

Chemical Engineering Thermodynamics

# Salting-out effect of ionic liquids on isobaric vapor-liquid equilibrium of acetonitrile-water system<sup>☆</sup>

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## ABSTRACT

This paper presents the vapor-liquid equilibrium (VLE) data of acetonitrile-water system containing ionic liquids (ILs) at atmospheric pressure (101.3 kPa). Since ionic liquids dissociate into anions and cations, the VLE data for the acetonitrile + water + ILs systems are correlated by salt effect models, Furter model and improved Furter model. The overall average relative deviation of Furter model and improved Furter model is 5.43% and 4.68%, respectively. Thus the salt effect models are applicable for the correlation of IL containing systems. The salting-out effect theory can be used to explain the change of relative volatility of acetonitrile-water system.

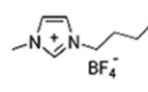
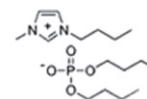
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## 1. Introduction

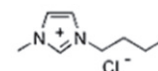
At room temperature, ionic liquids (ILs) are one of novel “green solvents”. They have many special properties, such as negligible vapor pressure, good thermal stability, and environmental friendliness, so they have more potential to be used in some special distillation processes. Recently, extractive distillation with ionic liquids as entrainers is more and more popular. The phase behavior of the systems containing ionic liquids in extractive distillation has been studied [1–10], but the thermodynamic data in this field are still insufficient, so it is necessary to investigate the phase behavior of more IL containing systems. For analyzing the VLE data, activity coefficient equations are usually used to simulate ionic liquid systems, such as the Wilson equation, NRTL equation, UNIQUAC equation, UNIFAC equation, and modified UNIFAC equation, which are based on the concepts of local composition and group contribution methods. Since various components in the mixture can be considered as a whole molecular group, these activity coefficient equations are usually obtained by the excess Gibbs free energy equation of the liquid mixture. However, ILs as a kind of molten salt can naturally dissociate into anions and cations, so these equations cannot fit ionic liquid systems efficiently.

Salt effect is a phenomenon that the composition of the vapor phase in equilibrium in a binary solution usually changes by adding a salt with volatile components to the system due to interactions between the salt and solvent components [11–13]. Salt effect is mainly caused by electrostatic interactions of ions. When ILs dissociate into anions and cations, the hydration between these ions and water molecules takes place due to electrostatic interactions, the result of which is that the number of free water molecules as solvent is reduced, the relative volatility of acetonitrile to water is improved, and the separation of materials is promoted. The salt effect theory is often applied to predict vapor-liquid equilibrium with inorganic salt solution, and the prediction is acceptable [14–17]. Literally ionic liquids are a kind of molten salt with similar nature as inorganic salt solution.

In this work, the isobaric VLE data for ternary systems of acetonitrile + water + different ionic liquids are measured at 101.3 kPa, which are 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]), 1-butyl-3-methylimidazolium dibutyl phosphate ([Bmim][DBP]), and 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]). They have the same cation but different anions. Their structures are as follows.

[Bmim][BF<sub>4</sub>]

[Bmim][DBP]



[Bmim][Cl]

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The salting-out effect of ILs on the separation performance of acetonitrile–water system will be discussed. The salt effect models, Furter model and improved Furter model, are used to correlate the vapor–liquid equilibrium of acetonitrile–water system containing IL.

## 2. Materials

The chemical reagents used in this work were acetonitrile, redistilled water, Karl-Fischer reagent and ILs. The analytical grade acetonitrile with purity of 99% was purchased from Jiangtian Chemical Reagents Co., Tianjin, China and used without further purification. ILs [Bmim][BF<sub>4</sub>], [Bmim][DBP] and [Bmim][Cl] were provided by Chengjie Chemical Co., Shanghai, China, with a minimum mass fraction of 99%. The purity of reagents was checked by gas chromatography (GC SP-3420, China). The properties of materials are shown in Table 1.

**Table 1**  
Properties of the pure components

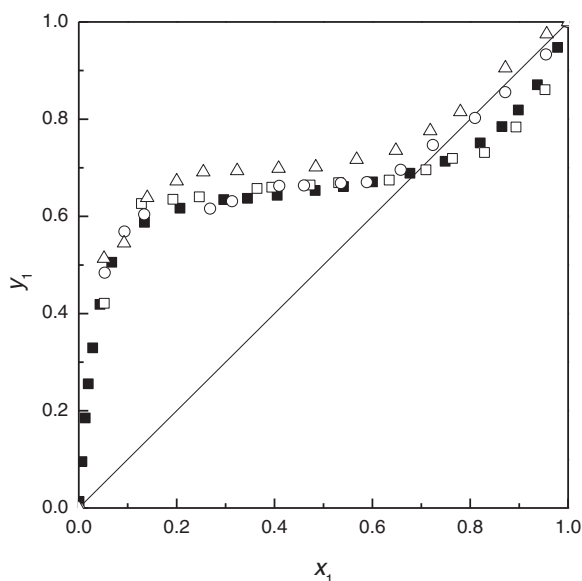
	Formula	$M_{w/g} \cdot \text{mol}^{-1}$	$T_b/\text{K}$	$T_c/\text{K}$	$p_c/\text{MPa}$
Acetonitrile	CH <sub>3</sub> CN	41.05	354.25	547.85	4.83
Water	H <sub>2</sub> O	18.01	373.15	647.35	22.12

