



## Separation of acetone and methanol azeotropic system using ionic liquid as entrainer



Wenxiu Li, Dezhang Sun, Tao Zhang, Shangwu Dai, Fenjin Pan, Zhigang Zhang\*

Liaoning Provincial Key Laboratory of Chemical Separation Technology, Shenyang University of Chemical Technology, Shenyang 110142, China

### ARTICLE INFO

#### Article history:

Received 10 July 2014

Received in revised form 10 September 2014

Accepted 6 October 2014

Available online 29 October 2014

#### Keywords:

Separation factor

Phase equilibrium

Ionic liquid

NRTL model

### ABSTRACT

In this work, three ionic liquids (ILs), namely monoethanolamine chloride ([HMEA][Cl]), monoethanolamine acetate ([HMEA][OAc]) and 1-ethyl-3-methylimidazole acetate ([EMIM][OAc]), were studied as entrainers to separate acetone + methanol azeotropic mixture by extractive distillation. Isobaric vapor liquid equilibrium of ternary systems containing ILs was investigated to examine the effect between the structure of ionic liquids and separation performance on acetone + methanol. The measurements were carried out at 101.3 kPa and the headspace chromatograph was employed to analyze the VLE data. From the experimental results, it is found that the addition of ILs can remarkably increase the separation factor (relative volatility) of acetone to methanol. The azeotropic point is pulled up and the azeotropy is even eliminated eventually. Comparison of the separation effect of ILs is that [EMIM][OAc] outperforms [HMEA][Cl] and [HMEA][OAc]. The experimental VLE data are well correlated using nonrandom two-liquid model (NRTL).

© 2014 Published by Elsevier B.V.

### 1. Introduction

The separation of azeotropic mixtures has conventionally been one of the most challenging tasks in industrial processes due to the fact that their separation by common distillation is almost impossible. Extractive distillation as a special distillation is the most widely used method to separate azeotropes. With the addition of a third solvent (entrainer), the relative volatility can be altered which makes the azeotropy broken. Thus, the selection of optimal entrainer is a significant step. Organic solvents [1], solid salts [2] and hyper-branched polymers [3] as traditional entrainers have been investigated before. However, the traditional entrainer comprises some disadvantages such as solvent loss, highly corrosive, difficulty in recycling, which has been a handicap for further application of extractive distillation.

Efforts to make existing separation method of extractive distillation more efficient and eco-friendly will get a boost from the use of a new class of compounds known as ILs. The addition of ILs can offer technologically and environmentally favorable alternatives to traditional entrainers in separation of organic substances. As new and potential solvents, IL has attracted much attention because of the unique chemical and physical merits, such as: no effective vapor pressure, less corrosive, high selectivity and solubility, high thermal stability and distinctive design-ability. Plenty of imidazole [4] and pyridine based [5] ILs as entrainers

used in the extractive distillation have been investigated and the superiorities they displayed were uplifting.

The vapor liquid equilibrium of acetone and methanol system may be one of the most studied binary systems owing to its industrial importance and promising applications. To the best of our knowledge, Seiler et al. [6], and Kurzin et al. [7] have reported the isothermal VLE data of 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]) and N-butylpyridinium hexafluorophosphate ([BPY][PF<sub>6</sub>]) presented in acetone + methanol mixture at temperature of 328.15 K and 313.15 K, respectively. Meanwhile, Vincent Liebert studied the influence of two sulfate-based anion ionic liquids 1-ethyl-3-methylimidazole hydrogensulfate ([EMIM][HSO<sub>4</sub>]) and 1-ethyl-3-methylimidazole methylsulfate ([EMIM][MeSO<sub>4</sub>]) [8] on vapor-liquid equilibrium of the system and compared the separation effect. A. Vicent Orchilles reported isobaric VLE data of ternary systems containing 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) [9], 1-butyl-3-ethylimidazolium trifluoromethanesulfonate ([beim][triflate]), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate]) [10] and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) [11] at a pressure of 101.3 kPa. In this paper, [HMEA][Cl], [HMEA][OAc] and [EMIM][OAc] have been selected as entrainer to separate acetone + methanol azeotropic system and to determine, if any [HMEA][Cl], [HMEA][OAc] or [EMIM][OAc] are capable of breaking the azeotropy. The separation effect is compared among the three ILs to select the potential entrainer. Finally the effect of potential entrainer for separating acetone from methanol is compared with the reported effect of ILs in the previous literature.

\* Corresponding author. Fax: +86 024 89384726.

E-mail address: [zhzhgang@126.com](mailto:zhzhgang@126.com) (Z. Zhang).

