phase diagram at $T = (288.15 \text{ and } 308.15)$ K. The experimental data were further correlated with the NRTL model.

1. Introduction

Glycol ethers are widely used as solvents in cleaning formulations, such as glass and all purpose cleaners. It has been shown that in a binary (water + glycol ether) system, the effects of propylene oxide groups $-OCH(CH_3)CH_2-$ and ethylene oxide groups $-OCH_2CH_2-$ on the lower critical solution temperature are different [1]. The (liquid + liquid) equilibrium data of several ternary (water + oil + ethylene glycol ether) systems have been measured in our laboratory [2–7]. The difference between ethylene glycol ether and propylene glycol ether triggers our interests to investigate the phase behaviour of the ternary (water + oil + propylene glycol ether) system. Recently, we have presented the (liquid + liquid) equilibrium measurements for ternary systems (water + hexadecane + propylene glycol *n*-propyl ether) and (water + tetradecane + propylene glycol *n*-propyl ether) [8,9]. In this work, (liquid + liquid) equilibrium measurements of the ternary system (water + dodecane + propylene glycol *n*-propyl ether) $CH_3(CH_2)_2(OCH(CH_3)CH_2)OH$ (symbolized by C_3P_1 hereafter) were performed at $T = (288.15, 298.15, \text{and } 308.15)$ K under atmospheric pressure. The NRTL (nonrandom, two-liquid) model of Renon and Prausnitz [10] were used to correlate the experimental data by using the commercial simulator Aspen Plus.

2. Experimental section

Dodecane ($C_{12}H_{26}$) oil was purchased from Merck Chemical Co. with a mass fraction purity of 0.99 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 mass fraction purity of >0.995 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. The comparison of measured density (DMA 4500M, Anton-Paar) and refractive index (NAR-3T, Atago) of dodecane and propylene glycol *n*-propyl ether with literature values [11–13] is shown in table 1. In addition, the water contents of dodecane and propylene glycol *n*-propyl ether analysed by a coulometric Karl Fischer moisture titrator (MKC-501, Kyoto Electronics Manufacturing Co.) are also reported in table 1.

The gas chromatograph (China Chromatography 9800, China Chromatography Co.) equipped with a thermal conductivity detector was used to analyse the composition of the sample. The peak area was calculated and recorded by the computer equipped with a data acquisition interface card (Scientific Information Service Co., Taiwan). The stainless steel column was 2 m length and packed with Poropak P 80/100 mesh. Both the injection-port temperature and the detector temperature were held at $T = 563.15$ K, while the oven temperature was fixed at $T = 513.15$ K. The flow rate of the carrier gas, helium, was maintained at

* Corresponding author.
E-mail address: ljchen@ntu.edu.tw (L.-J. Chen).

0021-9614/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2011.11.013

TABLE 1
Comparison of the experimental results and literature data [11–13] of densities, ρ, and refractive index, n_D, of the pure compounds at $T = (293.15$ and $298.15)$ K.

Compound	10^6 (Water content)	T/K	$\rho/(g \cdot cm^{-3})$		n_D	
			Exptl.	Lit.	Exptl.	Lit.
Propylene glycol *n*-propyl ether	250.13	293.15	0.88588	0.8886 [11] 0.885 [12]	1.4118	1.4130 [11] 1.4110 [12]
		298.15	0.88111	*a*		*a*
Dodecane	49.246	293.15	0.74886	0.74875 [13]	1.4212	1.42167 [13]
		298.15	0.74523	0.74518 [13]	1.4196	1.41952 [13]

[a] No literature data available.

TABLE 2
Experimental mole fraction of equilibrium liquid phases for the ternary system (water + dodecane + C_3P_1) at $T = 288.15$ K.

Composition in mole fractions			
Dodecane-rich phase		Water-rich phase	
H_2O	C_3P_1	H_2O	C_3P_1
0.002	0.024	0.988	0.012
0.005	0.072	0.977	0.023
0.014	0.138	0.962	0.038
0.030	0.201	0.950	0.050
0.045	0.242	0.932	0.068
0.049	0.252	0.908	0.091
0.049	0.253	0.868	0.129
0.050	0.254	0.799	0.194
0.051	0.257	0.757	0.233
0.056	0.268	0.669	0.310
0.091	0.326	0.495	0.435

TABLE 3
Experimental mole fraction of equilibrium liquid phases for the ternary system (water + dodecane + C_3P_1) at $T = 298.15$ K.

