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Liquid–liquid equilibria for ternary systems ethanol + heptane + phosphoric-based ionic liquids

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ABSTRACT

This work demonstrates the capabilities of three phosphoric-based ionic liquids (ILs) as solvents for the extraction of ethanol from its mixture with heptane. The knowledge of liquid–liquid equilibria (LLE) of this mixture is essential for the design of the extraction separation process. For this reason, the experimental LLE data were measured for the ternary systems, {ethanol + heptane + 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]), or 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), or 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP])}, at $T = 298.2$ K and atmospheric pressure. The thermodynamic nonrandom two-liquid (NRTL) model was used to correlate the experimental results for the studied ternary systems. The extraction capabilities for the studied ILs were evaluated by solute distribution ratios of ethanol and ethanol/heptane selectivities. Moreover, this extraction capability was also compared with other ILs obtained from the literature. The experimental results show that the studied ILs can be suitable to act as solvents for the separation of the ethanol and heptane in the extraction process. The extraction capabilities for the studied ILs decrease in the following order [MMIM][DMP] > [EMIM][DEP] > [BMIM][DBP].

1. Introduction

The azeotrope ethanol and heptane is present in industrial production processes of oxygenated additives for unleaded gasoline [1]. For the separation of ethanol and heptane, ordinary distillation cannot yield high purity components. However, separation of this mixture is important because pure components can be reused in further applications. Extractive distillation is currently the most widely used process to separate the components in the azeotropic systems [2–4]. Nevertheless, this process shows some serious disadvantages such as need high energy to achieve a fluid phase system, and the use of volatile compounds. The liquid–liquid extraction, based on the immiscibility of two liquid phases, provides an environmentally friendly process as an alternative to extractive distillation [5–7]. Liquid–liquid extraction can be carried out under ambient conditions, and reduces the energy consumption and corresponding environmental impact. But the selection of an efficient and suitable solvent is the paramount to ensure an economic operation.

Ionic liquids (ILs) have received considerable attention to act as potential substitutes for classical organic solvents in the extraction processes in the past decade. Their notable properties include negligible vapor pressure at room temperature, wide liquid range, high thermal/chemical stability, excellent solubility for organic/inorganic compounds, and superior regeneration ability [8–10]. Apart from that, the ILs are being considered as "designer" solvents because they can be synthesized for a specific task by using different anion–cation combinations. Therefore, they have been extensively used as extraction solvents to separate different mixtures in recent years [11–16].

For the azeotrope ethanol and heptane, the requirement of a suitable IL for the separation of this mixture is: high solubility of the ethanol in the IL, absence or low solubility of heptane in the IL; high solute distribution ratio and selectivity values, etc. Currently, there are a few publications concerning the extraction of ethanol from its mixture with heptane using ILs as solvents. Pereiro et al. [17–19] focused on the separation of ethanol from heptane using the ILs, 1,3-dimethylimidazolium methyl sulfate ([MMIM][$MeSO_4$]), 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][$EtSO_4$]), and 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][$MeSO_4$]). Seoane et al. [20] studied the effect of the alkyl chain length of the imide-based ILs, [AMIM][NTf_2], in the separation of ethanol and heptane by solvent extraction. Petera and co-workers [21,22] investigated the extraction of ethanol from its mixture with heptane using [BMIM][$MeSO_4$] on a new electrostatic spray extraction column. Letcher et al. [23] published the LLE data for the ternary systems involving ethanol + heptane with 1-methyl-3-octylimidazolium chloride. González and co-workers [24–26] analyzed the effect of amide-based ILs on the LLE data of ethanol + heptane at $T = 298.15$ K and atmospheric pressure.

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Nomenclature

List of symbols

x_i	Mole fraction of component i
w_i	Mass fraction of component i
S	Ethanol/heptane selectivities
Δg_{ij}	Binary interaction parameter of NRTL model
T	Equilibria temperature (K)
R	Ideal gas constant (J mol^{-1} K^{-1})
p	Pressure (kPa)
k	Number of experimental tie-lines
x_i^{I}	Mole fraction of component i in the upper layer
x_i^{II}	Mole fraction of component i in the lower layer
W_i^{I}	Mass fraction of component i in the upper layer
W_i^{II}	Mass fraction of component i in the lower layer
$x_{1i}^{\mathrm{I}}, x_{2i}^{\mathrm{I}}, x_{1i}^{\mathrm{II}}, x_{2i}^{\mathrm{II}}$	Experimental mole fractions
$x_1^{\mathrm{I}}(\mathrm{calc}), x_2^{\mathrm{I}}(\mathrm{calc}), x_1^{\mathrm{II}}(\mathrm{calc}), x_2^{\mathrm{II}}(\mathrm{calc})$	Calculated mole fractions

Greek letters

β	Solute distribution ratios of ethanol
α_{ij}	Nonrandomness factor of NRTL model
γ_i	Activity coefficient of component i
τ_{ij}	Parameter of NRTL model
σ	Root mean square deviation

Superscripts

I, II	Upper and lower layers, respectively

Subscripts

1	Ethanol
2	Heptane
3	Ionic liquid
i	Component
l	Phase
m	Tie-lines
exptl, calc	Experimental and calculated

Finally, Rodríguez and co-workers [27,28] studied the extraction of ethanol from heptane using 1-alkyl-3-methylimidazolium hexafluorophosphate.

Phosphorus-containing imidazolium derivatives [29–34] 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. In this work, three phosphoric-based ILs, [MMIM][DMP], [EMIM][DEP], and [BMIM][DBP], were used as solvents for the extraction of ethanol from its mixture with heptane. The experimental LLE data for the ternary systems {ethanol + heptane + [MMIM][DMP], or [EMIM][DEP], or [BMIM][DBP]} were measured at T = 298.2 K and atmospheric pressure. The NRTL [35] model was used to correlate the experimental results for the studied ternary systems. The solute distribution ratios of ethanol and ethanol/heptane selectivities, derived from the experimental LLE data, were calculated and analyzed to evaluate the capabilities of the studied ILs as solvents in the extraction process. Meanwhile, this extraction capability was compared with that of other ILs reported in the literature.

2. Experimental

2.1. Chemicals

Ethanol (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), heptane (Aladdin Industrial Corporation, Shanghai, China), and 1-propanol (Aladdin Industrial Corporation, Shanghai, China) were used in this work with stated purities of 99.7% (mass), 99.0% (mass), and 99.9% (mass), respectively. The studied ILs, [MMIM][DMP], [EMIM][DEP] and [BMIM][DBP], were synthesized in the laboratory according to the procedure reported in the literature [36]. The IL was subjected to heating at T = 393.2 K under high vacuum (0.2 kPa) for 48 h to remove possible traces of solvents and moisture, prior to use. The structure of the ILs was confirmed by ^{1}H NMR spectrum (Bruker AV-600 NMR spectrometer) with a certified purity higher than 98.0% mass fraction. The specifications of the chemicals used in this work are listed in Table 1, and the structure formulas of the studied ILs are shown in Fig. 1. All chemicals are kept in a glove box under inert nitrogen atmosphere to avoid moisture.

2.2. Apparatus and experimental procedure

The measurement of experimental LLE data was performed into a 50 mL glass cell containing a magnetic stirrer and thermostatically controlled at T = 298.2 K. A schematic diagram of the experimental apparatus is shown in Fig. 2. In the experimental LLE data measurement, 30 mL of an immiscible ternary mixture of known composition was put into the glass cell and stirred by the

Table 1
The specifications of the chemicals used in this work.

Chemical name	Molecular formula	CAS number	Source	Mass fraction purity	Final water mass fraction	Analysis method
Ethanol	C_2H_6O	64-17-5	Sinopharm Chemical Reagent Co., Ltd.	≥0.997		GC[d]
Heptane	C_7H_{16}	142-82-5	Aladdin Industrial Corporation	≥0.990		GC[d]
1-Propanol	C_3H_8O	71-23-8	Aladdin Industrial Corporation	≥0.999		GC[d]
[MMIM][DMP][a]	$C_7H_{15}N_2O_4P$	654058-04-5	Prepared in the lab	≥0.980	<0.0005	KF[e], NMR[f]
[EMIM][DEP][b]	$C_{10}H_{21}N_2O_4P$	848641-69-0	Prepared in the lab	≥0.980	<0.0005	KF[e], NMR[f]
[BMIM][DBP][c]	$C_{16}H_{33}N_2O_4P$	663199-28-8	Prepared in the lab	≥0.980	<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.