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Application of 1-hexyl-3-methylimidazolium trifluoromethanesulfonate to the removal of alcohol from mixtures with heptane

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ABSTRACT

An ionic liquid (IL) of 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate [Hmim][OTf] was investigated as a possible extraction solvent in petrochemical processes for the removal of alcohol from an azeotropic mixture with heptane. Liquid–liquid equilibrium (LLE) experiments of three ternary systems, hexane + ethanol, 1-propanol, or 2-propanol + [Hmim][OTf], were conducted at 298.15 K and atmospheric pressure. The efficiency of [Hmim][OTf] as an extraction solvent was determined by calculating the solute distribution ratio, β, and selectivity, S, and this efficiency was compared to other ionic liquids from the literature. The structural volume (r) and surface area (q) of [Hmim][OTf] were determined using a quantum chemistry approach. The LLE data of the three ternary systems were correlated using NRTL and UNIQUAC models, and the UNIFAC model was used to predict the phase behavior compared to the experimental data.

1. Introduction

Alkanol and alkane mixtures that produce oxygenated additives have been widely used in industry for the reduction of lead in gasoline [1]. As a result, various azeotropic mixtures of alcohols and alkanes are present, and the separation of alkanol and alkane mixtures into pure components is necessary for their reuse. Because the separation of azeotropic mixtures by ordinary distillation processes is difficult or even impossible, extractive distillation is currently used instead. However, liquid-liquid extraction represents a cost- and environment-friendly alternative to extractive distillation because the process reduces the energy consumption and avoids the release of volatile solvents into the atmosphere [2].

As a result, ionic liquids (ILs) have attracted the interest of many researchers as potential substitutes for classical organic solvents in extraction processes due to numerous advantages, namely, good thermal stability, negligible vapor pressure, wide liquid range polarities, and thermal and chemical stability [3]. Thermodynamic liquid–liquid equilibrium (LLE) data are essential for the design, optimization and operation of extraction processes using ILs as solvents. A number of studies have investigated the LLE for the separation of alkanol and alkane using an IL as an extraction agent [2,4–18]. Begoña González and Sandra Corderí [10] investigated the ionic liquids 1-butyl-1-methylpyrrolidinium dicyanamide and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate as green solvents for the separation of ethanol from heptane and hexane. The efficacy of the extraction of ethanol from the alkanes was evaluated using the solute distribution ratios and selectivity values. Fufeng Cai and Guomin Xiao [16] analyzed the ILs 1,3-dimethylimidazolium dimethylphosphate, 1-ethyl-3-methylimidazolium diethylphosphate, and 1-butyl-3-methylimidazolium dibutylphosphate as solvents for the extraction of methanol from its mixtures with hexane and heptane. The authors concluded that ILs with shorter chains have a greater extracting potential and that the IL 1,3-dimethylimidazolium dimethylphosphate is the best candidate for the separation of methanol from its mixtures with hexane and heptane.

For the UNIQUAC [19] and UNIFAC [20] models, basic data such as structural volume (r) and surface area (q) parameters of the ILs are necessary for further study. Sandra Corderí et al. [9,21] utilized [Hmim][OTf] for the separation of toluene/alkanes and hexane/

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ethanol mixtures. However, they only used the NRTL model [22] to regress their systems involving [Hmim][OTf] for the absent and q values. Therefore, in this work, we used a quantum chemistry approach for determining the values of r and q, which are not present in the literature for IL 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate ([Hmim][OTf]). The validities of the r and q values that were obtained from the quantum chemistry approach and applied to the UNIQUAC model were proven by several experts [23–27].

In this work, LLE data were experimentally determined for three ternary systems: heptane (1) + ethanol, 1-propanol or 2-propanol (2) + [Hmim][OTf] (3) at T = 298.15 K and atmospheric pressure. The solute distribution ratios and the selectivities of the ternary systems involving [Hmim][OTf] were obtained from the LLE data and were compared with other ILs to analyze the separation efficiency with alcohol-heptane azeotropic mixtures. The experimental LLE data were correlated with NRTL and UNIQUAC models, and relevant binary interaction parameters for the models were obtained. The UNIFAC model was used to predict the LLE phase equilibria, which were compared to the experimental data, and the predictive ability of the UNIFAC model for the studied systems was also revealed.

2. Experimental

2.1. Chemicals

The IL [Hmim][OTf] was supplied by the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences with a stated purity of >0.990 mass fraction. The study was conducted using chromatography grade ethanol, 1-propanol and 2-propanol, of which the purities were checked by gas chromatography. The suppliers and mass fraction of chemical reagents are listed in Table 1. All materials were used without further purification. The 3D molecular structure of [Hmim][OTf] was optimized through a Density Functional Theory (DFT) calculation and is shown in Fig. 1.