Composition in mole fractions					
Dodecane-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
Three-liquid-phase-coexisting					
0.117	0.364	0.564	0.384	0.959	0.041
Two-liquid-phase-coexisting region on dodecane/C_3P_1 side					
0.178	0.396	0.480	0.425		
Two-liquid-phase-coexisting region on water/dodecane side					
0.087	0.332			0.960	0.040
0.047	0.260			0.965	0.035
0.024	0.180			0.971	0.029
0.008	0.101			0.979	0.021
0.003	0.040			0.989	0.011
Two-liquid-phase-coexisting region on water/C_3P_1 side					
		0.646	0.326	0.953	0.047
		0.741	0.251	0.950	0.050

TABLE 4
Experimental mole fraction of equilibrium liquid phases for the ternary system (water + dodecane + C_3P_1) at $T = 308.15$ K.

Composition in mole fractions			
Dodecane-rich phase		Water-rich phase	
H_2O	C_3P_1	H_2O	C_3P_1
0.004	0.054	0.989	0.011
0.012	0.129	0.982	0.018
0.028	0.214	0.977	0.023
0.059	0.300	0.972	0.028
0.099	0.376	0.971	0.029
0.171	0.430	0.970	0.030
0.234	0.463	0.970	0.030
0.308	0.482	0.970	0.030
0.364	0.478	0.970	0.030
0.432	0.463	0.970	0.030
0.537	0.415	0.967	0.033
0.808	0.192	0.955	0.045

30 $cm^3 \cdot min^{-1}$. Single-phase binary mixtures of (C_3P_1 + water) and (C_3P_1 + dodecane) with known compositions were used to calibrate the gas chromatography in the composition range of interest.

For each tie line, the (water + dodecane + C_3P_1) mixtures were prepared in three test tubes with the same total composition. These samples were placed in a computer-controlled water thermostat [8], whose temperature was controlled within ±0.005 K, for at least 12 h to allow the system to reach equilibrium. All samples were shaken vigorously several times to ensure thorough mixing. The variation of composition as a function of time was carefully examined and the system could reach equilibrium within 6 h. After equilibrium was reached, all liquid phases were transparent and interfaces were sharp and mirror-like. Following equilibration, each phase in every sample was analysed at least three times by gas chromatography. The experimental uncertainty of the gas chromatography was within ±0.001 mole fraction.

3. Results and discussion

The experimental equilibrium compositions of the ternary system (water + dodecane + C_3P_1) at $T = (288.15,$ 298.15, and 308.15) K are given in tables 2 to 4, respectively. At $T = 288.15$ K, there is only one two-liquid-phase-coexisting envelop in the phase diagram, as shown in figure 1. The system exhibits one three-

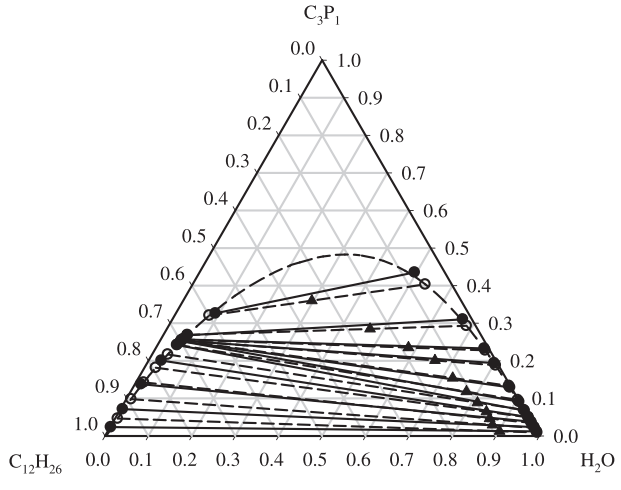

FIGURE 1. Ternary (liquid + liquid) equilibria (in mole fraction) for the system (water + *n*-dodecane + C_3P_1) at $T = 288.15$ K: experimental tie lines (•, solid lines); calculated binodal curve (dashed curve) and tie lines (○, dashed lines); and total compositions (▲).