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Isobaric vapor–liquid equilibria for water + n-propanol + n-butanol ternary system at atmospheric pressure

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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) data for water + n-propanol + n-butanol ternary system have been extensively measured at 99.2 kPa using a recirculating still. The experimental data were then correlated using the extended UNIQUAC model, in which the binary interaction energy parameters between the three components were obtained through a simplex fitting method. The results showed that the calculated data by the extended UNIQUAC model using the same interaction energy parameters agree well with both the experimental data and the literature data. It demonstrated that the experimental data are very consistent with the literature data; and the extended UNIQUAC model is reliable to predict the VLE of the ternary system using the obtained interaction energy parameters.

1. Introduction

1,4-Butanediol (BDO) is the main intermediate for the manufacture of tetrahydrofuran, γ-butyrolactone, polybutylene terephthalate and polyurethane [1,2] and a widely used industrial solvent. The majority of the word's BDO is produced via the Reppe process that involves the reaction of formaldehyde with acetylene and subsequent stages of hydrogenation to produce BDO [3], in which a significant amount of liquid mixtures of n-propanol + n-butanol + water are generated during the product purification. To recycle these by-products, the primary consideration is distillation since the three components have significant boiling temperature differences (water, 100 °C; n-propanol, 97.19 °C; n-butanol, 117.7 °C) [4], while the prerequisite for the process design and calculation is the vapor–liquid equilibrium (VLE) data of the system.

VLE data of the binary systems between water, n-propanol and n-butanol are fairly complete in the literatures [5], while only two groups of isobaric data of the ternary system in a very narrow temperature range are available, which cannot meet the requirement of engineering calculations. Therefore, it is very necessary to measure and extend the VLE data of water + n-propanol + n-butanol ternary system to a broader temperature and concentration range.

In this paper, the isobaric VLE data of water + n-propanol + n-butanol ternary system were measured at 99.2 kPa and extensive concentration and temperature ranges, and the experimental data were then correlated using the extended UNIQUAC model, in which the binary interaction energy parameters were obtained through a simplex fitting method. The aim of the study is to enrich the VLE database and establish a reliable model to predict the VLE of water + n-propanol + n-butanol ternary system.

2. Experimental

2.1. Materials

n-Propanol (analytical reagent grade, AR, mass fraction > 99.5%) is purchased from Tianjin Guangfu Fine Chemical Ltd. (Tianjin, China,), n-butanol (AR, mass fraction > 99.5%) is from Chongqing Chuandong Chemical Reagent Plant (Chongqing, China). The water content, determined using a Karl Fischer volumetric automatic titrator (2DJ-2S, Beijing Xianqu), was small in the two chemicals (mass fraction < 0.0005). The two reagents were used without further purification after chromatography failed to show any significant impurities, however, the reagents were degased in vacuum before measurements. The double distilled water used in the measurements is self-made in the lab.

2.2. Apparatus and procedure

2.2.1. VLE data measurement

The binary mixtures of water + n-propanol and n-propanol + n-butanol are totally miscible, while water and n-butanol is partially miscible. The addition of a suitable amount of n-propanol in the

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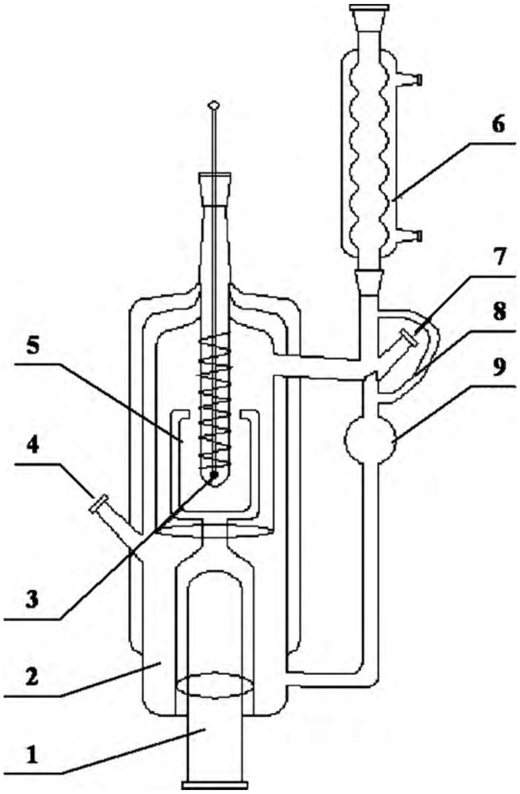

Fig. 1. Experimental set-up for VLE measurement. (1) Heating mantle; (2) boiling chamber; (3) thermometer, (4) liquid phase sampling port/liquid mixture input; (5) equilibrium chamber; (6) condenser; (7) vapor phase sampling port; (8) equilibrium tube; (9) mixing chamber.

