



Phosphoric-based ionic liquids as solvents to separate the azeotropic mixture of ethanol and hexane



Fufeng Cai^a, Min Zhao^b, Yuan Wang^a, Fei Wang^a, Guomin Xiao^{a,*}

^a School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China

^b Analysis and Test Center, Chinese Academy of Tropical Agricultural Sciences, Hainan Provincial Key Laboratory of Quality and Safety for Tropical Fruits and Vegetables, Laboratory of Quality and Safety Risk Assessment for Tropical Products, Haikou 571101, Hainan, PR China

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ABSTRACT

Ethanol and hexane mixtures are present in industrial processes producing oxygenated additives for unleaded gasoline. The separation of ethanol and hexane is important but challenging due to the formation of an azeotropic mixture. This research focuses on the study of phosphoric-based ionic liquids (ILs) as green solvents for the separation of ethanol from hexane in a liquid extraction process. The knowledge of the (liquid + liquid) equilibrium (LLE) of this mixture is essential for the design of the extraction separation technique. Hence, the experimental determination of the LLE data for the ternary system {ethanol + hexane + 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP])}, {ethanol + hexane + 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP])} and {ethanol + hexane + 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP])} at $T = 303.2$ K and atmospheric pressure was carried out. The reliability of the experimental LLE data was confirmed by applying the Othmer–Tobias and Hand equations, and the NRTL model was used to correlate the experimental results for the studied ternary system. The solute distribution ratio and selectivity, derived from the experimental LLE data, were calculated and analyzed to evaluate the capacity of the investigated ILs as solvents in liquid extraction process. This capacity was also compared with that of other ILs. The experimental results show that the studied ILs can be suitable solvents in a (liquid + liquid) extraction for the separation of azeotropic mixtures of ethanol and hexane.

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1. Introduction

As a result of the reduction of lead in gasoline, an increasing number of processes in which alkanols and alkanes co-exist to produce oxygenated additives for gasolines have been widely applied in industry [1]. Different azeotropes, e.g., ethanol and hexane, are present in these industrial processes. In this case, the separation of an ethanol and hexane mixture into pure components is necessary for their reuse. However, the separation of ethanol and hexane has been a challenging task in industrial processes because the azeotropic separation of this mixture cannot be done in ordinary distillation.

Extractive distillation, which combines the advantages of solvent extraction and distillation, has been used in the separation of ethanol from its azeotropic mixture with hexane [2]. In this process, a new solvent is added to the liquid mixture, altering the relative volatilities of the components and making the separation more efficient. However, this type of distillation method has a

few significant disadvantages namely requiring a higher energy cost to achieve a fluid phase system, and the use of volatile compounds. (liquid + liquid) extraction, based on the immiscibility of two liquid phases, is a potential alternative separation process to extractive distillation [3]. (Liquid + liquid) extraction can be carried out under ambient conditions, does not require specialized equipment and reduces the required energy consumption and corresponding environmental impact. However, the selection of an efficient and suitable solvent is the key to ensure an economic operation. Fortunately, (liquid + liquid) equilibrium (LLE) data can supply the information necessary to determine the appropriate solvents to accomplish the separation target. Additionally, the LLE data provides information relevant to the design of extraction process. Therefore, an examination of LLE data is necessary and important to understand the role of various solvents in the separation processes.

The search for more environmentally friendly solvents has gained interest in the past decade. Solvents like ionic liquids (ILs) show notable properties such as an extremely low vapor pressure, non-flammability, recyclability and excellent dissolving powers for a wide range of inorganic and organic compounds [4–7].

* Corresponding author. Tel./fax: +86 25 52090612.

E-mail address: xiaogm@seu.edu.cn (G. Xiao).

Additionally, ILs are considered “designer solvents” because they can be synthesized for a specific task by employing different (anion + cation) combinations [8]. Thus, ILs have attracted increased interest as novel substitutes of many traditional organic solvents.

For the azeotropic system ethanol and hexane, a suitable IL for the separation of this mixture must have the following properties: a high solubility of ethanol and an absence or low solubility of hexane; high solute distribution ratio and selectivity; and an easy recovery from both the extract and raffinate phases. Currently, there are only a few publications investigating ILs as solvents for the separation of azeotropic mixtures of ethanol and hexane. Rodríguez and co-workers [9–12] investigated the separation of ethanol from hexane using the ILs 1,3-dimethylimidazolium methyl sulfate ([MMIM][MeSO₄]), 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO₄]) and 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][MeSO₄]) at $T = 298.15$ K and atmospheric pressure. Corderí *et al.* [13,14] analyzed the effect of bis(trifluoromethylsulfonyl)imide-based ILs on the LLE data of ethanol + hexane. González *et al.* [15,16] published the LLE data for the ternary systems containing pyridinium-based ILs with ethanol + hexane at $T = 298.15$ K and atmospheric pressure. Finally, Pereiro *et al.* [17] focused on the effect of the alkyl chain length of 1-alkyl-3-methylimidazolium hexafluorophosphate IL in the separation of ethanol and hexane by solvent extraction. The ILs with fluorine-containing anions such as [PF₆][−] can undergo hydrolysis and produce HF in contact with water and at high temperatures [18,19]. Phosphorous-containing imidazolium derivatives [20–23] are promising ILs and are used in industrial processes. These ILs are not only chemically and thermally stable, with low melting points and relatively low viscosities, but can also be easily synthesized in a halide-free way at a reasonable cost. These advantages make them particularly attractive for the separation of ethanol and hexane.

