Fluid Phase Equilibria 466 (2018) 14–18

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Isobaric vapor-liquid equilibrium for chloroform + ethanol + 1,3-dimethylimidazolium dimethylphosphate at 101.3 kPa

Kun Yue [a], Chengjingyan Luo [a], Jiujuan Zhu [b], Zhongqi Ren [a], Ruiqi Qiao [a], Qunsheng Li [a, *]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, China
[b] School of Science, China University of Geoscience, Beijing, 100083, China

ARTICLE INFO

Article history:
Received 23 November 2017
Received in revised form
18 March 2018
Accepted 19 March 2018
Available online 20 March 2018

Keywords:
Vapor-liquid equilibrium
ChloroForm
Ethanol
Ionic liquids
NRTL

ABSTRACT

In this study, isobaric vapor-liquid equilibrium (VLE) data for ternary systems of chloroform + ethanol + 1,3-dimethylimidazolium dimethylphosphate ([MMim][DMP]) were measured with a modified Othmer still at 101.3 kPa. VLE data were correlated with the nonrandom two-liquid (NRTL) model and the fitted results showed that [MMim][DMP] produced a crossover effect between salting-in and salting-out on chloroform. Moreover, the minimum concentration of [MMim][DMP] needed to break the azeotrope of the chloroform + ethanol system was 0.058 (mole fraction). In the current work, the effects of [MMim][DMP] were analyzed and compared with that of other ionic liquids (ILs), and [MMIM][DMP] found to be an effective candidate entrainer.

1. Introduction

In recent years, the separation of binary azeotropic systems containing low-carbon alcohol has become a hot topic. Chloroform and ethanol are important organic solvents, with wide applications in the pharmaceutical and chemical industries [1]. The mixture of chloroform and ethanol at 101.3 kPa can form an azeotrope, which is difficult to efficiently separate by ordinary distillation. At present, common methods for separating azeotropes include azeotropic, extractive, and pressure distillation, among which extractive distillation is a generally applied method for breaking the azeotropic point of azeotropes. In addition, organic solvents and solid salts are commonly used as entrainers [2].

Ionic liquids are potential entrainers for separating azeotropes [3–8]. As a new type of green solvent, ILs have wide temperature ranges, low vapor pressure, and good thermal stability [9–12]. These advantages have identified ILs as potential entrainers as substitutes for organic solvents and solid salts. As ILs are widely applied in extractions and azeotrope separations, VLE data regarding ILs are essential for understanding the separation rule regarding ILs as well as for developing a thermodynamic model of VLE [13–16].

In this work, the VLE data for the binary system chloroform + ethanol and ternary systems containing [MMim][DMP] were obtained at 101.3 kPa. The effects of [MMim][DMP] on the chloroform + ethanol system were discussed and its separation ability discussed compared with other recently studied ILs.

2. Experimental section

2.1. Chemicals

The chemicals used in this study included chloroform, ethanol and [MMim][DMP] (Table 1). Both chloroform and ethanol (>99.9%, mass fraction) were obtained from Beijing Chemical Works (Beijing, China) and purity checked by gas chromatography (GC). The IL [MMIM][DMP] (>99%, mass fraction) was supplied by Shanghai Cheng Jie Chemical Co. Ltd.(Shanghai, China) and also purity checked by GC analysis. The water mass fractions, assessed using the Karl Fischer titration (KF), for chloroform, ethanol, and [MMIM][DMP] were 100, 150, and 450 ppm, respectively. Before experiments, volatile solvents were removed from the ILs by rotary evaporation under vacuum at 423 K for more than 24 h.

---

* Corresponding author.
E-mail address: buctcts@163.com (Q. Li).

https://doi.org/10.1016/j.fluid.2018.03.015
0378-3812/

Table 1
Specifications of used chemical samples.

Chemical name	Source	Mass fraction	Purification method	Final water mass fraction	Analysis method
chloroform	Beijing chemical works	0.999	None	0.00010	GC[a] , KF[c]
ethanol	Beijing chemical works	0.999	None	0.00015	GC[a] , KF[c]
[MMim][DMP]	Shanghai Cheng Jie chemical Co. LTD.	0.99	rotary evaporation under a vacuum	0.00045	LC[b] , KF[c]

[a] GC = gas chromatography.
[b] LC = liquid chromatography.
[c] KF = Karl Fischer titration.

2.2. Apparatus and procedure

In this work, the experimental data were obtained at 101.3 kPa using a modified Othmer equilibrium still made of quartz glass and each sample in the experiment is about 60 mL (Fig. 1). This equipment maintained pressure at 101.3 kPa via a pressure control system, with the system's pressure measured using a digital manometer with a standard uncertainty of 0.1 kPa. More details regarding the apparatus can be found in our previous publications [17–21].

Each sample for the present experiments was gravimetrically prepared using an analytic balance (Satorius, Germany) with a standard uncertainty of 0.1 mg. The equilibrium temperature was measured using a mercury thermometer, with a standard uncertainty of 0.1 K. The chloroform and ethanol content was analyzed by GC (SP7800, China), whose attachment was a thermal conductivity detector and a packed column (Porapak-Q, 3m × 3 mm). The GC carrier gas was high-purity hydrogen (99.999%, mass fraction) at 40 $cm^3\ min^{-1}$. The GC temperature settings included the injector and detector temperatures both at 443.15 K and the oven temperature at 403.15 K. Standard data were measured to establish a calibration curve, for determining the chloroform and ethanol mole fraction in each sample. Thus, the standard uncertainty in chloroform and ethanol mole fractions were estimated to be 0.002. In liquid phase containing ILs, the samples were also directly injected into the GC. The ILs could not be vaporized in GC due to their nonvolatility and only chloroform and ethanol were observed. As a result, the chloroform and ethanol mole fractions in liquid phase on an IL-free basis were obtained. At the same time, samples of liquid phase containing ILs were dried in an oven for 10 h to remove volatile components. The masses of original samples and treated samples were measured and the IL content in liquid phase obtained.

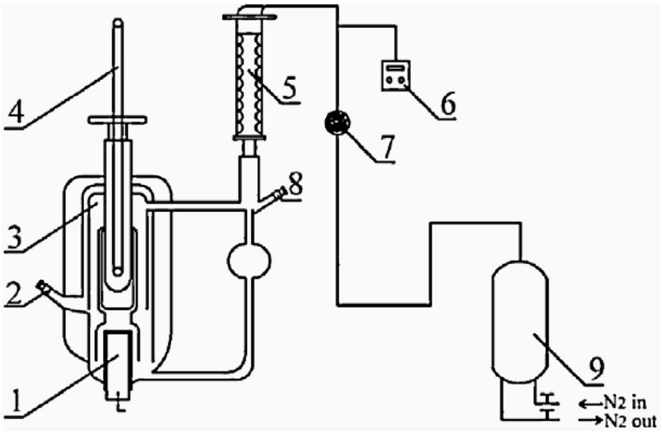

Fig. 1. Schematic diagram of vapor–liquid equilibrium still: (1) heating rod; (2) liquid-phase sample point; (3) equilibrium chamber; (4) thermometer; (5) condenser; (6) digital manometer; (7) desiccators; (8) vapor-phase sampling point; (9) gas buffer.

3. Result and discussion

3.1. Experimental data

The activity coefficient (γ_i) and relative volatility (α_{12}) was introduced to explore the effects of different ILs on chloroform + ethanol azeotropes. Considering the vapor phase ideal, the equations of γ_i and α_{12} are shown as follows:

$$\gamma_i = \frac{y_i P}{x_i P_i^S} \tag{1}$$

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^S}{\gamma_2 P_2^S} \tag{2}$$

where x_i and y_i represents the component i mole fraction in the liquid and vapor phase, respectively, P_i^S the component i vapor pressure, which was calculated by Antoine equation [22,23], and P the system pressure (101.3 kPa).

VLE data for the binary system of chloroform (1) + ethanol (2) were obtained at 101.3 kPa (Table 2). The experimental data in this paper agreed well with those published by A. Vicent Orchillês et al. [24] (Fig. 2), and the apparatus and experimental method were reliable.

Differential test for the thermodynamic consistency was conducted to verify the reliability of experimental data [25], and the data found to be thermodynamically consistent. More details can be found in the Supplementary Information, Fig. 1.

VLE data for the ternary system of chloroform (1) + ethanol (2) + [MMim][DMP] (3) were obtained at 101.3 kPa and [MMim][DMP] mole fraction held constant in each data set (Table 3). In addition, in the three sets of data x_3 was 0.05, 0.10 and 0.15. In IL-

Table 2
The VLE results for temperature T, liquid-phase mole fraction x, vapor-phase mole fraction y, activity coefficient γ, and relative volatility α_{12}, for the binary system of chloroform (1) + ethanol (2) at 101.3 kPa.[a]

T/K	x_1	y_1	γ_1	γ_2	α_{12}
346.40	0.085	0.229	1.880	1.033	3.194
341.95	0.183	0.415	1.815	1.056	3.171
338.65	0.280	0.543	1.722	1.077	3.065
336.15	0.362	0.624	1.651	1.117	2.918
334.35	0.472	0.695	1.495	1.185	2.545
333.15	0.567	0.738	1.376	1.307	2.154
332.55	0.679	0.784	1.244	1.499	1.710
332.25	0.776	0.819	1.149	1.822	1.304
332.25	0.881	0.870	1.075	2.466	0.901
332.65	0.951	0.926	1.046	3.339	0.645

[a] Standard uncertainties: u(T) = 0.1 K, u(P) = 0.1 kPa, u_c (x_1) = u_c (y_1) = 0.002.