



Effect of water on extractive desulfurization of fuel oils using ionic liquids: A COSMO-RS and experimental study☆



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ABSTRACT

When evaluating ionic liquids (ILs) for extractive desulfurization (EDS) of fuel oils, the inevitable presence of water in the system may have a significant and in many cases strongly negative effect. However, few studies have considered this particular issue and a promoted water effect on EDS is scarcely reported. In this work, COSMO-RS was firstly employed to calculate the capacity and selectivity for EDS of various IL/H₂O mixtures, which cover different IL characters and a wide water concentration range. Experiments were then conducted with a representative IL [C₄MIM][H₂PO₄], whose stable and even promoted extraction performance with a small amount of water was suggested by COSMO-RS. Through analyses of the desulfurization ratio, the cross-solubility and the water content in the desulfurized fuel, the promoted effect of water within a certain range (<10 wt%) was experimentally demonstrated. Moreover, such effect of water was explained combining the viscosity, the solvent–solute interactions and the COSMO-RS based analysis.

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1. Introduction

Ionic liquids (ILs), known as molten salts at or around room temperature, possess many unique physical and chemical properties, such as non-volatility, non-flammability, high thermal/chemical stability, wide liquid range, and so on [1]. Because of these attractive characters, ILs are regarded as promising alternatives for volatile organic solvents and thus have been extensively studied in various separation processes in the past few decades [2–10]. Among them, deep desulfurization of fuel oils, which faces the difficulty in effective removal of aromatic sulfur compounds (thiophenes and their derivatives) by conventional hydrodesulfurization methods, has been widely focused on. Extractive desulfurization (EDS) with ILs which has the advantages of mild process conditions, facile operation options and high selectivity for aromatic sulfur compounds, is consequently proposed [10] and many studies are successively carried out.

In 2001, Bösmann *et al.* reported the first attempt of EDS with ILs, in which [C₄MIM][AlCl₄] shows the best extractive ability for selective removal of sulfur compounds from diesel fuel among all the tested ILs [10]. However, the chloroaluminate ILs are not suitable in practice as they are strongly sensitive to water, even moisture and air [11]. Since then, ILs comprising anions of [BF₄][−], [PF₆][−] and [TF₂N][−] have been

intensively studied [12–18]. But the [BF₄][−] and [PF₆][−] based ILs are easily hydrolyzed in the presence of water, especially at elevated temperature, forming toxic and highly corrosive HF. Though the [TF₂N][−] based ILs appear to be more stable against hydrolysis, they are expensive and also potentially environmental pollutant, which restrict their practical application in large scale [11]. Considering such problems, halogen-free ILs with anions of alkylsulfate, alkylphosphate, [OAc][−], [N(CN)₂][−], etc. are further suggested [19–23]. With respect to the selection of cation, imidazolium and pyridinium based cations are the most commonly studied, while cations based on pyrrolidinium, piperidinium, quinolinium and ammonium have also been reported [24,25]. The detailed summary of the experimentally tested ILs for EDS can be found elsewhere [26].

Currently, most contributions on IL-based EDS focus on the selection of different ILs [17,27]. But an important concern in practical IL-based EDS process, *i.e.* the potential effect of water in IL or in the system, is rarely reported. However, as a matter of fact, the presence of water is to some extent inevitable in EDS systems with IL solvent. Firstly, most ILs initially contain more or less water (range from 10² mg·kg^{−1} level to 10⁴ mg·kg^{−1} level due to their different hydrophilicity and hydrophobicity), which is very hard and cost-intensive to remove completely [11]. Moreover, water usually exists as atmospheric moisture or at a low concentration in the fuel feed, which could be absorbed by IL solvent and accumulated during the extraction process. Besides, in many cases, IL-based EDS processes can be integrated with oxidation process to intensify the desulfurization performance [16,28]. This will also introduce a certain concentration of water into the system since 30 wt% hydrogen peroxide is usually employed as the oxidant.

