Available online at www.sciencedirect.com
ScienceDirect
Fluid Phase Equilibria 266 (2008) 42–46
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Liquid–liquid equilibria of water + 2,3-butanediol + ethyl acetate at several temperatures

Yan-Yang Wu [a], Jia-Wen Zhu [a,*], Kui Chen [a], Bin Wu [a], Ya-Ling Shen [b]

[a] *Chemical Engineering Research Center, East China University of Science & Technology, Shanghai 200237, China*
[b] *State Key Laboratory of Bio-Reactor Engineering, East China University of Science & Technology, Shanghai 200237, China*

Received 5 December 2007; received in revised form 9 January 2008; accepted 13 January 2008
Available online 19 January 2008

Abstract

Liquid–liquid equilibrium (LLE) data of the solubility curves and tie-line compositions have been determined for mixtures of (water + 2,3-butanediol + ethyl acetate) at 298.15, 308.15 and 318.15 K and atmospheric pressure. Distribution coefficients and separation factors have been evaluated for the immiscibility region. The reliability of the experimental tie lines has been confirmed by using Othmer–Tobias correlation. The LLE data of the ternary systems have been predicted by UNIFAC method.

Keywords: Liquid–liquid equilibria; 2,3-Butanediol; Ethyl acetate; UNIFAC

1. Introduction

The production of 2,3-butanediol by fermentation has been considered as a potential source of fuels [1,2] or chemical feedstock [3]. Its microbial preparation has been observed in several yeasts and bacteria from various genera such as Klebsiella, Bacillus, Serratia and Pseudomonas [4–10]. The separation and purification of 2,3-butanediol from fermentation broth is essential to realize the industrial production for 2,3-butanediol [11–13].

Since the fermented liquors contain only a few percent of 2,3-butanediol along with various other materials which cause difficulty in separation and since 2,3-butanediol has a much higher boiling point than that of water and may not be distilled out directly, extraction from the fermentation liquors by a suitable solvent seems to be a feasible method. Various organic solvents have been investigated and reported for 2,3-butanediol extraction [14,15]. Ethyl acetate used in this study may be a suitable solvent for extraction of 2,3-butanediol from water, being capable of forming azeotropic mixtures with water to take it from 2,3-butanediol.

The aim of this work is to present the phase behavior of liquid–liquid equilibrium (LLE) for the (water + 2,3-butanediol + ethyl acetate) ternary system at 298.15, 308.15 and 318.15 K and atmospheric pressure. The tie lines have also been predicted using the UNIFAC method (a group contribution method) developed by Fredenslund et al. [16] and compared with the experimental data.

2. Experimental

2.1. Chemicals

All the chemicals used in this study were purchased from commercial sources. 2,3-Butanediol was supplied by Sinopharm Chemical Reagent Co. Ltd. with a minimum mass fraction purity of 99.2%. Ethyl acetate was provided by Shanghai Chemical Reagent Co. Ltd. with a minimum mass fraction purity of 99.5%. They were used directly without further treatment in this study. Water was distilled twice before utilization. The purity of these materials was checked and assured by gas chromatography. The normal boiling point and refractive index values were measured in this study and reported in Table 1 in comparison with the literature data so as to demonstrate the purity of the compounds.

* Corresponding author. Tel.: +86 21 64253003; fax: +86 21 64253914.
E-mail address: jwzhu@ecust.edu.cn (J.-W. Zhu).

0378-3812/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2008.01.009

Table 1
Refractive indexes at $T = 293.15$ K and boiling points at 101.3 kPa, of the compounds

Component	Refractive indexes		Boiling points (K)	
	Experimental	Literature [a]	Experimental	Literature [a]
2,3-Butanediol[b]	1.4375	1.4366	454.21	454.20
Ethyl Acetate	1.3701	1.3704	350.24	350.21
Water	1.3325	1.3325	373.30	373.26

[a] Ref. [17].
[b] Ref. [18].

2.2. Equilibrium measurements

Three different temperatures (298.15, 308.15 and 318.15 K) at atmospheric pressure were selected to study the ternary equilibrium system in order to observe the evaluation of the binodal curves and tie lines.

