Vapor pressure measurements and predictions for the binary systems containing ionic liquid [EMIM][BF$_4$] and formic acid/acetic acid

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ABSTRACT

The vapor pressures of the binary systems formic acid/acetic acid +1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF$_4$]) were measured using a modified equilibrium still at temperatures ranging from 323.15 to 358.15 K and IL contents ranging from 0.1 to 0.9 in mass fraction. The predictive thermodynamic models (i.e., UNIFAC-Lei and COSMO-RS models) were used to predict the vapor pressures with the ARDs of 4.54% and 22.24% for formic acid, respectively, and 6.38% and 16.43% for acetic acid, respectively. This indicates that the UNIFAC-Lei model can give a quantitative description with high accuracy, while the COSMO-RS model can only be used as a prior model to give a qualitative prediction. Moreover, the excess enthalpies and σ-profiles were calculated by the COSMO-RS model to achieve further understanding on the thermodynamic behavior at molecular scale. It was found that the hydrogen bonding interaction (H_{HB}) plays a dominant role to the total excess enthalpy, and the H_{HB} is mainly dependent on acid components. For IL, the contribution of anion is larger than that of cation as confirmed by the σ-profiles.

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1. Introduction

Ionic liquid (IL) is a relatively new class of solvent composed of organic cation and inorganic or organic anion, most of which have a melting point below 100 °C [1]. It has caused extensive concern in many fields, especially in separation processes [2–10], due to the unique properties such as negligible vapor pressure and potential as "designer solvent".

Ester compounds are widely applied in many fields as common organic solvents and industrial raw materials, while acid impurities must be removed by special equipment to obtain refined products during the preparation process [11]. In many other industrial processes, the existing acid impurities must be deacidified to prevent pipe lines and devices from corrosion and blockage [12]. Moreover, the acid must be recovered from acidic waste water before discharge, avoiding the pollution of environment and waste of resources. Thus, the study about the separation of acid is significant in the protection of environment and utilization of resources. However, due to the low relative volatility of some acid with other components, the general distillation equipment can't fulfill the separation [13].

Extractive distillation is a special separation method commonly applied in the mixtures that can't be separated by conventional distillation. The entrainer or solvent is usually a volatile organic solvent, while its recovery may cause high energy consumption and environment problems sometimes. Thus, extractive distillation with ILs as entrainers as a new separation technology was proposed in recent years [14–18]. Compare to traditional extractive distillation, the negligible vapor pressure of IL entrainer makes it easily recovered by a simple flash tank instead of a distillation recovery column. Thus, this technology can save the equipment investment and energy consumption, which is promising to be applied in the deacidification process. Until now, many studies have been carried out on the separation processes involving ILs. Undoubtedly, the thermodynamic properties such as phase equilibria (GLE, VLE, LLE, etc.) data, activity coefficient data, and excess enthalpy of the systems containing ILs are necessary for the design and optimization of separation processes and other applications of ILs [19–27]. However, the reports on vapor-liquid equilibrium (VLE) data of acid (formic acid and acetic acid) and IL binary systems are still scarce. In this work, the common ionic liquid [EMIM][BF$_4$] was selected as the representative to investigate the VLE with the organic acids because of its economical price, good thermal stability, and relatively low viscosity.

The aim of this work is to measure the vapor pressures of the binary systems of formic acid/acetic acid + [EMIM][BF$_4$] at different temperatures and concentrations to study the effect of IL on VLE. Moreover, two predictive thermodynamic models (i.e., UNIFAC-Lei and COSMO-RS models) were used to predict the vapor pressures. To a further step, the COSMO-RS model was applied to analyze the excess enthalpies and σ-profiles of these two systems to investigate the molecular interactions at microscopic level.

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2. Experimental section

2.1. Materials

Formic acid (mass fraction >0.985%) was obtained from Tianjin Guangfu Fine Chemical Research Institute, and acetic acid (mass fraction >99.5%) was obtained from Being Chemical Works. They were used directly without further purification. [EMIM][BF$_4$] was obtained from Shanghai ChengJie Chemical Co., Ltd. with a purity >99.0 wt%. It was dried over a vacuum rotary evaporator at 358.15 K for 24 h to remove traces of water and other volatile impurities. The chemicals used in this work are listed in Table 1.