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From the practical point of view, the existence of water in ILs may bring about a significant and in many cases strongly negative impact on EDS process. For instance, Gao *et al.* demonstrated the dramatic decrease of the desulfurization performance of $[\text{C}_6\text{PY}][\text{BF}_4]$ with a low water content in the IL [14]. The strong dependence of the desulfurization efficiency on the water concentration in solvents of $[\text{C}_4\text{MIM}][\text{DBP}]$, $[\text{C}_2\text{MIM}][\text{DEP}]$, $[\text{C}_1\text{MIM}][\text{DMP}]$ and $[\text{C}_2\text{DMAPY}][\text{N}(\text{CN})_2]$ was also reported [19,20,23]. For such ILs, the water content in the EDS systems should be strongly restricted which makes the process complex to deal with water and may greatly obstruct their practical applicability. It should be noted that only ILs of different hydrophilicity are covered in these studies and such dramatic effect of water on the desulfurization ability of these ILs was roughly explained by the hydrophilicity of IL and hydrophobicity of sulfur compounds. Although the effect of water on the EDS performance of hydrophobic ILs was scarcely considered, it has already been proved that even the most hydrophobic ILs can dissolve a certain amount of water [29,30]. This indicates, in the long run, that the water content in hydrophobic ILs can still increase because of the absorption of atmospheric moisture and the trace water in the fuel, which may also give rise to decrease in the EDS performance. If the water content increases to a certain amount, even multiphase systems can be formed and may lead to more complex effect on the EDS process.

Taking account of these facts, it is necessary to carefully consider the effect of water concentration in ILs (especially in the low range) when evaluating their suitability for an EDS process. Moreover, proper ILs that can present stable or even promoted EDS performance with water content in a certain range are highly desirable [18]. However, so far, studies on EDS mainly care about the extractive efficiency of ILs, e.g., the desulfurization ratio, extraction capacity and selectivity, whereas very few of them concern about the effect of water concentration.

In this contribution, the extraction capacity and selectivity of different IL/ H_2O mixtures for EDS were calculated by COSMO-RS. The EDS system is simulated with heptane and toluene as model fuel components and thiophene as the representative sulfur compound. These IL/ H_2O mixtures cover a broad range of water concentration and various IL characters, and thus the effect of water on the EDS performance of different ILs can be suggested. Afterwards, experiments with a representative IL $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ were carried out to verify the COSMO-RS predictions. Moreover, the viscosity of IL, the solvent-solute interactions and the COSMO-RS based analysis were combined to interpret the effect of water.

2. Method Description

2.1. COSMO-RS prediction and analysis

The Conductor-like Screening Model for Real Solvent (COSMO-RS) is a well-established and fully predictive thermodynamic model. A detailed description of the COSMO-RS model has already been given in literature [31,32] and only the major features for understanding the involved prediction and analysis are briefly provided.

In the COSMO-RS theory, the sigma (σ) profile is one of the most important molecule-specific properties. It 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, that is, the nonpolar region ($-1.0 \text{ e} \cdot \text{nm}^{-2} < \sigma < 1.0 \text{ e} \cdot \text{nm}^{-2}$), the hydrogen-bond donor region (HB-donor, $\sigma < -1.0 \text{ e} \cdot \text{nm}^{-2}$), and the hydrogen-bond acceptor region (HB-acceptor, $\sigma > 1.0 \text{ e} \cdot \text{nm}^{-2}$). A broader distribution and/or high peaks of σ -profile outside the nonpolar region usually indicate a higher polarity of the molecule. The properties of liquid or liquid mixtures can be calculated based on interacting molecular surfaces combining the σ -profile with the statistical thermodynamic treatment. 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, anions are strong HB acceptors but weaker donors, and cations can act as strong HB donors but weaker acceptors [30–32]. In this work, the COSMO-RS calculations are made using the COSMOthermX (Version C30_1401) with BP_TZVP_C30_1401 parameterization. All the σ -profiles of involved cations and anions of ILs, as well as conventional compounds are taken from the standard database of the software.

