



# Vapor pressures, excess enthalpies, and specific heat capacities of the binary working pairs containing the ionic liquid 1-ethyl-3-methylimidazolium dimethylphosphate

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## ABSTRACT

In present research the binary solutions containing ionic liquid (IL), 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM] [DMP]), are considered as new working pairs for absorption heat pumps or absorption refrigerators. The IL was synthesized in the lab and mixed with water, ethanol, or methanol. Experimental (vapor + liquid) equilibrium (VLE) of these binary systems was measured at different mole fractions ranging from 0.1 to 0.5 and was correlated by the NRTL equation within the average relative deviation of 2%, which means that the (vapor + liquid) equilibrium of these binary solutions containing ionic liquid can be predicted by traditional non-electrolyte solution model. Meanwhile these binary solutions are a negative deviation from Raoult's law. Excess enthalpy of these binary systems was measured at the temperature of  $T = 298.15$  K and at the pressure of 1 atm. The results indicate that the mixing processes of [EMIM] [DMP] with water, ethanol, or methanol are exothermic, which is a very important characteristic for working pairs used in absorption heat pumps or in absorption refrigerators.

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## 1. Introduction

With rapid economic growth, human beings will face more serious environmental and energy issues. The ways to solve these problems are multiple, including developing, and utilizing renewable energy resources, increasing renewable energy ratio in the energy structure, enhancing energy utilization efficiency, and so on. Absorption heat pumps or absorption refrigerators are important energy-saving devices that can reuse a lot of low grade thermal energy, such as solar energy and industrial waste heat for heating or refrigerating, so the application of absorption heat pumps or absorption refrigerators will play an important role in increasing energy utilization efficiency and reducing environmental pollution.

The performance of absorption cycles depends on the thermodynamic properties of working pairs composed of refrigerant and absorbent. The commonly-used working pairs are ammonia–water solution ( $\text{NH}_3\text{--H}_2\text{O}$ ) and aqueous solution of lithium bromide ( $\text{LiBr--H}_2\text{O}$ ). However, corrosion, crystallization, and toxicity are their great disadvantages in application, respectively. Therefore, seeking more advantageous working pairs with good thermal stability, no corrosion and no crystallization has become the research focus in recent years.

Ionic liquids (ILs) are room-temperature melting salts that remain in liquid state at near or below room temperature [1]. In recent years, ILs have attracted considerable attention because of their unique properties, e.g. negligible vapor pressure [2], negligible flammability and thermal stability [3], low melting temperatures and liquid state over a wide temperature range and good solubility [4]. Upto now, extensive research focuses on the property of ILs where ILs act as reaction solvent, extraction agent for separation process [5–8].

Because of excellent properties of IL, it is possible that IL is a new absorbent of coolants for absorption heat pump or refrigeration. However, the reports on IL used as absorbent in absorption heat pump or absorption refrigeration are very limited. The pressure and heat capacity of binary solution of TFE + [bmim][BF<sub>4</sub>] and TFE + [bmim][Br] were researched and the negative deviation from Raoult's law of these binary solution was found [9]. The solubility and diffusivity of HFCs in [bmim][BF<sub>4</sub>] and [bmim][BF<sub>6</sub>] and predicted qualitatively excess properties GE, HE and S<sup>E</sup> of the solution of R-134a and [bmim][BF<sub>6</sub>] by NRTL active coefficients models were given [10]. The solubility of NH<sub>3</sub> in [emim][Ac], [emim][EtOSO<sub>3</sub>], [emim][SCN], and [DMEA][Ac] was also researched, respectively [11]. The vapor pressure and specific heat capacity of binary solution, 1-ethyl-3-methylimidazolium ethylsulfate and water, were researched as a new working pair [12]. The vapor pressure, excess enthalpy and specific heat capacity of binary solution ILs 1,3-dimethylimidazolium dimethylphosphate

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([MMIM][DMP]) with water, ethanol or methanol were also studied and they exhibit the negative deviation from Raoult's law [13].

In the present research on ionic liquid, 1-ethyl-3-methylimidazolium dimethylphosphate [EMIM] [DMP] was proposed as a new absorbent of coolants, such as water, ethanol or methanol for absorption cycle rather than as a salt in distillation process for breaking the azeotropes in an extractive distillation process, where IL mole fraction range from 0.02 to 0.24 [7,8]. Obviously in that case the IL mole fraction is lower than that in absorption heat pump or absorption refrigerator.

In order to prove whether the binary solution composed of [EMIM] [DMP] and water, ethanol, or methanol has the potential to be a working pair for absorption heat pump and refrigeration, it is necessary to know the thermodynamic properties, such as vapor pressure, excess enthalpy, and specific heat capacity, especially to know whether these binary solutions are a negative deviation from Raoult's law and to know whether mixing processes of [EMIM] [DMP] with water, ethanol, or methanol, respectively, are exothermic because these two properties are necessarily met for the working pair of absorption cycle.

In the present research the VLE of binary solution composed of the [EMIM] [DMP] and water, ethanol, or methanol, respectively, at mole fraction of ionic liquid ranging from 0.1 to 0.5 was measured by bubble point method and was correlated by NRTL equations. The mixing enthalpy of [EMIM] [DMP] with water, ethanol, or methanol at different ionic liquid concentrations and at  $T = 298.15$  K was also measured, respectively.

