Fluid Phase Equilibria 472 (2018) 212–217

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Effect of bis(trifluoromethylsulfonyl)imide-based ionic liquids on the isobaric vapor - liquid equilibrium behavior of ethanol + dimethyl carbonate at 101.3 kPa

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ARTICLE INFO

Article history:
Received 8 April 2018
Received in revised form
8 May 2018
Accepted 23 May 2018
Available online 25 May 2018

Keywords:
Vapor - liquid equilibrium
Ethanol
DMC
Ionic liquids
NRTL model

ABSTRACT

Isobaric vapor - liquid equilibrium (VLE) data for the binary system of ethanol + dimethyl carbonate (DMC) and the ternary systems of ethanol + DMC + 1-hexyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl] imide ([HMIM][NTf$_2$]) and ethanol + DMC + 1-butyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl] imide ([BMIM][NTf$_2$]) were obtained by using a modified Othmer still at a constant pressure of 101.3 kPa. The experimental results indicated that both [HMIM][NTf$_2$] and [BMIM][NTf$_2$] had a notable effect on the azeotropic system of ethanol - DMC. The NRTL model was used in this work to correlate VLE data and the calculated data agreed well with the experimental value. The minimum mole fractions of [HMIM][NTf2] and [BMIM][NTf2] needed to eliminate azeotrope were 0.125 and 0.170 calculated by NRTL model, respectively. And the [HMIM][NTf2] was found to be a better candidate of entrainer for separating the ethanol - DMC azeotrope.

1. Introduction

Ionic liquids (ILs), which are usually liquids at room temperature, have become a popular research field of green chemistry because of their unique properties, such as thermal and chemical stabilities, extremely low vapor pressure, designability, good solubility [1–4]. Moreover, it has found that the using of the appropriate ionic liquid as the extractant for extractive distillation can significantly increase the relative volatility of the azeotropic system. Moreover, some specific entrainer could break the azeotrope and make the separation of the azeotropic system possible by extractive distillation since it was first researched by Arlt et al. [5,6].

Although the number of works related to the separation of azeotropic system by using ILs has been growing in recent years [7–12], the experimental data are still not enough and only a few research groups are studying on it [3,13]. Thus the thermodynamic behavior of multi-component systems, especially the VLE data of systems containing ILs, as well as the correlation of the experimental data with activity coefficient model are essential to study.

DMC, widely used in pesticides, pharmaceuticals, polymer synthesis, fuel additives and solvents, can react to make some important chemical products, instead of the hyper toxic or carcinogenic substances like phosgene and dimethyl sulfate [14–17]. Separation of ethanol and DMC will be inevitable in the synthesis of diethyl carbonate or methyl ethyl carbonate. The mix of ethanol and DMC can form an azeotrope at normal pressure, and it is impossible to separate them by ordinary distillation. Although some scholars have studied the VLE data of the ethanol + DMC binary system [18,19], there is little research has been reported on the separation of the ethanol and DMC. What's more, there is no report on the VLE data for the ternary systems of ethanol + DMC + ionic liquids.

In this work, isobaric VLE data for binary systems of ethanol + DMC, ternary systems of ethanol + DMC + [HMIM][NTf$_2$] and ethanol + DMC + [BMIM][NTf$_2$] were presented at 101.3 kPa. The influence of different concentrations and kinds of ILs on the thermodynamic behavior of ethanol + DMC were discussed. The VLE experimental data were correlated with NRTL activity coefficient model.

2. Experimental

2.1. Materials

Ethanol (analytical grade) and DMC (analytical grade) were supplied by Beijing Chemical Reagents Company and Aladdin

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https://doi.org/10.1016/j.fluid.2018.05.024
0378-3812/

Table 1
Specifications of chemical samples.

Chemical name	CAS	Source	Mass fraction	Purification method	Final water mass fraction	Analysis method
Ethanol	64-17-5	Beijing Chemical Reagents Company	0.999	None	0.00032	GC[c], KF[e]
DMC	616-38-6	Aladdin Industrial Corporation	0.999	None	0.00035	GC[c], KF[e]
[HMIM][NTf$_2$][a]	382150-50-7	Shanghai Cheng Jie chemical Co. LTD.	0.99	Rotary evaporation under vacuum	0.00048	LC[d], KF[e]
[BMIM][NTf$_2$][b]	174899-83-3	Shanghai Cheng Jie chemical Co. LTD.	0.99	Rotary evaporation under vacuum	0.00051	LC[d], KF[e]

[a] [HMIM][NTf$_2$] = 1-hexyl-3- methylimidazolium bis[(trifluoromethyl) sulfonyl] imide.
[b] [BMIM][NTf$_2$] = 1-butyl-3- methylimidazolium bis[(trifluoromethyl) sulfonyl] imide.
[c] GC = gas chromatography.
[d] LC = liquid chromatography.
[e] KF = Karl Fischer titration.