The molar-based solubility of an arbitrary solute i in any pure or mixed solvent (x_i) is calculated by

$$\lg(x_i) = (\mu_i^{\text{pure}} - \mu_i^{\text{sol}} - \Delta G_{i,\text{fusion}}) / RT \ln 10 \quad (1)$$

where μ_i^{pure} and μ_i^{sol} represent the chemical potential of solute i in the pure solute and in the solvent, respectively, and $\Delta G_{i,\text{fusion}}$ is the Gibbs free energy of fusion. The μ_i^{pure} and μ_i^{sol} can be directly calculated by COSMOthermX, and $\Delta G_{i,\text{fusion}}$ is zero for liquid solutes. The thus computed solubility is a zeroth order approximation ($x_i^{(0)}$), which is valid only for small concentrations of the solute. To improve the accuracy of prediction, x_i can be refined iteratively into the solubility calculation as expressed by

$$\lg(x_i^{(n+1)}) = (\mu_i^{\text{pure}} - \mu_i^{\text{sol}(n)} - \Delta G_{i,\text{fusion}}) / RT \ln 10 \quad (2)$$

This procedure can be repeated until the differences in the computed value of x_i are below a certain threshold. The solubility of the solute i in the solvent in mass ratio (w_i) can be automatically provided by COSMO-RS, which is converted as follows,

$$w_i = \frac{x_i \times M_i}{(1 - x_i) \times M_{\text{sol}}} \quad (3)$$

where M_i and M_{sol} are the molar weight of the solute and solvent, respectively. The extraction capacity of IL/ H_2O mixtures for thiophene was estimated by its mass-based solubility in the corresponding mixtures. The extraction selectivities (S_1 and S_2) of IL/ H_2O mixtures to thiophene are then calculated as Eqs. (4)–(5),

$$S_1 = \frac{w_{\text{thiophene}}}{w_{\text{heptane}}} \quad (4)$$

$$S_2 = \frac{w_{\text{thiophene}}}{w_{\text{toluene}}} \quad (5)$$

where S_1 and S_2 refer to the selectivity of ILs to thiophene against heptane and toluene respectively. The reliability of the predictions in this work can be validated by previous contributions, which demonstrate that COSMO-RS can provide a right qualitative trend and in many cases also quantitative description of liquid–liquid equilibria of hydrocarbons and ILs, and capacities of ILs for different solutes (including thiophene) [18,22,30,33]. For more details about COSMO-RS model for ILs, please see the website at https://www.scm.com/documentation/Tutorials/COSMO-RS/Ionic_Liquids/.

2.2. Experimental

Heptane, toluene and thiophene were purchased from Aladdin Chemical Co., Ltd. with purity above 99.0 wt%, and were used as received without further purification. The IL $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ was supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences with purity higher than 98.5 wt%, which was confirmed by ^1H -NMR with an AVANCE III 400 MHz digital spectrometer (Bruker, Germany). Before use, the IL was 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 IL was determined to be below $4000 \text{ mg} \cdot \text{kg}^{-1}$ with an AQV-300 Karl-Fischer volumetric titration (Hiranuma, Japan).

Model fuel with sulfur content of $500 \text{ mg} \cdot \text{kg}^{-1}$ was prepared by dissolving a certain amount of thiophene into the mixture of 80 wt% heptane and 20 wt% toluene. In a typical run, a specific mass ratio of water and IL were first added to a 25 ml screw-capped vial and mixed together. Then, a certain amount of model fuel was charged into the vial. After tightly sealed, the mixture was agitated with a magnetic stirrer for a certain time. The stirring speed was set to $800 \text{ r} \cdot \text{min}^{-1}$, at which complete dispersion of the biphasic system can be visually observed. After stirring, the mixture was left to settle for a certain time. During the experiments, the liquid temperature was controlled by an oil bath with a temperature fluctuation of $\pm 0.1^\circ \text{C}$ (Huber Ministat 230, Germany). All weighing involved was carried out in a Sartorius BSA224S-CW balance with a precision of $\pm 0.0001 \text{ g}$.

