



Separation of 2-propanol and water azeotropic system using ionic liquids as entrainers



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ABSTRACT

2-propanol and water form an azeotropic mixture of the minimum boiling point at constant pressure. In this work, three ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) and 1-ethyl-3-methylimidazolium bromide ([EMIM][Br]), were used as entrainers to separate the azeotropic mixture by the method of extractive distillation. Isobaric vapor–liquid equilibrium (VLE) data for the ternary systems of 2-propanol + water + [EMIM][OAc], 2-propanol + water + [BMIM][OAc], and 2-propanol + water + [EMIM][Br] were measured at 101.3 kPa. The results demonstrate that the relative volatility of 2-propanol to water is dramatically enhanced with the addition of ILs at areas of 2-propanol molar fraction higher than 0.2. As the amounts of ILs increase, the azeotropic point is pulled up and the azeotropy is even eliminated gradually. The separation effect (namely the effect of ILs on enhancement of the relative volatility) of the three ILs follows the order: [EMIM][OAc] > [BMIM][OAc] > [EMIM][Br]. Moreover, The experimental VLE data were well correlated with the nonrandom two-liquid model (NRTL).

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1. Introduction

2-propanol is an important chemical product and raw material. Due to its excellent physico-chemical properties, 2-propanol finds its use in various areas, such as used as an intermediate or a solvent in pharmaceutical industry [1], applications in biofuels [2], and other engineering applications [3,4]. Generally, there are two commercial routes to produce 2-propanol, namely direct hydration and indirect hydration of propylene [5]. Therefore, it becomes necessary to separate 2-propanol from water. However, a separation problem occurs because 2-propanol and water form a minimum azeotrope at 2-propanol mass fraction of 87.4%, and the azeotropic temperature is 353.45 K at 101.3 kPa [6].

Due to the inefficiency of conventional distillation for azeotrope separation, it is indispensable to turn to special distillations, such as extractive distillation, pressure swing distillation, azeotropic distillation, salt adding distillation and so on [7]. In this study, the extractive distillation separation method draws our attention, for

its high-efficiency separation capacity for binary azeotropes and other close boiling point mixtures. Extractive distillation, by adding a third solvent (namely entrainer) to the separated mixtures, achieves the goal of valid separation [8]. Hence, the selection of entrainers should be paid more attention. Traditional entrainers such as salts [9] and organic solvents [10] have been applied to separate the azeotropic mixture, but they have the disadvantages of corrosivity, pollution to the environment and difficulty in recycling.

In this work, ionic liquids (ILs) are proposed as entrainers because of their attractive advantages, such as non-volatility, non-flammability, high chemical and thermal stability, convenient recycling and tailorable structures [11]. During the past years, the isobaric or isothermal vapor–liquid equilibrium data for 2-propanol and water containing ionic liquids have been reported. Various ionic liquids have been investigated to test their abilities to break the azeotropy, including 1-ethyl-3-methylimidazole tetrafluoroborate [12], 1-butyl-3-methylimidazole tetrafluoroborate [6], 1-butyl-3-methylimidazole chloride [13] and 1-butyl-3-methylimidazole acetate [14]. The ILs [EMIM][OAc], [BMIM][OAc] have also been used to separate the mixture [15], but the experiment conclusion only can be made at the 2-propanol-rich region. In this study, the ILs [EMIM][OAc], [BMIM][OAc], [EMIM][Br] were utilized to separate the azeotropic mixture of 2-propanol and

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water. The VLE data expanded to water-rich region were measured at 101.3 kPa and were correlated with the non-random two liquid (NRTL) model. By analyzing the results, we tried to find the potential entrainers for the system.

2. Experimental section

2.1. Material

2-propanol (mass fraction $\geq 99.7\%$) used in this work was provided by Sinopharm Group without further purification. Water used in this work was ultrapure water produced by Water purification system (Direct-Q3UV). The ILs, [EMIM][OAc], [BMIM][OAc], and [EMIM][Br] were synthesized in our lab, and the mass purities of them were determined by Liquid Chromatography. The ILs were dried in a vacuum desiccator at 373 K for 24 h before experiment with the purpose of making the moisture content down to 0.003 (mass fraction) checked by Karl Fischer titration. Specifications of the chemicals utilized in this work are listed in Table 1.

