Available online at www.sciencedirect.com

ScienceDirect

Fluid Phase Equilibria 260 (2007) 262–265

FLUID PHASE EQUILIBRIA

www.elsevier.com/locate/fluid

Liquid–liquid equilibria of ternary mixture (propargyl alcohol + diisopropyl ether + water)

Kongmeng Ye, Jia Wu*, Guo’an Deng

Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, PR China

Received 24 April 2007; received in revised form 28 June 2007; accepted 6 July 2007

Abstract

The liquid–liquid equilibria (LLE) of ternary mixture (propargyl alcohol + diisopropyl ether + water) were measured under atmospheric pressure and at different temperatures of 297.25, 304.35, 313.15, and 323.25 K. It was found that the end points of tie-lines at the four temperatures were located almost on a common solubility curve but the tie-lines possessed different slopes that described different equilibrium relations. A comparison of the predicted values through use of UNIFAC method with the measured LLE data was carried out but the predicted values showed remarkable deviations from the experimental data.

Keywords: Liquid–Liquid equilibria; Propargyl alcohol; Diisopropyl ether; Water; UNIFAC

1. Introduction

Propargyl alcohol (PA) derivatives are useful compounds in fine chemical synthesis which can be readily activated by transition metals and allow the preparation of a variety of multiple metal–carbon bond species such as vinylidene, alkenylidene and alkenylcarbene complexes [1]. Because PA forms a binary azeotrope with water, it is hard to purify PA up to 99.9% only by distillation. Liquid extraction provides a cheaper and energy-saving precursor to distillation in industrial applications [2].

It is reported that diisopropyl ether (DIPE) is an effective extractant in separating alkanol [3], toluene [4], 2-propanol [5], methanol [6], phenol [7–9] and so on. However, there is no published research work related to the liquid–liquid equilibria (LLE) behavior of the ternary mixture of PA, DIPE and water. This study is part of an ongoing investigation to check the efficiency of DIPE as solvent for extracting PA from water.

In this work, LLE data were measured under atmospheric pressure and at temperatures of 297.25, 304.35, 313.15, and 323.25 K. A comparison of the LLE data with the predicted values by using UNIFAC method was also carried out.

2. Experiments

2.1. Chemicals

The suppliers and purity specifications of the chemicals used in experiments are listed in Table 1 together with the measured purities determined using a gas chromatography (GC) with a thermal conductivity detector (TCD). The chemicals were used without further purification.

2.2. Procedure

The general procedure of experimental operation was as follows.

Necessary quantities of PA, DIPE and water were weighted with an electronic balance (BS224S, accuracy ±0.1 mg, Sartorious AG, Germany) and dosed in a set of test tubes according to the desired compositions of ternary mixtures. The total quantity in a test tube was about 11–17 g. The tubes were sealed with silicon rubber stops and weighted again, and then were fixed horizontally onto an oscillator installed in a thermostatic oven with PID temperature controller of accuracy ±0.1 K.

The tubes in thermostat oven were preheated 30 min to let the temperature keep steady at the desired values, and then were oscillated for 60 min to approach phase equilibria. After stopping

---

* Corresponding author. Tel.: +86 571 8795 1230.
E-mail address: wujia@zju.edu.cn (J. Wu).

0378-3812/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2007.07.015

Table 1
Suppliers and purity of the used chemicals

Chemical	Supplier	Specifications[a] (%)	Measured purity (%)
PA	Northeast Pharmaceutical Factory Fushun Branch, China	>99.50	>99.09[b]
DIPE	Wulian Chemical, China	>99.90	>99.84

[a] The purity reported by the supplier.
[b] The only impurity detected was water.

oscillation, the tubes were set to vertical positions and kept static for 30 min to break the liquid in tubes clearly into two phases. The tubes were weighted again to ensure that the loss of contents was negligible (less than 0.01 g). Then the two phases were carefully sampled with a micro injector and analyzed at once using a GC (GC 1690T, Kexiao Science Apparatus Co. Ltd., China) with Ø 2 mm × 2000 mm column (packed with Porapak Q, 80/100 Mesh, USA).