After settling, the upper desulfurized fuel phase was carefully removed from the lower aqueous IL phase first by an injection syringe and followed by a microsyringe, and the IL phase was again weighted by the mass balance. The sulfur content of the model fuel and desulfurized fuel was precisely determined by a sulfur analyzer (Antek 9000, USA). The specified measuring range of the sulfur analyzer is $20 \mu\text{g} \cdot \text{L}^{-1}$ –40%, and different calibration lines can be adopted at each small interval within the range to ensure the accuracy of analysis. For the sulfur content analysis in the work, the calibration lines of 1 – $10 \text{ mg} \cdot \text{L}^{-1}$, 10 – $100 \text{ mg} \cdot \text{L}^{-1}$, and 100 – $500 \text{ mg} \cdot \text{L}^{-1}$ were employed and the uncertainty of the determined sulfur content was estimated to be within $\pm 2\%$. The desulfurization capacity was estimated by the desulfurization ratio (D), which is defined as

$$D = \frac{C_i - C_f}{C_i} \times 100\% \quad (6)$$

where C_i is the initial sulfur content of model fuel and C_f is the final sulfur content of desulfurized fuel. The solubility of model fuel in the IL phase ($W_{\text{fuel-in-IL}}$) was determined to evaluate the effect of water on the extraction selectivity. Here, $W_{\text{fuel-in-IL}}$ in mass ratio ($\text{g} \cdot \text{g}^{-1}$) was gravimetrically determined as literature [14,23,24], and can be expressed as follows

$$W_{\text{fuel-in-IL}} = \frac{m_{\text{fuel}}^i - m_{\text{fuel}}^f}{m_{\text{IL}}} \quad (7)$$

where m_{fuel}^i and m_{fuel}^f represent the mass of the fuel phase before and after EDS respectively, and m_{IL} represents the mass of IL in the process. The errors of the determined $W_{\text{fuel-in-IL}}$ were estimated to be within $\pm 3\%$ due to the variance of the separation of the two phases.

In addition, another two aspects, i.e., the IL solubility and the water content in the desulfurized fuel were also analyzed in the experiments. The solubility of the IL in the desulfurized fuel was estimated by the

difference of the nitrogen content in the fuel phase before and after the EDS process, which can be precisely determined by a chemiluminescence nitrogen analyzer (Antek 9000, USA) with a specified measuring range of $20 \mu\text{g} \cdot \text{L}^{-1}$ –17%. For the analysis of the IL solubility in the fuel, the calibration line of 0.5 – $2.5 \text{ mg} \cdot \text{L}^{-1}$ was adopted and the estimated uncertainty for the determined nitrogen content was less than $\pm 2\%$. The water content in the desulfurized fuel was analyzed by Karl-Fischer volumetric titration with estimated deviations within $\pm 4\%$.

The other involved experimental details, i.e., the analyses of solvent-solute interactions and the viscosity of IL, the multistage extractions and regeneration of IL were provided in Supplementary Material, S1.

3. Results and Discussion

3.1. COSMO-RS predicted capacity and selectivity of IL/H₂O mixtures for EDS

As suggested by previous contributions, the effect of water on the desulfurization performance of IL may be closely related to the IL hydrophilicity [19,20]. Moreover, it has been demonstrated that the anion and the cation alkyl chain length of IL play a major role in determining its hydrophilicity [29,30]. Therefore, the effect of water concentration on the EDS performance of IL/H₂O mixtures in the cases of different anion characters and cation alkyl chain lengths was evaluated by COSMO-RS, respectively.

Firstly, eight [C₄MIM]-based ILs paired with the anions of [H₂PO₄][−], [HSO₄][−], [DEP][−], [DBP][−], [N(CN)₂][−], [BF₄][−], [PF₆][−], and [TF₂N][−] were selected, and the extraction capacity and selectivity of their mixtures with different concentrations of water for the model EDS system were calculated at 25°C . These anions range from strong hydrophilic ones ([H₂PO₄][−] and [HSO₄][−]) to high hydrophobic ones ([PF₆][−] and [TF₂N][−]), which can be demonstrated by their σ profiles in Fig. S1 and σ moments in Table S1 (Supplementary Material).

As illustrated in Fig. 1(a), in the case of ILs comprising moderate hydrophilic anions ([DEP][−], [DBP][−], [N(CN)₂][−], [BF₄][−]), a gradually decreasing tendency of their capacity for thiophene is observed with rising water concentration in the IL/H₂O mixtures. For instance, the capacity for thiophene remarkably declines from 0.673 of neat [C₄MIM][DBP] to 0.062 of [C₄MIM][DBP]/H₂O mixture with water concentration of 50 wt%. Such negative effect of water on the capacity of these ILs predicted by COSMO-RS agrees well with the available experimental studies on similar systems [14,19,20,23]. For ILs with strong hydrophobic anions ([PF₆][−] and [TF₂N][−]), the decreasing capacity with higher water concentration is also found. Especially for [C₄MIM][TF₂N], a sharp drop is witnessed from 0.501 of neat IL to 0.320 of IL/H₂O mixture with a low water concentration of only 2.6 wt%. These facts suggest

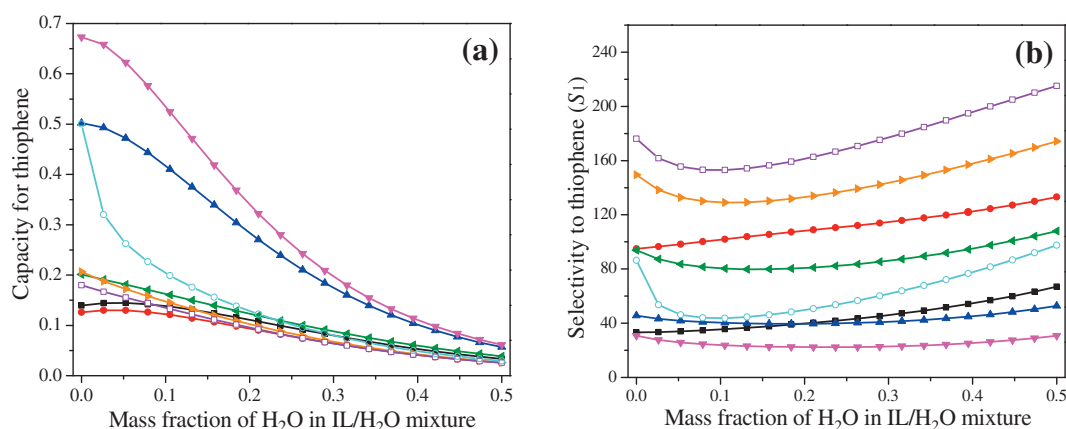


Fig. 1. COSMO-RS predicted capacity (a) and selectivity (b) for thiophene of different anion-based IL/H₂O mixtures as a function of the mass fraction of water in the mixture. (■) [C₄MIM][H₂PO₄]; (●) [C₄MIM][HSO₄]; (▲) [C₄MIM][DEP]; (▼) [C₄MIM][DBP]; (◆) [C₄MIM][N(CN)₂]; (▴) [C₄MIM][BF₄]; (□) [C₄MIM][PF₆]; (○) [C₄MIM][TF₂N].

that water is also dramatically unfavorable in the EDS systems based on hydrophobic ILs. On the contrary, for ILs based on strong hydrophilic anions $[\text{H}_2\text{PO}_4]^-$ or $[\text{HSO}_4]^-$, the capacity of IL/ H_2O mixtures slightly grows at first within a small water concentration range and then gradually decreases with further rising water concentration. For example, for $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$, the capacity slightly increases from 0.139 of neat IL to 0.144 with water concentration of 5.3 wt% in the IL/ H_2O mixture, and afterwards slowly decreases to 0.033 when increasing water concentration to 50 wt%. This observation is interesting since it indicates a certain concentration of water in EDS systems based on such ILs is acceptable and even favorable with respect to the extraction capacity.

The effect of water on the selectivity to thiophene of IL/ H_2O mixtures also depends on the anion character of IL to some extent (see Fig. 1(b)). For ILs with anions $[\text{H}_2\text{PO}_4]^-$ or $[\text{HSO}_4]^-$, the S_1 of their aqueous solutions almost increases linearly with higher water concentration. Such increasing tendency can be attributed to their stable capacity for thiophene and on the other side decreasing capacity for heptane. In the cases of ILs with other anions, the S_1 of the IL/ H_2O mixtures changes to different extents with varying water concentration, but generally it drops within a certain water concentration range and then grows with further increasing the water concentration. The S_2 of different IL/ H_2O mixtures is in a close range of [2.50, 4.60] with a similar dependency on the water content as that of S_1 (Fig. S2, Supplementary Material). Therefore, a certain concentration of water in EDS systems based on $[\text{H}_2\text{PO}_4]^-$ and $[\text{HSO}_4]^-$ is also beneficial from the selectivity point of view.

Combining both the capacity and selectivity, two distinct effects of water on the EDS performance of IL/ H_2O mixtures are observed in the cases of strong hydrophilic anions ($[\text{H}_2\text{PO}_4]^-$ and $[\text{HSO}_4]^-$) and moderate hydrophilic or hydrophobic anions (the other studied anions), respectively. Thus, $[\text{DEP}]^-$ and $[\text{H}_2\text{PO}_4]^-$ were selected as two representative anions and their combinations with $[\text{C}_n\text{MIM}]^+$ ($n = 1, 2, 4, 6, 8, 10$) were investigated to further evaluate the effect of water in the cases of ILs with different cation alkyl chain lengths.

As depicted in Fig. 2, for ILs based on the same anion (i.e., $[\text{DEP}]^-$ or $[\text{H}_2\text{PO}_4]^-$), similar dependencies of the capacity and selectivity of the IL/ H_2O mixtures on the water concentration was found, respectively, which is almost irrespective of the cation alkyl chain length. For instance, the capacity of $[\text{C}_n\text{MIM}][\text{DEP}]/\text{H}_2\text{O}$ mixtures ($n = 1, 2, 4, 6, 8, 10$) has a very close decreasing tendency with higher water concentration (see Fig. 2(a)). Moreover, their S_1 to thiophene nearly shares the same trend, i.e., it firstly decreases in a certain water concentration range and then increases with further rising water concentration (Fig. 2(c)). Although slight differences are observed for the trends of the capacity and S_1 of $[\text{C}_n\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ ($n = 1, 2, 4, 6, 8, 10$) mixtures, they also present similar dependencies on the water concentration, respectively. As seen in Fig. 2(b), except for $[\text{C}_1\text{MIM}][\text{H}_2\text{PO}_4]$, the capacity of all $[\text{C}_n\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ ($n = 2, 4, 6, 8, 10$) mixtures slightly increases within a small water concentration range and then gradually decreases with higher water concentration in the mixtures. Furthermore, the S_1 of all these IL/ H_2O mixtures increases with growing water concentration (see Fig. 2(d)). The S_2 of $[\text{C}_n\text{MIM}][\text{DEP}]/\text{H}_2\text{O}$ and $[\text{C}_n\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ mixtures ($n = 1, 2, 4, 6, 8, 10$) is also depicted in Fig. S3 (Supplementary Material), which almost shows the same tendencies as their S_1 with increasing the water concentration.

The above COSMO-RS predictions demonstrate that the effect of water on the EDS performance of IL/mixtures may vary with different anions of IL, but it is less dependent on the cation alkyl chain length.