2.2. Apparatus and procedure

The experiment was performed in our unique equilibrium cell that was described in our previous work [26]. An HX-105 low-temperature thermostat that was purchased from the Changliu Instrument Factory of Beijing in China was used to maintain a constant temperature. The uncertainty in the temperature was ±0.05 K. Prior to the experiment, the scope of the two-phase region was determined and the ratio for every component was determined according to the results. The mixture was then stirred vigorously with a stir bar for 3 h to ensure good contact and left to settle for 15 h to ensure complete separation of the liquid phases. Samples were removed from both layers to analyze the compositions.

The composition of alcohol and heptane was analyzed using gas chromatography (GC-2014C) with helium as the carrier gas. The chromatograph was equipped with a thermal conductivity detector (TCD) and a GDX-104 (3 m × 4 mm) packed column connected to a pre-column. The stationary phase of the packed pre-column was Porapak Q, which prevented the nonvolatile IL from reaching and contaminating the packed column. Ethanol was used as the internal standard for heptane + 1-propanol/2-propanol and 1-propanol was used for heptane + ethanol in the GC analysis. GC conditions were as follows: helium was used (>99.999% purity) as the carrier gas, the temperature of the injector was 503.15 K, the column oven was maintained at 438.15 K for 3 min and subsequently submitted to the following heating program: from 438.15 K to 503.15 K at a rate of 15 K/min, maintained at 503.15 K for 3 min, and the detector was at 523.15 K. A vacuum drying oven (DZF-6020 from Shanghai Boxun China) was used to determine the IL content in the sample. The mass difference in the liquid samples before and after vaporization at 308.2 K in the vacuum oven was calculated to determine the IL composition, as described in our previous work [26]. All of the data were measured at least three times.

3. Results and discussion

3.1. Experimental data

The experimental ternary LLE values for heptane (1) + ethanol, 1-propanol, or 2-propanol (2) + [Hmim][OTf] (3) at T = 298.15 K are presented in Table 2, where x_i represents the mole fraction of component *i*. The corresponding ternary phase diagrams are displayed in Figs. 2–4. The solubility of heptane in [Hmim][OTf] [21] is shown in the figures. The two-phase region and the slopes of the experimental tie-line are represented in Figs. 2–4. The mixtures studied in this work show Treybal's Type I behavior. The binary systems of heptane + ethanol/1-propanol/2-propanol were completely miscible at 298.15 K, which indicated that ethanol, 1-propanol and 2-propanol had higher affinity toward [Hmim][OTf] than heptane based on the slopes of the tie-lines.

3.2. LLE correlation

The NRTL and UNIQUAC models were used to calculate the experimental data because both models have previously provided adequate correlations for LLE [18,28–36]. MATLAB was used to regress the parameters from both the NRTL and UNIQUAC models via the nonlinear least squares method. The non-randomness parameter α_{ij} of the NRTL model was optimized and is given in Table 3. The molecular volume structure parameter *r* and the molecular surface area parameters *q* and *q'* of [Hmim][OTf] are listed in Table 4 and were determined using the quantum chemical calculation method that was thoroughly described in a previous report [26]. After optimization of the equilibrium geometry of [Hmim][OTf] using Density Functional Theory (DFT), the values of r and q were calculated using the Polarizable Continuum Model (PCM) with the GEPOL algorithm in the Gaussian 09 package. The overall surface (A) and the overall volume (V) were then obtained from their relationships with r and q as follows:

$$r = \frac{V(1\times10^{-8})^3 N_A}{V_{VW}} \quad q = \frac{A(1\times10^{-8})^2 N_A}{A_{VW}} \tag{1}$$

where N_A is Avogadro's number (6.023×10^{23} mol^{-1}) and the standard segment volume V_{VW} and area A_{VW} were set at 15.17 cm^3/mol and 2.5×10^9 cm^2/mol, respectively, as suggested by Bondi [37]. Table 4 lists the *r* and *q* values for the solvents [23,24].

The binary interaction parameters of the NRTL and UNIQUAC models were determined by minimizing the objective function as follows:

$$OF = \sum_{k=1}^{M}\sum_{j=1}^{2}\sum_{i=1}^{3}\left(x_{ijk}^{exp} - x_{ijk}^{calc}\right)^2 \tag{2}$$

where *M* represents the number of tie-lines, x^{exp} and x^{calc} indicate the experimental and calculated mole fractions, respectively, and subscripts *i*, *j*, and *k* denote the component, phase, and tie-line, respectively.

The binary interaction parameters for the NRTL and UNIQUAC models are listed in Table 3. The values of *rmsd* between the experimental and calculated data were calculated from the following equation: