Ternary liquid–liquid equilibrium of an azeotropic mixture (hexane + methanol) with different imidazolium-based ionic liquids at $T = 298.15$ K and $101.325$ kPa

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A B S T R A C T

The recovery and purification of methanol from its mixtures is of great importance; to this end, liquid-liquid extraction is an effective method for the separation of azeotropes. In this work, three imidazolium-based ionic liquids were used to separate a hexane-methanol azeotropic mixture, and the ternary liquid-liquid equilibria (LLE) data for the systems of hexane + methanol + [MIM][HSO4] (1-methylimidazole hydrogen sulfate), [BMIM][HSO4] (1-Butyl-3-methylimidazolium hydrogen sulfate), [BMIM][OTf] (1-Butyl-3-methylimidazolium trifluoromethansulfonate) were measured at $298.15$ K and atmospheric pressure. The separation factor and distribution coefficient were calculated from the experimental LLE data to evaluate the separation performance. The influence of the anions and mono-/di-substituted hydrocarbon chains on the imidazolium cation ring of the LLE was investigated. The experimental LLE data were successfully correlated by non-random two liquid (NRTL) and universal quasi-chemical (UNIQUAC) models, and the binary interaction parameters were obtained.

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1. Introduction

Liquid-liquid extraction is a widely used method for separating azeotropes and for certain extraction process, the determination of a suitable solvent is the most important factor. Ionic liquids (ILs) are of great interest and potential in the liquid-liquid extraction due to their excellent properties [1], such as low vapor pressure, non-flammability and chemical/thermal stability, which make them to a favorable solvent compared to traditional organic solvents [2,3]. Additionally, ILs are a “Designer Solvent,” which is a combination of an anion and cation; therefore, a variety of ILs can be synthesized for a particular purpose. Therefore, the primary objective is to know exactly what is being designed to meet the requirements of a specific separation process. In the last two decades, the applications of ILs as solvents have drawn extensive attention, in which many liquid-liquid equilibria systems containing ILs have been investigated [2–6].

There are a number of alcohol and alkane mixtures that can exist in the industrial production processes of oxygenated additives for unleaded gasoline [78]. Methanol is one of the basic organic raw materials in the chemical industry, in which it has been widely used in the organic synthesis industry, as well as acting as a good solvent. Therefore, the recovery of pure methanol from mixtures is of great economic significance. Due to the close boiling point and formation of azeotropes, ordinary distillation encounters difficulty in separating the mixtures. Liquid-liquid extraction is an effective method for the separation of azeotropes [9] and is an energy-saving process [10]. Liquid–liquid equilibrium (LLE) data of ternary systems are the primary consideration for the design of a separation process [11], in which a large number of LLE data are required for the separation of alcohol from its mixture.

Currently, research regarding the purification of alcohol by liquid-liquid extraction has included Gao et al., who studied the recovery of methanol/ethanol at different temperatures [12,13]. Marciniak et al. [14] analyzed the separation of methanol from alkanes using ILs as solvents, and Cai et al. [15] measured the LLE data for the ternary systems of methanol + hexane/heptane + IL.
Pereiro et al. [16,17] tested the recovery of ethanol from hexane/heptane by ILs and Revelli et al. [18], and Letcher et al. [19] reported the LLE for the mixtures of 1-methyl-3-octylimidazolium chloride + alkanol + alkane. Lastly, González et al. [20–22] published the LLE data for the ternary systems of alcohols + alkanes.

Imidazolium-based ILs are considered to have a moderate viscosity and low melting point [23,24]. In this work, three imidazolium-based ILs were studied for their use in the separation of methanol from a methanol-hexane mixture, and liquid-liquid equilibrium data for ternary systems of {hexane + methanol + [MIM][HSO4], hexane + methanol + [BMIM][HSO4], hexane + methanol + [BMIM][OTf]} were measured at 298.15 K (atmospheric pressure). Through the comparison of three ILs with different anions, we observed that the anion has a strong effect on the separation capacity. Two ILs with the same anionic substituents and mono-/di-substituted hydrocarbon chains on the imidazolium cation ring were applied in the separation process, and the influence of alkyl chains of the imidazole ring was discussed. Separation factors (S) and distribution coefficients (β) were calculated from the experimental tie-lines data to evaluate the separation capacity. The experimental tie-line data were correlated by use of the universal quasi-chemical (UNIQUAC) [25] and non-random two liquid (NRTL) [26] models, and the interaction parameters were obtained.

### 2. Experiment

#### 2.1. Chemicals

Hexane, methanol and ethanol were provided by Tianjin Kermel Chemical Reagent Co., Ltd., with a purity of 99.5%, 99.5% and 99.8%, respectively, and all of the purities were checked by gas chromatography (GC-2014C). ILs were supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, with a stated purity of 98%. All chemicals were used without further purification. Detailed information, including source, purity and suppliers of chemical reagents, is shown in Table 1, and the ionic liquid structures were given in Fig. 1.

#### 2.2. Apparatus and procedure

The LLE for the systems of (hexane + methanol + IL) was determined at 298.15 K and atmospheric pressure. The equipment and experimental procedure for the measurement of LLE data were detailed in our previous work [27–30]. The mixtures were prepared by mass and placed into the equilibrium cell [31], which was self-designed. The three components were mixed together and agitated by a stir bar. After intense agitation (3 h, approximately

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Table 1

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>CAS number</th>
<th>Molar mass/ (g mol⁻¹)</th>
<th>Mass purity stated by supplier</th>
<th>w_m/10⁶</th>
<th>Analysis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>Tianjin Kermel Chemical Reagent Co., Ltd.</td>
<td>64-17-5</td>
<td>46.07</td>
<td>0.998⁺</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>hexane</td>
<td>Tianjin Kermel Chemical Reagent Co., Ltd.</td>
<td>110-54-3</td>
<td>86.18</td>
<td>0.995⁺</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>Tianjin Kermel Chemical Reagent Co., Ltd.</td>
<td>67-56-1</td>
<td>32.04</td>
<td>0.990⁺</td>
<td>GC</td>
<td></td>
</tr>
<tr>
<td>[MIM][HSO4]</td>
<td>Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.</td>
<td>681281-87-8</td>
<td>180.18</td>
<td>0.980⁺</td>
<td>&lt;500⁺</td>
<td></td>
</tr>
<tr>
<td>[BMIM][HSO4]</td>
<td>Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.</td>
<td>262297-13-2</td>
<td>236.29</td>
<td>0.980⁺</td>
<td>&lt;500⁺</td>
<td></td>
</tr>
<tr>
<td>[BMIM][OTf]</td>
<td>Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.</td>
<td>174899-66-2</td>
<td>288.29</td>
<td>0.980⁺</td>
<td>&lt;500⁺</td>
<td></td>
</tr>
</tbody>
</table>

+ Analysis by supplier.

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Fig. 1. Ionic liquids structures. (a) [MIM][HSO4]; (b) [BMIM][HSO4]; (c) [BMIM][OTf].