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Effect of cation alkyl chain length on liquid-liquid equilibria of {ionic liquids + thiophene + heptane}: COSMO-RS prediction and experimental verification

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ABSTRACT

When selecting ionic liquid (IL) as solvent for extraction processes, the cation alkyl chain length is an important structural variation, while research particularly concerning its effect is lacking. In this work, the effect of cation alkyl chain length on the liquid-liquid equilibria of {IL + thiophene + heptane}, an example for extractive desulfurization, was systematically investigated. The COSMO-RS model was employed to calculate the distributional coefficient (β^∞) and selectivity (S^∞) at infinite dilution for thiophene of the combinations of 17 cations and 63 anions. Two different anion-dependent tendencies of the β^∞ with increasing the cation alkyl chain length were identified and analyzed by COSMO-RS theory. To verify the scarcely-reported decreasing β^∞ with longer cation alkyl chain, acetate ($[OAc]^-$) was selected as representative and liquid-liquid equilibria {$[C_nMIM][OAc]$ + thiophene + heptane} (n = 2, 4, 6, 8) were experimentally determined, which validate the anion-dependency and demonstrate the highest extraction performance of $[C_2MIM][OAc]$.

1. Introduction

Ionic liquids (ILs) possess several unique properties, such as non-volatility, high thermal stability, wide liquid range, high solvent capacity, etc. More importantly, desired properties of ILs can be achieved by judicious selection of cation, anion and substitution groups, making them 'designer' solvents [1]. Due to these attractive characters, ILs have attracted significant interest as promising alternatives for volatile organic solvents as greener reaction or separation media [2–8].

The exploration of ILs as solvent for several difficult extraction tasks have been widely investigated [7–11]. Among them, extractive desulfurization (EDS) of fuel oils is one of the most extensively studied systems because of its advantages of mild process conditions, facile operation options and high selectivity towards aromatic sulfur compounds. So far, many studies on IL-based EDS have been carried out, where the desulfurization performance varies remarkably with different IL solvents [11–19]. Therefore, taking account of the large number of possible cation-anion combinations, many researchers are still striving to find more suitable ILs for EDS through both experimental and theoretical approach [11,19–23].

For the selection of ILs for EDS, the alkyl chain length on the cation is among the most commonly considered structural variations. Generally, it is believed that a longer alkyl chain is favorable for a higher distribution coefficient (β) for sulfur compounds or desulfurization ratio, but on the other hand leads to a decreasing selectivity (indicating higher amount of fuel components co-extracted by IL) [12–16]. For example, Wlazło et al. demonstrated the ranking of $[C_3MPIP][Tf_2N] < [C_4MPIP][Tf_2N] < [C_6MPIP][Tf_2N]$ for β and the reverse ranking of $[C_3MPIP][Tf_2N] > [C_4MPIP][Tf_2N] > [C_6MPIP][Tf_2N]$ for S in the ternary liquid-liquid equilibria of {$[C_nMPIP][Tf_2N]$ + thiophene + heptane} [12]. Gao et al. reported that for the removal of thiophene, benzothiophene and dibenzothiophene from dodecane with $[C_nPY][BF_4]$ (n = 4, 6, 8), both the desulfurization ratio and the solubility of model fuel in ILs follow the order of $[C_4PY][BF_4] < [C_6PY][BF_4] < [C_8PY][BF_4]$, which also suggest the converse tendencies of β and S [13]. Similarly, the increasing order of the desulfurization efficiency, namely $[C_2MIM][BF_4] < [C_4MIM][BF_4] < [C_6MIM][BF_4]$ [14], $[C_1MIM][MeSO_4] < [C_2MIM][MeSO_4] < [C_4MIM][MeSO_4]$ [15], $[C_4MPY][BF_4] < [C_6MPY][BF_4] < [C_8MPY][BF_4]$ [16] were experimentally

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proved, respectively. Moreover, for the separation of aromatic/aliphatic hydrocarbons with $[C_nMIM][Tf_2N]$ (which are similar to the EDS system), the continuously increasing β and decreasing S towards aromatic hydrocarbons from $[C_2mim]^+$ to $[C_{10}mim]^+$ was also observed [8–10]. Such effect of cation alkyl chain length was also roughly found by some theoretical works on these systems [20,23,24].

On the contrary, the consistent behaviors of β and S with the change of alkyl chain length were also found in some EDS literature. Song et al. found the decreasing ranking of $[C_2MIM][H_2PO_4] > [C_4MIM][H_2PO_4] > [C_5MIM][H_2PO_4]$ of β and S for thiophene/heptane separation by COSMO-RS prediction [11]. Chen et al. experimentally investigated the removal of thiophene and dibenzothiophene from model fuel and demonstrated the higher desulfurization ratio of $[C_4MIM][HSO_4]$ (28.5% for thiophene and 30.6% for dibenzothiophene) than $[C_6MIM][HSO_4]$ (13.7% for thiophene and 15.5% for dibenzothiophene) [25]. The following ranking of capacity for thiophene and dibenzothiophene: $[C_2MIM][Cl] > [C_6MIM][Cl]$, $[C_2MIM][MeSO_3] > [C_6MIM][MeSO_3]$, $[C_2MPYR][MeSO_3] > [C_6MPYR][MeSO_3]$ was also obtained by the COSMO-RS simulation of Gao et al. [23]. These results imply that the shorter cation alkyl chain is favorable for the β of such EDS systems.