Industrial Corporation, respectively, and they were used without further purification. The mass fraction of ethanol and DMC were both 99.9% and no impurities were detected by GC.

[HMIM][NTf$_2$] and [BMIM][NTf$_2$] were bought from Shanghai Cheng Jie Chemical Co. LTD, China and reused in a vacuum rotary evaporator operated under the temperature of 390 K for at least 24 h. The purity of ILs used in this study was checked by liquid chromatography (LC) and the mass fraction were both 99.0%.

The water concentration of all chemicals used in this work was measured by Karl Fischer titration (KF) and the specifications of chemical samples were listed in Table 1.

2.2. Experimental apparatus and procedure

The equilibria data were measured by a modified Othmer still, which was purchased from Peiyang Chemical ENG. Co. (China), under a constant pressure of 101.3 kPa, and more details about the apparatus could be found in our previous works [20–22]. The equilibrium temperature was measured by a precision mercury thermometer with an error temperature of ±0.1 K. The pressure was measured by a digital manometer with a standard uncertainty of ±0.1 kPa.

The gas chromatography (GC, SP7800, China) was used to analyze the experimental data. The column of GC was filled with Porapak-Q (4 m × 3 mm) and the carrier gas was hydrogen (99.99%) with a flow rate of 38 cm^3 min^{-1}. The operating conditions were as follows: the column temperature was 413.15 K, the injector temperature was 443.15 K, the detector temperature was 443.15 K and the bridge current was 80 mA.

Table 2
Isobaric vapor-liquid equilibria data for temperature T, liquid-phase mole fraction x_1, and gas-phase mole fraction y_1, for the binary system ethanol (1) + DMC (2) at 101.3 kPa.[a]

T/K	x_1	y_1
360.25	0.056	0.164
357.15	0.119	0.291
354.65	0.192	0.386
352.95	0.251	0.444
351.85	0.306	0.485
351.25	0.338	0.509
350.25	0.399	0.549
349.55	0.449	0.578
349.15	0.497	0.605
348.75	0.543	0.635
348.55	0.582	0.650
348.25	0.639	0.679
348.15	0.687	0.706
348.25	0.725	0.728
348.45	0.776	0.758
348.75	0.816	0.786
349.15	0.861	0.822
349.75	0.917	0.878
350.35	0.955	0.926

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.1$ kPa, and the combined standard uncertainties are $u_c(x_1) = u_c(y_1) = 0.002$.

Because the boiling point of the ionic liquid is much higher than the equilibrium temperature, it is generally considered that the gas phase does not contain ionic liquids and chromatographic workstation only has two chromatographic peaks of ethanol and DMC. Although the liquid phase contains ionic liquids, because of its null volatility, the chromatographic workstation also has only two chromatographic peaks of ethanol and DMC. The contents of ethanol and DMC could be determined by using the area normalization method and we prepared a series of standard solutions and got a calibration curve to calculate the mole fraction of ethanol and DMC. With this analysis method, the maximum deviation of the mole fraction of composition in the samples could be estimated to be 0.002. In order to calculate the mole fraction of ILs in liquid phase, samples were dried in an oven for 24 h to remove the volatile components, and then the data could be obtained by measuring the mass difference of original samples and treated samples. And the standard uncertainty in mole fraction of ILs was 0.001.

3. Result and discussion

3.1. Experimental data

The VLE data for ethanol (1) + DMC (2) binary system measured at 101.3 kPa were listed in Table 2, in which T was the equilibrium temperature and x_1, y_1 represented the mole fraction of ethanol in liquid and vapor phase, respectively, and the experimental data showed an azeotropic point at $x_1 = 0.726$ and T = 348.25 K. Differential test [23] was used to perform thermodynamic consistency test on experimental data and proved to be thermodynamically consistent. As shown in Fig. 1, the experimental data were in good agreement with the previous works. The little differences were

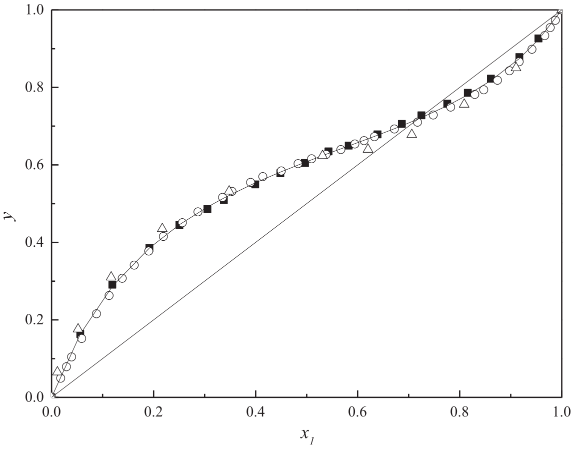

Fig. 1. Y-x diagram for ethanol (1) + DMC (2) system at 101.3 kPa: ■, this work; ○, ref [18]; △, ref [19]; solid line, correlated using NRTL model.