The binodal (solubility) curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. Temperature in the cell was kept constant by circulating water from a water bath (SUPER-CONSTANTTEP BATH, Shanghai precision science instrument Co. Ltd.), which is equipped with a temperature controller capable of maintaining the temperature within ±0.1 K. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of water + ethyl acetate with 2,3-butanediol until the turbidity had disappeared. For the water-side and solvent-side, regions in which the curve and the sides of the triangle are close and exhibit similar slopes, binary mixtures of either (water + 2,3-butanediol) or (ethyl acetate + 2,3-butanediol) were titrated against the third component until the transition from homogeneity to heterogeneity was observed.

All mixtures were prepared by weighing with a Sartorius scale accurate to within $\pm 10^{-4}$ g. Mutual solubility values of the (water + 1-butanol) binary were measured using the method based on the detection of the cloud point [19–21]. The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the microburette with an accuracy of ±0.01 cm^3, and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting approximately 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times in order to acquire high accuracy.

End-point determinations of the tie lines were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium. For this purpose, mixtures of known masses of water, 2,3-butanediol, and ethyl acetate lying within the heterogeneous zone were introduced into the equilibrium cell and were agitated for not less than 2 h with a magnetic stirrer vigorously, and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The compositions of liquid samples withdrawn from conjugate phases were analyzed by a gas chromatograph (GC112A) with a thermal conductivity detector (TCD), after calibration with gravimetrically prepared standard solutions. A GDX-102 packed column (3 m × Φ3 mm × 0.5 mm) was used to separate components. They were all produced by Shanghai Hengping Scientific Instrument Co. Ltd. The oven, injector and detector temperatures were 453.15, 473.15 and 493.15 K, respectively. High-purity hydrogen (99.9999% purity) was used as the carrier gas at a constant flow rate of 30 mL min^{-1}. The detector was connected to a FJ-2003B integrator. Each sample was analyzed at least thrice to ensure accuracy. The uncertainty in mass fractions was within ±0.001.

3. Results and discussion

The LLE measurements were made for the ternary system of (water + 2,3-butanediol + ethyl acetate) at 298.15, 308.15 and 318.15 K and atmospheric pressure. The experimental binodal curves for this ternary system at each temperature are listed in Table 2, for which W_i refers to the mass fraction of i-th component. The experimental tie-line compositions of the equilibrium phases are shown in Table 3, for which W_{i1} and W_{i3} refer to the mass fractions of the i-th component in the aqueous and solvent phases, respectively.

The experimental and predicted equilibrium data through UNIFAC model of the ternary system at $T = 298.15$ K are plotted in Fig. 1. As can be seen from Fig. 1, the system

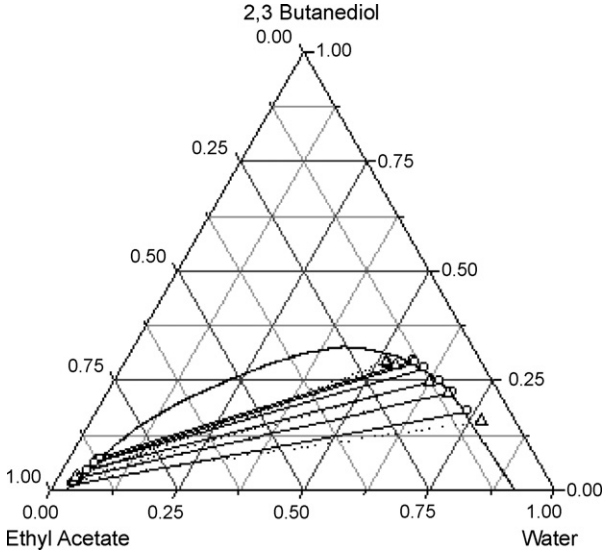

Fig. 1. Ternary diagram for LLE of (water + 2,3-butanediol + ethyl acetate) at 298.15 K: (—) experimental solubility curve; (◯) experimental tie-line data; (△) calculated (UNIFAC) tie-line data.