The temperatures of TCD, column and injection port of GC were all kept at $T = 463.15$ K. The bridge current of TCD was 150 mA. The pre-column pressure of carrier gas hydrogen was kept at 0.264 MPa.

3. Results and discussion

3.1. LLE measurements

The measured data of tie-lines at four different temperatures are listed in Table 2. Every value was an average of those from three repeated experiments. The root mean square deviation $\mathrm{RMSD_R}$ for all repeated data was 0.077% which was calculated by following formula.

$$\mathrm{RMSD_R} = \left[\frac{\sum_k^N \sum_j^2 \sum_i^3 \sum_r^R (x_{ijkr}^{\mathrm{mea}} - x_{ijk}^{\mathrm{exp}})^2}{2 \times 3 \times N \times R} \right]^{1/2} \quad (1)$$

Table 2
Phase compositions of water (1) PA (2) DIPE (3) ternary mixtures (mass percentage)

DIPE rich phase			Water rich phase			Total		
X1	X2	X3	X1	X2	X3	X1	X2	X3
$T = 297.25$ K								
1.35	5.72	92.93	86.41	13.00	0.60	44.91	9.32	45.77
2.15	12.21	85.64	77.54	21.39	1.07	41.52	16.99	41.49
3.10	17.50	79.40	70.69	27.90	1.41	38.49	22.99	38.51
4.16	22.92	72.93	63.84	33.64	2.52	35.94	28.55	35.51
5.53	27.61	66.85	56.99	38.55	4.47	33.24	33.43	33.33
7.18	31.94	60.89	51.34	42.33	6.34	31.18	37.52	31.30
9.14	35.80	55.07	45.01	45.71	9.28	29.52	41.22	29.26
$T = 304.35$ K								
1.11	5.75	93.14	87.07	12.36	0.57	45.01	9.32	45.67
2.02	11.84	86.14	77.81	21.15	1.04	41.64	16.82	41.54
2.82	17.11	80.08	70.20	28.20	1.60	38.39	23.02	38.59
4.08	22.35	73.57	63.49	33.96	2.54	35.70	28.65	35.64
5.40	27.08	67.51	56.82	39.02	4.18	33.16	33.48	33.36
7.07	31.38	61.55	50.57	43.00	6.43	31.11	37.66	31.23
8.72	35.26	56.03	44.61	46.24	9.15	29.31	41.29	29.41
$T = 313.15$ K								
1.32	5.52	93.16	86.94	12.45	0.61	45.41	9.05	45.54
1.93	11.19	86.88	76.81	21.97	1.22	41.41	16.80	41.80
2.76	16.17	81.06	69.02	29.16	1.82	38.68	23.01	38.31
3.66	20.81	75.53	62.13	34.95	2.92	35.79	28.48	35.73
4.74	24.88	70.37	55.39	39.83	4.78	33.24	33.26	33.51
5.95	28.65	65.41	49.59	43.74	6.67	31.56	37.40	31.05
7.61	32.79	59.60	43.21	47.07	9.72	29.29	41.22	29.49
$T = 323.25$ K								
1.25	5.06	93.69	87.05	12.49	0.46	45.41	9.05	45.54
1.98	10.16	87.86	77.04	22.02	0.93	41.41	16.80	41.80
2.65	14.88	82.46	68.90	29.54	1.57	38.68	23.01	38.31
3.50	19.24	77.26	61.02	35.76	3.22	35.79	28.48	35.73
4.38	23.02	72.60	54.73	40.42	4.85	33.24	33.26	33.51
5.47	26.99	67.54	48.55	44.32	7.13	31.56	37.40	31.05
6.65	30.55	62.80	42.58	47.48	9.93	29.42	41.11	29.46