2.2. Apparatus and procedure

In this work, an all-glass dynamic recirculating still (NGW, Wertheim, Germany), which has been described in detail in the previous literature [16] [17], was used to conduct the experiment. The pressure of the apparatus was kept at 101.3 kPa by controlling a gas buffer connected with the still. A manometer with an uncertainty of 0.1 kPa was used to measure the pressure of the apparatus. A precise and calibrated thermometer with an uncertainty of 0.01 K was used to measure the temperature of the apparatus. The experiment was performed in the way that the binary mixture of water and defined mole fraction of ILs were added in batches into the other mixture of 2-propanol and the same mole fraction of IL continuously, with the purpose of changing the mole fraction of 2-propanol from zero to unity and keeping the mole fraction of IL in each series constant in the ternary system. Only when the temperature was constant for more than 30 min, was the VLE assumed.

Both the vapor and liquid phases were detected by a gas chromatograph (Model 7890A, Agilent Technologies) equipped with a 30 m, 0.32 mm i.d., and 0.25 μm Agilent 19091J-413 capillary column and a TCD detector for which the carrier gas is N_2 . The operating conditions were as follows: the temperatures of oven, injector, and detector were 373, 473, and 473 K, respectively. The samples were injected into the headspace sampler (G1888 Network, headspace Sampler Agilent Technologies) before being injected into the GC. Due to the non-volatility of ILs, only the peaks of 2-propanol and water were observed. A digital balance (CAV264C OHAUS America) with a standard uncertainty of 0.001 g was used to measure the content of ILs by weighting the sample before and after vaporizing the volatile component in a vacuum desiccator. And the standard uncertainty of the content of the component in the liquid and vapor phase is 0.001 (mole fraction).

Table 1
Overviews of the chemical samples.

Chemical name	Source	Purity	Purification method	Analysis method
2-propanol	Sinopharm Group	0.997	None	GC ^a
[BMIM][OAc]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b
[EMIM][OAc]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b
[EMIM][Br]	Synthesized own	0.990	Vacuum desiccation	LC ^c KF ^b

^a GC = gas chromatography.

^b KF = Karl Fisher titration.

^c LC = liquid chromatography.

Table 2

The isobaric VLE data for the binary system of 2-propanol (1) + Water (2) at 101.3 kPa.

T (K)	x_1	y_1
365.42	0.023	0.307
358.73	0.049	0.433
356.22	0.078	0.502
354.91	0.126	0.522
354.34	0.248	0.544
354.15	0.373	0.554
353.82	0.448	0.574
353.43	0.562	0.624
353.36	0.625	0.645
353.32	0.675	0.674
353.45	0.747	0.710
353.76	0.825	0.790
353.88	0.865	0.831
354.65	0.948	0.928

Standard uncertainty $u(x_1) = u(y_1) = \pm 0.001$, $u(T) = \pm 0.01$ K.

3. Results and discussion

3.1. Experimental data

With the purpose of verifying the reliability of the still used in this work, the binary VLE data of 2-propanol and water were determined at 101.3 kPa. The VLE data, listed in Table 2, were compared with the data calculated by the NRTL model and the data from literature [12]. As shown in Fig. 1, the VLE data of 2-propanol and water system measured in this work agree well with the literature and the calculated data, indicating that the still used in the work is reliable.

As mentioned above, the relative volatility α_{12} is considered as an important indicative quantity to evaluate the separation effect of an entrainer, and is defined as

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (1)$$

where $x_1(x_2)$ and $y_1(y_2)$ are the mole fractions of component 1(2) in the liquid phase and vapor phase, respectively.

Since the experimental data were measured at 101.3 kPa, the assumption of the ideal vapor phase could be made. After neglecting the fugacity coefficients and the Poynting correction, the VLE equation can be simplified as:

$$y_i P = x_i \gamma_i P_i^s \quad (2)$$

where y_i and x_i represent the mole fraction of components i in the vapor phase and the liquid phase, respectively, P is the total pressure of 101.3 kPa, γ_i is the activity coefficient of component i in the liquid phase, P_i^s is the saturated vapor pressure of component i at equilibrium temperature which can be calculated using the Antoine equation:

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