## 3. Results and Discussion

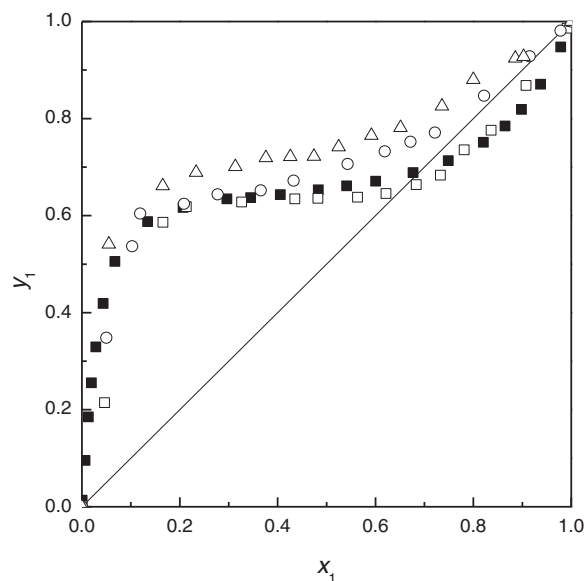
### 3.1. Experimental data

In order to check the reliability of the experimental set-up, the isobaric VLE data for acetic acid–water system at atmospheric pressure (101.3 kPa) were measured and compared with those in literature [18]. The apparatus and adjusted results were given in our previous work [19]. The isobaric VLE data for acetonitrile–water system containing different ILs at various IL contents (20% and 30%, by mass) were measured.

The  $x$ – $y$  diagrams are plotted in Figs. 1 and 2 to describe the salting-out effect caused by ILs, where  $x_3$  represents the mass fraction of IL in the liquid phase,  $x_1$  is the mole fraction of acetonitrile in the liquid



**Fig. 1.** Isobaric VLE diagram for system acetonitrile (1) + water (2) + IL (3) at 20% mass fraction. ■ IL free; □ [Bmim][BF<sub>4</sub>]; ○ [Bmim][DBP]; △ [Bmim][Cl].



**Fig. 2.** Isobaric VLE diagram for system acetonitrile (1) + water (2) + IL (3) at 30% mass fraction. ■ IL free; □ [Bmim][BF<sub>4</sub>]; ○ [Bmim][DBP]; △ [Bmim][Cl].

phase excluding IL, and  $y_1$  is the mole fraction of acetonitrile in the vapor phase. [Bmim][BF<sub>4</sub>] is ineffective to enhance the relative volatility of the acetonitrile–water system, while [Bmim][DBP] and [Bmim][Cl] increase the relative volatility of acetonitrile in the whole concentration range. The salting-out effect for acetonitrile with [Bmim][Cl] is more effective than that with [Bmim][DBP]. The azeotropic point for acetonitrile–water binary mixture shifts upwards with the addition of ILs and the azeotropic phenomenon even disappears at specific IL content in the cases of [Bmim][DBP] and [Bmim][Cl].

As organic molten salts, the influence of ionic liquids on the VLE of acetonitrile–water system can be explained by the hydration theory and electrostatic interaction theory. The hydration theory indicates that the salting-out effect is the interaction between water molecules and ions, which is reduced if the salt is hydrated by water molecules. In this experimental system, the polarization parameter of water is greater than that of acetonitrile, so the dipole moment of water molecules is towards to the hydrate of salt in the formation of hydrates. The relative volatility of acetonitrile to water is enhanced because of the precipitation of acetonitrile as a result of weak polarity. According to the electrostatic interaction theory, ILs can produce an electric field in the solution. Due to different polarities and dielectric constants of acetonitrile and water, water molecules tend to gather in the neighborhood of ions while acetonitrile molecules are expelled from the ions. In this way, the composition of acetonitrile–water system should change with the addition of ionic liquids and the relative volatility of acetonitrile to water is enhanced as observed in the experiments.

Vapor–liquid equilibrium is generally expressed by the relative volatility  $\alpha$ ,

$$\alpha = \alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \quad (1)$$

where  $y$  and  $x$  represent the mole fraction of specific component in the vapor and liquid phases, respectively.

To further investigate the salting-out effect of ILs on acetonitrile–water system, the relative volatilities of acetonitrile to water with different ILs are plotted in Fig. 3. The results show that the salting-out effect of ILs follows the order: [Bmim][Cl] > [Bmim][DBP] > [Bmim][BF<sub>4</sub>].

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