2.2. Apparatus and procedure

The experimental vapor pressures of binary systems were measured by a modified equilibrium still, the details of which can be seen in our previous work [31]. Before experiments, the U-type equilibrium still was thoroughly washed by anhydrous ethanol and then dried using air oven. The mixtures of (formic acid + [EMIM][BF$_4$]) and (acetic acid + [EMIM][BF$_4$]) with different compositions were prepared by weighting the IL and solutes with an electronic balance (type FA2104B, Shanghai Precision Scientific Instrument Co., China) with the precision of 0.001 g. About 15 mL formic acid/acetic acid + [EMIM][BF$_4$] mixture were added into the equilibrium still, filling with two thirds of the vacuole in volume. Connected the equilibrium still well, and put it into the thermostatic water bath at a given temperature measured by a digital temperature indicator (Type DP–AF, Nanning Sangli Electronic Equipment Company, China, 2014) with a precision of 0.01 K. Opened the condensed water, stirrer and heater, when the temperature reached the desired value. Opened the vacuum pump until the liquid mixture boiled in the equilibrium still. Then, the needle valve was slowly opened to leak into the air until the U-type tube was kept at the same level height on both sides. If the liquid level didn't change within 20 min, it was considered to reach the vapor-liquid equilibrium. The pressure of equilibrium still was measured by a precision digital pressure gauge (Type DP–AF, Nanjing Sangli Electronic Equipment Company, China, 2014) with a precision of 0.01 kPa.

The vapor pressures of formic acid and acetic acid were first measured from 303.15 to 358.15 K to check the reliability of experimental apparatus.

3. Thermodynamic models

For the binary system containing IL, the vapor-liquid equilibrium for solute i can be expressed as

$$\phi_i y_i P = \gamma_i x_i P_i^s \tag{1}$$

where x_i and y_i and are the mole fractions of solute i in liquid and vapor phases, respectively; ϕ_i is the fugacity coefficient of solute i in vapor phase calculated by the Peng-Robinson (PR) equation of state at a certain temperature and pressure; P is the system pressure; and γ_i is the activity coefficient of solute i in liquid phase. P_i^s is the saturated

pressure of pure solute i, which can be calculated by Antoine equation as follows

$$\log(P_i^s / \text{bar}) = A_i - \frac{B_i}{T/K + C_i} \tag{2}$$

where the Antoine constants (A_i, B_i, and C_i) for formic acid and acetic acid were given in Table 2 [32,33].

The vapor phase is assumed to be pure solute ($y_i = 1$) because of the negligible volatility of IL. Therefore, Eq. 3 can be simply rewritten as.

$$\phi_i P = \gamma_i x_i P_i^s \tag{3}$$

where i represents the component formic acid or acetic acid.

3.1. UNIFAC-Lei model

The UNIFAC-Lei model was used to describe the vapor-liquid equilibrium of binary system containing IL, which has been applied by many authors [34–38]. In this model, components are divided as interaction groups, and the thermodynamic properties of components are the addition of group properties. The activity coefficient of component i is written as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{4}$$

where $\ln \gamma_i^C$ represents the combinatorial contribution, which is relevant to the shape and size of functional groups, and is a function of two group parameters (R_k and Q_k) for group k; and $\ln \gamma_i^R$ represents the residual contribution due to the interaction between functional groups, and is a function of a pair of group interaction parameters (a_{mn} and a_{nm}) between groups m and n. There are five groups (CH$_3$, CH$_2$, HCOOH, COOH, and [MIM][BF$_4$]) concerned in this work, and their group parameters (R_k and Q_k) are listed in Table 3, which come from previous works [39,40]. The unknown group interaction parameters between main group COOH and [MIM][BF$_4$] were obtained by correlating the experimental VLE data of formic acid + [EMIM][BF$_4$] and acetic acid + [EMIM][BF$_4$] binary systems as measured in this work, using the minimized average relative deviation between the experimental and calculated vapor pressures as objective function (OF) (OF = $\min\{\frac{1}{N}\sum_1^N |\frac{P_{cal} - P_{exp}}{P_{exp}}|\}$). The new obtained parameters as well as the old parameters from references are given in Table 4.

3.2. COSMO-RS model

In the COSMO-RS calculation, the IL molecular was described as a cation and an anion. Therefore, the binary mixture of IL and solute was considered as a hypothetical ternary system, which consists of cation, anion and solute. A transform between activity coefficient of solute i in the binary and ternary mixture should be made by

$$\gamma_i^{bin} = \frac{\gamma_i^{tern} x_i^{tern}}{x_i^{bin}} = \frac{\gamma_i^{tern}}{2 - x_i^{bin}} \tag{5}$$

Table 1
The properties (CAS-register number, water mass fraction ω_{H2O}, density ρ, and refractive index n_D) of used chemicals at $T = 298.15$ K and atmospheric pressure.

Compounds	CAS	Purity[a]	ω_{H2O} (ppm)[b]	ρ (g·cm^{-3})		n_D	
				Exp.	Lit.	Exp.	Lit.
Formic acid	64–18–6	98.5	14,030	1.21380	1.21410 [28]	1.36916	1.36939 [28]
Acetic acid	64–19–7	99.5	1387	1.04341	1.04330 [29]	1.36975	1.36960 [29]
[EMIM][BF$_4$]	N.F.	99.0	280[c]	1.28253	1.28230 [30]	1.41097	1.41090 [30]

[a] Information provided by supplier.
[b] Water content was measured by Karl-Fischer titration.
[c] Water content was measured after drying over a vacuum rotary evaporator.