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Liquid–liquid equilibria for ternary mixtures of water + 2-propanol + 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids at 298.15 K

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ABSTRACT

Ternary liquid–liquid equilibria for three systems of water + 2-propanol + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][NTf_2]), 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Omim][NTf_2]), and 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Dmim][NTf_2]) ionic liquids (ILs) have been determined at T = 298.15 K and atmospheric pressure. The solute distribution coefficient and the selectivity were calculated for all systems. Influence of ILs with different length of alkyl chain on the liquid–liquid equilibria was revealed. The nonrandom two liquid (NRTL) model was used to correlate ternary systems. Three ILs were studied to determine the parameters of structural volume (r) and surface area (q) by quantum chemistry approach. According to the calculated values of r and q, the universal quasichemical (UNIQUAC) model was also applied to correlate three ternary systems. The results show that both NRTL and UNIQUAC models are capable of correlating the studied systems with reasonable accuracy.

1. Introduction

2-propanol is an important organic synthetic raw material and solvent widely used in the production of many chemicals and intermediates [1]. It can be produced by biomass-fermentation process where the mixtures of water and 2-propanol are always generated simultaneously. The separation of these mixtures and related thermodynamic physical properties are important for engineering application. Among different available separating technologies, liquid–liquid extraction is a potential method for its unique assets. Thus, it is important to study the liquid–liquid equilibrium (LLE) of water and 2-propanol and give relevant thermodynamic data for us.

Many papers about the LLE containing alcohols and water have been reported recent years [2–21]. Some researchers among these papers present the influences of traditional organic solvent on the LLE of alcohols and water [3–7,14]. For example, H Ghanadzadeh Gilani et al. [7] investigated ternary equilibrium data of mixtures consisting of 2-butanol, water, and heavy alcohols at T = 298.15 K. Amparo Cháfer et al. [14] presented LLE data of systems 4-methyl-2-pentanone + water + 1-propanol, 2-propanol. Comparing with the organic solvent, ionic liquids (ILs) have been causing researchers' attention in the application of LLE containing alcohols and water [2,19,22–34] for their advantages, such as negligible vapor pressure, non-flammability, and tunable physiochemical properties [35]. For example, Catarina M. S. S. Neves et al. [31] showed the separation of ethanol of water using phosphonium-based ILs by liquid–liquid extraction. Dharamashi Rabari et al. [34] obtained successful recovery of butanol and propanol from aqueous solution by introducing phosphonium-based ILs that has density lower than water. Few scholars have concentrated on the LLE of water + 2-propanol + ILs comparing with the ternary systems of water + 1-butanol + ILs that show the Treybal's Type II [26,27,29]. Thus, the ternary systems of water + 2-propanol based on different ILs are studied in this paper.

Researchers are apt to correlate LLE data of ternary systems by the nonrandom two liquid (NRTL) [36] and universal quasichemical (UNIQUAC) [37] models after the LLE data were reported. Both models can correlate the LLE data of ternary systems containing no ILs well [15,38–43]. The application of the UNIQUAC model for correlating the LLE data containing ILs, however, is narrower than that of the NRTL model for the former requires the structural volume (r) and surface area (q) parameters of ILs and the parameters

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are missing in the published papers for the new ILs [44]. The calculations of the values of r and q for some ILs by quantum chemistry approach have been reported and the validities of the calculated values applied to the UNIQUAC model were testified [44–46]. Therefore, the quantum chemistry approach was applied for determining the values of r and q for the studied ILs by Gaussian 09 in this work.

The influences of some factors on the LLE of ternary systems were investigated by researchers [19,31,33,47–49]. For example, Amparo Chafer et al. [19] studied the impact of temperature on the phase equilibrium of Water + Ethanol + 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide. Alexander Nann et al. [33] presented the influences of ILs on the LLE of ternary system using the ILs based on different anion. In this paper, the ternary systems of water + 2-propanol + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][NTf_2]), 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([Omim][NTf_2]), and 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Dmim][NTf_2]) were investigated at T = 298.15 K and atmospheric pressure. According to the experimental data, the influences of the ILs with different length of alkyl chain on the LLE were revealed by calculating the solute distribution ratio (β) and the selectivity (S). Furthermore, the NRTL and UNIQUAC models with calculated r and q were applied to correlate the experimental data and to fit the interaction parameters of two models. The root-mean-square deviation ($rmsd$) between the experimental and predicted data calculated by two thermodynamic models using the fitted interaction parameters were also calculated.

2. Experiment

2.1. Chemicals

The ILs of [Hmim][NTf_2], [Omim][NTf_2], and [Dmim][NTf_2] with mass fraction purities higher than 0.990 were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The study was carried out using 2-propanol and ethanol whose purity was checked by gas chromatography. The suppliers and mass fraction of the chemical reagent are listed in Table 1. Water used in the whole experiment was doubly distilled deionized. All materials were used without further purification. Density Functional Theory (DFT) calculation is used to optimize the 3D molecular structures of the ILs and the results are shown in Fig. 1.

2.2. Apparatus and procedure

The experiment was performed in a customized LLE device, which has a 35 mL glass cell containing a mechanical stirring bar and was thermostatted by a water jacket connected to a bath. Fig. 2 shows the customized equilibrium cell that has a sample opening in the bottom of inner cell. The lower phase sample can be taken out without a contamination from the upper phase sample. A jacket around the inner cell has an inlet and an outlet used to pass though thermostatic water from a thermostat. A low temperature thermostat of THD-015 purchased from Tianheng Instrument Factory of Ningbo in China was used to control the temperature of the systems. The uncertainty of the temperature measurements was ±0.05 K. In order to make the LLE data cover the entire two-phase region as large as possible, during the mix of the pure components, the content of ILs was fixed and the proportion span of 2-propanol/water was determined by the pre-experiment using the cloud point method [50]. In the pre-experiment, the equilibrium time of the samples are determined within 10 h. 30 g mixture with explicit composition was put into the glass cell and stirred vigorously by the mechanical stirrer for 2 h to ensure a good contact between both phases and then settled overnight of 15 h to ensure a complete split of the equilibria phases at a constant temperature of 298.15 K. The samples were respectively taken out from the upper and lower layers to analyze specific phase composition.

The compositions of water and 2-propanol were analyzed by gas chromatography (GC-2014C) equipped with a Headspace Autosampler, a GDX-104 (2 m × 3 mm) packed column, and a thermal conductivity detector (TCD). Ethanol was added to the sample as an internal standard substance for the GC analysis. Operating conditions were described as following: the temperature of the injector was 383.2 K, the oven was 403.2 K, and the detector was 473.2 K. The IL composition in the sample was determined by calculating the mass difference of the liquid sample before and after the vaporization of solvents at 408.2 K in a vacuum drying oven (DZF-6020, Shanghai Boxun, China) until the constant weight was reached. All the measurements were repeated at least three times. The maximal standard composition uncertainty of the IL was ±0.001 in mole fraction.

3. Thermodynamic models

The experimental LLE data for the ternary systems have been correlated by the NRTL and UNIQUAC models (Table 2) which have provided adequate correlation for ternary systems containing ILs [34,49,51]. The molecular volume structure parameter r and the molecular surface area parameters q, q' of ILs in UNIQUAC model calculated are listed in Table 3. For most of substances, q is equal to q' except water and some small alcohols. The coordination number, z, is set to 10. Polarizable Continuum Model (PCM) [52] with the GEnerating POLyhedra (GEPOL) algorithm [53] was used to calculate the r and q in the UNIQUAC model after the ILs structures being optimized by Density Functional Theory (DFT) [54]. DFT based on a hypothesis that the electron density distribution completely characterizes the ground state of a many electron system is a most popular method for calculating the electronic structure of atoms, molecules, liquids, solids, and plasmas. As a valuable research tool,

Table 1
List of chemicals.

Chemical	Molecular formula	CAS number	Molar mass/ ($g \cdot mol^{-1}$)	Purity (mass fraction)	Manufacturer
2-propanol	C_3H_8O	67-63-0	60.10	0.992	Tianjin Bodi Chemical Holding Co., Ltd.
Ethanol	C_2H_6O	64-17-5	46.07	0.995	Sinopharm Chemical Reagent Co., Ltd.
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{12}H_{19}O_4N_3S_2F_6$	382150-50-7	447.42	0.990	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{14}H_{23}O_4N_3S_2F_6$	178631-04-4	475.47	0.990	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.
1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{16}H_{27}O_4N_3S_2F_6$	433337-23-6	503.52	0.990	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.