From above, the effect of cation alkyl chain length on the β and S of ternary LLE of EDS system may vary with different types of ILs. However, the available reports on this particular issue only cover a small range of ILs with limited anion types, and in most cases the S towards sulfur compounds is not considered [12–16,25,26]. Therefore, to better understand the effect of cation alkyl chain length, more studies taking account of the IL characters (e.g., anion type, cation family and cation alkyl chain number, etc.) are strongly desired.

In this work, the effect of cation alkyl chain length on the LLE of an example EDS system {IL + thiophene + heptane} was investigated. The distributional coefficient (β^∞) and selectivity (S^∞) for thiophene at infinite dilution of the combinations of 63 anions and 17 cations was calculated by COSMO-RS, thereby providing a prior prediction of the effect of cation alkyl chain length. The ternary LLE of $\{[C_nMIM][OAc] + \text{thiophene} + \text{heptane}\}$ ($n = 2, 4, 6, 8$) were then experimentally determined.

2. Simulation and experimental description

2.1. COSMO-RS prediction

The software COSMOthermX based on the COSMO-RS theory was adopted [27]. Since the full description of the COSMO-RS model has been already given in literature [28,29], only the major features for understanding the prediction and analysis are briefly provided as follows.

The capability of COSMO-RS to calculate the chemical potential of an arbitrary solute i in any pure or mixed solvent enables the prediction of thermodynamic properties. The activity coefficient at any concentration can be predicted by

$$\ln(\gamma_i) = \left(\mu_i^{sol} - \mu_i^{p}\right) / RT \tag{1}$$

where μ_i^{sol} and μ_i^{p} represent the chemical potential of the solute *i* in the solvent and in the pure solute, respectively.

The distributional coefficient (β^∞) and selectivity (S^∞) of ILs at infinite dilution for the solute of interest can be determined by

$$\beta^\infty = \left(1/\gamma_i^\infty\right)^{IL} \tag{2}$$

$$S^\infty = \left(\gamma_j^\infty / \gamma_i^\infty\right)^{IL} \tag{3}$$

where γ_i^∞ and γ_j^∞ are the infinite dilution activity coefficient of solute i and diluent j in the IL phase. In this case, i and j refer to thiophene and heptane, respectively. These two parameters are widely used to evaluate the separation ability of a solvent for a specific task [11,20,22,24].

In the COSMO-RS theory, the σ profile is one of the most important molecule-specific properties, which is derived from unimolecular quantum chemical calculations and can well characterize the electrostatic polarity and charge distribution of a molecule. Generally, the whole σ range can be divided into three different regions, i.e., the nonpolar region ($-0.01\ e/Å^2 < \sigma < 0.01\ e/Å^2$), the hydrogen-bond donor region ($\sigma < -0.01\ e/Å^2$) and the hydrogen-bond acceptor region ($\sigma > 0.01\ e/Å^2$). Based on the definition of σ profile, two important σ moments related to hydrogen bond (HB), namely HB-acc3 and HB-don3, can be used to quantify the HB acceptor strength and the HB donor strength, respectively. Because of the ionic characters of ILs, cations are strong HB donors but weak acceptors, and anions are strong HB acceptors but weak donors [28,30].

2.2. Experimental verification

Ternary LLE experiments of $\{[C_nMIM][OAc] + \text{thiophene} + \text{heptane}\}$ ($n = 2, 4, 6, 8$) were determined at 298.15 K and ambient pressure to validate the COSMO-RS prediction. Heptane and thiophene were purchased from Aladdin Chemical Co., Ltd. with purity above 99.0 wt%, and no impurities were detected by gas chromatograph. The ILs $[C_nMIM][OAc]$ ($n = 2, 4, 6, 8$) were supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences with purity higher than 98.5 wt%, which were verified by ^{1}H.NMR characterization. Before use, the ILs were dried for 48 h at room temperature under reduced pressure to remove possible volatile impurities and traces of water. After the drying procedure, the water content in the ILs was determined to be less than 1000 ppm with an AQV-300 Karl-Fischer volumetric titration (Hiranuma, Japan). The detailed information about the involved chemicals was tabulated in Table S1 (Supporting Information).

In the LLE experiment, the IL (1), thiophene (2) and heptane (3) were successively introduced into a screw-capped vial, where the mass of each chemical in the mixture (M_1, M_2, M_3) was determined gravimetrically by a Sartorius BSA224S-CW balance (Germany) with a precision of ±0.0001 g. After tightly sealed, the mixture was vigorously agitated with a magnetic stirrer for 3 h and then settled for 6 h to ensure complete thermodynamic equilibrium. The liquid temperature was controlled by an oil bath with a temperature fluctuation of ±0.1 K (Huber Ministat 230, Germany). After settling, samples of the raffinate (R) and extract phases (E) were withdrawn carefully with syringes and analyzed by a gas chromatograph (Agilent 7890 GC, USA) equipped with a flame ionization detector and a PEG-20M column. The non-volatile IL was collected in a pre-column (5 m × 0.250 mm, uncoated fused silica) in order not to disrupt the analysis. An internal standard method was applied to determine the mass ratio of thiophene-to-heptane in both phases (m_{2R}/m_{3R}, m_{2E}/m_{3E}). The concentration of IL in the raffinate phase (m_{1R}) was analyzed by the increase in nitrogen content, which can be precisely determined with a chemiluminescence nitrogen analyzer (Antek 9000, USA). The detection range of the nitrogen analyzer is 20 ppb − 17% and different calibration lines can be adopted at each small interval within the range to ensure the accuracy of analysis. The estimated errors of the determined IL