In this work, three phosphoric-based ILs with different structures have been selected: 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) and 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]). LLE data were measured for the ternary systems {ethanol + hexane + [MMIM][DMP]}, {ethanol + hexane + [EMIM][DEP]} and {ethanol + hexane + [BMIM][DBP]} at $T = 303.2$ K and atmospheric pressure. The capacities of the studied ILs as solvents in the liquid extraction process were analyzed by using the solute distribution ratio and selectivity values. These capacities were then compared with that of other ILs. The reliability of the LLE data was ascertained by applying the Othmer–Tobias [24] and Hand [25] equations. The non-random two liquid (NRTL) [26] model was used to correlate the experimental results for the studied ternary systems.

2. Experimental

2.1. Chemicals

Ethanol and hexane used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Their mass fraction purities were checked by gas chromatography (GC-6890, China) and were 0.997 and 0.99, respectively. The studied ILs, [MMIM][DMP], [EMIM][DEP] and [BMIM][DBP], were synthesized in the laboratory following procedures published in the literature [27]. Briefly, these ILs were subjected to heating at $T = 393$ K under high vacuum (0.2 kPa) for 48 h to remove residual traces of solvents and moisture. The mass fraction of water in the IL, measured by Karl Fischer titration (AKF-2010, China), was $x_w < 0.0005$. The structure of the final products was confirmed by ¹H NMR spectroscopy (AV-600 Bruker spectrometer), and their purities were found to be greater than 0.98 mass fraction. All chemicals were kept in a glove box under an inert nitrogen atmosphere to prevent moisture. The specifications of the chemicals used in this work are summarized in table 1, and the structures of the studied ILs are shown in figure 1.

2.2. Apparatus and experimental procedure

The determination of experimental LLE tie-lines was performed in a 50 mL glass cell containing a magnetic stirrer and thermostatically controlled at $T = 303.2$ K. For the experimental measurements of the LLE tie-lines, 30 mL of an immiscible ternary mixture of known composition was put into the glass cell and stirred using the magnetic stirrer, and the temperature in the glass cell was measured with a precise and calibrated thermometer with a standard uncertainty of $T = 0.1$ K. The sample mixture was stirred vigorously for 1 h to complete contact between the phases. Then, the sample mixture was left to settle for 4 h to ensure a complete separation between the equilibrium phases.

At the end of settling period, the samples were obtained from the upper and lower phases using a syringe, and compositional analysis was carried out. The compositions of ethanol and hexane

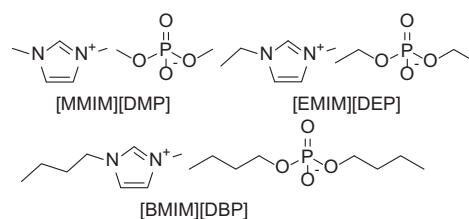


FIGURE 1. Structures of the ionic liquids studied in this work.

TABLE 1

The specifications of chemicals used in this work.

Chemical name	Source	Mass fraction purity	Final water mass fraction	Analysis method
Ethanol	Sinopharm Chemical Reagent Co., Ltd.	≥0.997		GC ^d
Hexane	Sinopharm Chemical Reagent Co., Ltd.	≥0.99		GC ^d
[MMIM][DMP] ^a	Prepared in this work	≥0.98	<0.0005	KF ^e , NMR ^f
[EMIM][DEP] ^b	Prepared in this work	≥0.98	<0.0005	KF ^e , NMR ^f
[BMIM][DBP] ^c	Prepared in this work	≥0.98	<0.0005	KF ^e , NMR ^f

^a [MMIM][DMP] = 1,3-dimethylimidazolium dimethylphosphate.

^b [EMIM][DEP] = 1-ethyl-3-methylimidazolium diethylphosphate.

^c [BMIM][DBP] = 1-butyl-3-methylimidazolium dibutylphosphate.

^d Gas chromatography.

^e Karl Fischer titration.

^f Nuclear magnetic resonance.

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