## 2. Experimental section

### 2.1. Materials

In this work, all chemical agents were of AR grade with purity of 99.8% and used without further purification. The ionic liquid, [EMIM] [DMP], was prepared according to the following method.

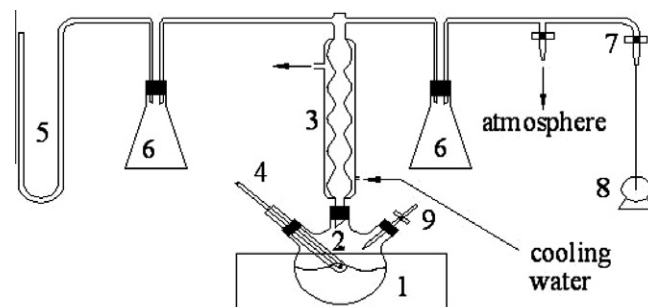
### 2.2. Preparation of [EMIM] [DMP]

First, an appropriate amount of N-ethylimidazole was put into a flask with a reflux condenser and then mixed with an equimolecular amount of methyl phosphate. After reacting for 10 h at  $T = 423.15$  K, the result mixture was cooled down to room temperature. Unreacted agents were extracted from the result mixture with ether. Then raffinate was treated using rotary vacuum evaporator for 24 h to remove all volatile components, such as water and remaining ether. The purity of the IL was better than 97.8% as determined by  $^1\text{H}$  NMR analysis.

In order to determine the thermal stability of [EMIM] [DMP], the d.s.c. curve of [EMIM] [DMP] was operated from  $T = (303.15$  to  $573.15)$  K with a heating rate of  $10 \text{ K min}^{-1}$  under an  $\text{N}_2$  flux of  $70 \text{ cm}^3 \text{ min}^{-1}$  by DSC 910S, and the TGA curve of [EMIM] [DMP] was also operated at a heating rate of  $5 \text{ K min}^{-1}$  with a nitrogen dynamic atmosphere by TGA/SDT851e.

### 2.3. Device and method for vapor pressure measurement of IL solution

The bubble point method for measuring vapor pressure was adopted the experimental apparatus used is shown in figure 1. It is composed of a three-necked flask, a mercury thermometer, a reflux condenser, a U-tube manometer with an uncertainty of 130 Pa, a buffer vessel, and pressure and temperature controlled devices. The mercury thermometer with an uncertainty of  $\pm 0.2$  K is adopted. In order to ensure the measuring accuracy, the seal fittings in the device should be kept in good connection to prevent the air leakage by using the vacuum silicon grease.



**FIGURE 1.** Schematic diagram of experimental apparatus for vapor pressure measurement: 1, constant temperature bath; 2, equilibrium vessel; 3, condenser; 4, temperature sensor; 5, U-tube manometer; 6, pressure buffer; 7, vacuum control valve; 8, vacuum pump, and 9, valve.

The vapor pressure of the binary solution was measured as follows: after the apparatus was well sealed and vacuum in apparatus could be created, the sample with an approximate volume of 200 ml was placed in the flask. The pressure was controlled to the desired value by a vacuum pump and a cock, and then the heating device was turned on. After about 10 min, the temperature of the solution was basically stable and the equilibrium was reached. A series of bubble point temperature and corresponding vapor pressure were obtained.

In order to check the reliability of the experimental apparatus, the vapor pressure of water at different temperatures was measured and compared with the calculated value by Antoine equation, as listed in table 1. It shows that the experimental data are in good agreement with the calculated ones with a maximum relative deviation of 1.76%, which implies that the experimental apparatus is reliable and applicable for the measurement of vapor pressure for IL-containing solution.

The non-ideality of a solution can be expressed by activity coefficient of component  $i$ ,  $\gamma_i$ , which can be computed as follows [14]:

$$\gamma_i = y_i \phi_i p / x_i \phi_i^s p_i^s, \quad (1)$$

where  $p$  and  $p_i^s$  are vapor pressure of liquid solution and saturation vapor pressure of pure component  $i$  at system temperature, respectively,  $y_i$  and  $x_i$  represent the mole fractions of component  $i$  in the vapor and liquid phases, respectively,  $\phi_i$  is the fugacity coefficient of component  $i$  in vapor phase, while  $\phi_i^s$  is the fugacity coefficient

**TABLE 1**  
Experimental and calculated vapor pressure of water at different temperature.

$T/\text{K}$	$p^{(\text{exp})}/\text{kPa}$	$p^{(\text{cal})}/\text{kPa}$	$\varepsilon = \left  \frac{p^{(\text{exp})} - p^{(\text{cal})}}{p^{(\text{exp})}} \right  / \%$
351.45	44.29	44.21	0.18
352.65	46.56	46.43	0.28
353.95	49.33	48.93	0.80
355.15	51.94	51.35	1.15
356.25	54.61	53.65	1.76
357.55	57.22	56.47	1.31
358.65	59.54	58.96	0.97
359.75	62.15	61.54	0.98
			$\varepsilon_{\text{ave}} = 0.93$

**TABLE 2**  
Constants of Antoine equation for water, ethanol, and methanol.

	A	B	C
Water	16.28837	3816.4	-46.13
Ethanol	16.89667	3803.98	-41.68
Methanol	16.57227	3626.55	-34.29

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