**List of symbols**

$\Delta g_{ij}$	Binary energy parameter of NRTL model
$x_i$	Mole fraction of solvent $i$ in the liquid phase
$y_i$	Mole fraction of solvent $i$ in the vapor phase
$T$	Equilibrium temperature
$P$	Total pressure in the equilibrium system
$P_i^s$	Saturated vapor pressure of component $i$
$S_{12}$	Selectivity of component 1 id=6#to component 2
Greek letters	
$\alpha_{12}$	Separation factor of component 1 id=6#to component 2
$\alpha_{ij}$	Non-randomness parameter of NRTL model
$\gamma_i$	Activity coefficient of component $i$

**2. Experimental section****2.1. Material**

The ILs [HMEA][Cl], [HMEA][OAc] and [EMIM][OAc] were synthesized in our own laboratory with mass purity greater than 99% checked by liquid chromatography. Besides, the ILs were dried in a vacuum desiccator at 393 K for 48 h before the experiments. The mass fraction of water in ILs, measured by Karl Fisher titration, is less than 0.005. The volatile chemicals used in this study were acetone (Sinopharm Group, minimum Wt 99.5%) and dried methanol (Sinopharm Group, minimum Wt 99.5%). The organic solvents were analyzed by gas chromatograph and no impurities were detected. Specifications of the chemicals used in this study are summarized in Table 1.

[EMIM][OAc] = 1-ethyl-3-methylimidazole acetate

**2.2. Apparatus and procedure**

An all-glass dynamic recirculating still (NGW, Wertheim, Germany) was used to operate the VLE experiments at atmospheric pressure. A detailed description of this apparatus is available in former literatures [12]. The pressure of this apparatus is measured by a manometer with an uncertainty of 0.1 kPa and kept constant at 101.3 kPa by controlling a gas buffer. Each experiment was replicated three times in a sequence and occasionally also two times during a longer period of time to check the reproducibility.

For ternary system, several mixtures of acetone and defined content IL were prepared, and different amounts of another mixture of methanol and same content IL were added to keep the mole fraction of IL in each series constant. For the measurements of ternary systems, a sample taken from the vapor phase was prepared in a 20 cm<sup>3</sup> glass vials when the VLE was reached. Then the sample was inserted into the headspace sampler (G1888 Network headspace sampler, Agilent Technologies) and

**Table 1**

Overviews of the chemical samples.

Chemical name	Source	Purity	Purification method	Analysis method
Acetone	Sinopharm group	0.995	None	GC <sup>a</sup>
Methanol	Sinopharm group	0.995	None	GC <sup>a</sup>
[HMEA][Cl]	Synthesized own	0.990	Vacuum desiccation	LC <sup>c</sup> KF <sup>b</sup>
[HMEA][OAc]	Synthesized own	0.990	Vacuum desiccation	LC <sup>c</sup> KF <sup>b</sup>
[EMIM][OAc]	Synthesized own	0.990	Vacuum desiccation	LC <sup>c</sup> KF <sup>b</sup>

[HMEA][Cl] = monoethanolamine chloride.

[HMEA][OAc] = monoethanolamine acetate.

<sup>a</sup> GC = gas chromatography.

<sup>b</sup> KF = Karl Fisher titration.

<sup>c</sup> LC = liquid chromatography.

**Table 2**

Isobaric vapor liquid equilibrium data for the system acetone (1)+methanol (2) at 101.3 kPa.

$x_1$	$y_1$	T/K
0	0	337.62
0.052	0.098	336.25
0.178	0.292	333.44
0.252	0.377	332.11
0.351	0.472	330.79
0.467	0.554	329.63
0.511	0.581	329.34
0.569	0.624	328.97
0.651	0.692	328.58
0.699	0.728	328.45
0.741	0.759	328.40
0.779	0.778	328.38
0.79	0.783	328.39
0.798	0.789	328.40
0.824	0.812	328.44
0.839	0.825	328.47
0.902	0.887	328.67
0.947	0.931	328.89
1.000	1.000	329.27

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

analyzed using gas chromatograph (Model 7890 A, Agilent Technologies). Since there is no effective pressure of IL, only two peaks can be observed. The determination of IL concentration was conducted with the help of digital balance (CAV264C OHAUS America) with a standard uncertainty of 0.0001 g after vaporizing the volatile component in a vacuum desiccator. The equilibrium temperature was determined using an accurate and calibrated thermometer with a standard uncertainty of 0.01 K. Composition of volatile component in the liquid phase was also determined by GC. The standard uncertainty of the content of the component in the liquid and vapor phase is 0.001.

**3. Result and discussion**

In the process of extractive distillation, two indicative quantities, relative volatility (or separation factor)  $\alpha_{12}$  [13] and selectivity  $S_{12}$  [14] are conventionally used to describe the separation effect of entrainer. The relative volatility of component 1 respect to component 2 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 and 2 in the liquid and vapor phase, respectively. That is to say, the higher the value of  $\alpha_{12}$ , the more effective the separation. On considering the vapor liquid equilibrium:

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

where  $\xi_i$  is the vapor phase non-ideality correction,  $P$  is the total pressure of 101.3 kPa.  $\gamma_i$  is the activity coefficient of component  $i$  in

Download English Version:

<https://daneshyari.com/en/article/201892>

Download Persian Version:

<https://daneshyari.com/article/201892>

[Daneshyari.com](https://daneshyari.com)