binary mixtures of water and n-butanol increases their mutual solubility, leading to the formation of water + n-propanol + n-butanol ternary system. However, liquid–liquid phase stratification could still occur in the ternary system at some ranges of concentration and temperature. While during the VLE measurements, the vapor phase was sampled at liquid state, consequently, liquid–liquid stratification could occur in vapor phase when it is cooled to the liquid state. Once it occurs, the accuracy of vapor phase sampling will be affected. In this study, the followed experimental procedures were followed to prevent the occurrence of phase stratifications in vapor samples. First, binary mixture of n-propanol + n-butanol at a specific volume ratio were prepared (at 1/4, 3/7, 2/3, 1/1 and 3/2, respectively), then water was added step by step and the VLE data were recorded at every step. Each group of VLE experiments were ended when phase stratification occurs in the vapor samples. Since phase stratification would not occur in the liquid phase in the experimental concentration and temperature ranges, the accuracy of the VLE measurements can be guaranteed.

The VLE data were measured using a CE-2 atmospheric pressure VLE detector (Beiyang Chemical Equipment Co., Ltd., Tianjin, China), which is a dual circulation glass VLE still showed in Fig. 1 [6]. During the measurements, the n-propanol + n-butanol binary mixture at a specific ratio was firstly added into the boiling chamber and heated. The mixture of the vapor and liquid was carried upward into the equilibrium chamber, where the vapor phase was separated with the liquid phase. The vapor was then condescended in the condenser and flowed back to the mixing chamber, where it mixed with the liquid from the equilibrium chamber and returned to the boiling chamber for recirculation. The equilibrium state was usually reached in 30–60 min, which was indicated by the steady temperature. After waiting for about another 30 min, the temperature was, then, recorded, the liquid and vapor phase was sampled and their composition was analyzed using GC. Afterwards, water was stepwisely added into the VLE chamber, and at every step, the previous procedure was repeated, the equilibrium temperatures were recorded and the vapor/liquid composition was determined. When liquid–liquid stratification occurred in the vapor sample, this group of experiments were completed. Then, the initial volume ratio of the binary n-propanol + n-butanol mixture was changed for the next group of experiments. The equilibrium temperature was measured by a precision and calibrated thermometer (Mercury, WNG-01, Hengshui Haiyang, Hebei, China) with an accuracy of ±0.05 K, which was checked against the ice and steam point of the double distilled water. The actual atmospheric pressure was measured by a mercury barometer with an accuracy of 0.01 kPa. Since the atmospheric pressure changed slightly during the experiments, the boiling temperatures at the actual pressures were adjusted to 99.20 kPa (the average value) according to the literature method [7,8]. The VLE data of the ternary system were measured when the initial volume ratio between n-propanol and n-butanol ($\nu_2 : \nu_3$) is at 1/4, 3/7, 2/3, 1/1 and 3/2, respectively.

2.2.2. *Composition analysis of the samples*

The composition of the samples was analyzed using a 102AT GC (Shanghai Precision Instrument Co., Ltd., Shanghai, China) equipped with a TCD detector and Porapak-P column. The operating conditions are column oven temperature, 180 °C; evaporation chamber temperature, 200 °C; detector temperature, 200 °C; H_2 (carrier gas) flowing rate, 55 ml/min.

In the experiments, two series of standard solutions of water + n-propanol and n-propanol + n-butanol were first prepared and analyzed using GC, two calibration curves were obtained by plotting the peak area ratio and molar ratio of the compositions. Then, the composition of the samples was determined according to the calibration curves by analyzing the peak areas in the chromatograms. The standard deviation in the mole fraction was less than 0.001.

3. VLE correlation using the extended UNIQUAC model

For experimental data to be applied in engineering calculations, it is preferred to correlate them into a model. Considering that water, n-propanol and n-butanol are all polar chemicals, the extended UNIQUAC equation was selected as the correlation model. The extended UNIQUAC model was originally proposed by Sander et al. [9] to solve complex VLE equations involving electrolytes, and later modified by several authors to extend its applicability and improve the accuracy [10,11]. It has been demonstrated that the extended UNIQUAC model is able to accurately describe the solid–liquid, liquid–liquid, and vapor–liquid equilibria of various systems [12–17].

Table 1
Interaction energy parameters used in the extended UNIQUAC calculation.

Parameter	a_{ij}^0			a_{ij}^T		
Material	Water (1)	n-Propanol (2)	n-Butanol (3)	Water (1)	n-Propanol (2)	n-Butanol (3)
Water (1)	0.000	−1605.658	4688.950	0.000	−2.523	−9.606
n-Propanol (2)	−319.780	0.000	−57.214	0.856	0.000	0.000
n-Butanol (3)	−674.420	−0.598	0.000	1.900	0.000	0.000