3.2. Experimentally determined effect of water on EDS of IL/ H_2O mixtures

The COSMO-RS predicted negative effect of water on the EDS performance of ILs with moderate hydrophilic or hydrophobic anions ($[\text{DEP}]^-$, $[\text{DBP}]^-$, $[\text{N}(\text{CN})_2]^-$, $[\text{BF}_4]^-$) can be basically verified by the available experimental reports based on similar systems [14,19,20,23]. For instance, for $[\text{C}_2\text{EIM}][\text{DEP}]$, even a water concentration of 1 wt% in the IL can cause 17% decrease of its sulfur partition coefficient (K_N) for DBT;

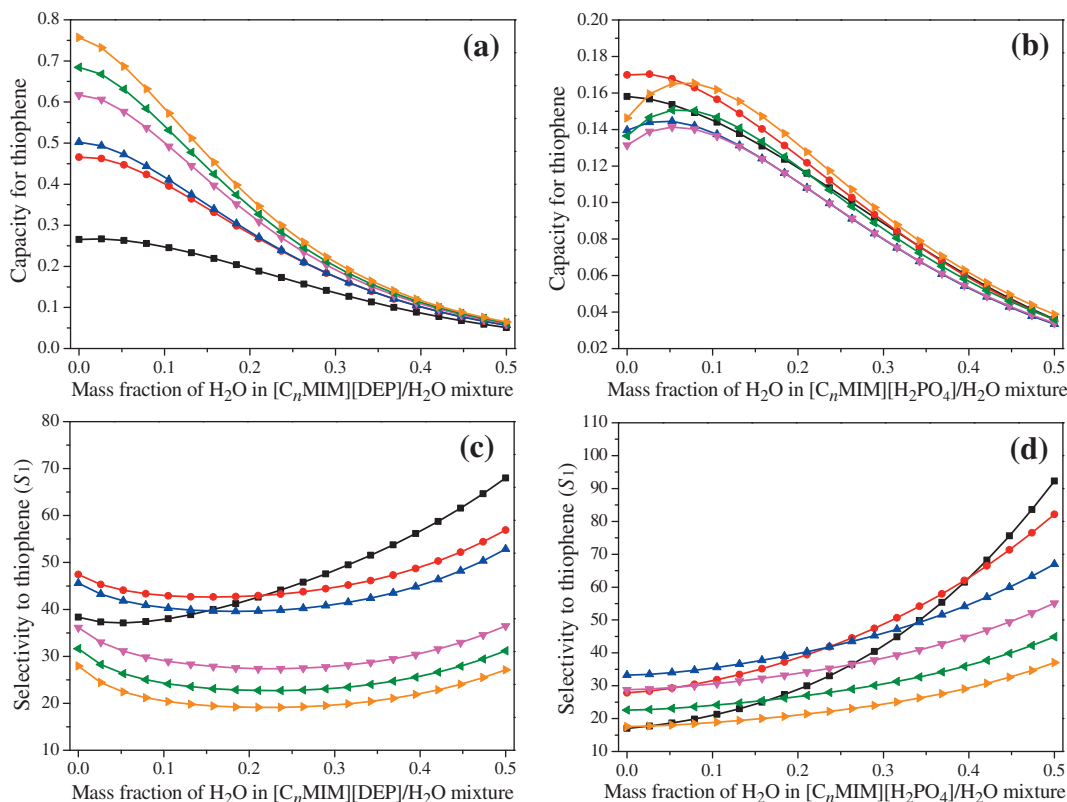


Fig. 2. COSMO-RS predicted capacity (a, b) and selectivity (c, d) for thiophene of different cation-based IL/ H_2O mixtures as a function of the mass fraction of water in the mixture. (■) $[\text{C}_1\text{MIM}]^+$; (●) $[\text{C}_2\text{MIM}]^+$; (▲) $[\text{C}_4\text{MIM}]^+$; (▼) $[\text{C}_6\text{MIM}]^+$; (◆) $[\text{C}_8\text{MIM}]^+$; (▶) $[\text{C}_{10}\text{MIM}]^+$.

and its K_N quickly approaches to 0 when the water content increases to 50 wt%, implying complete loss of its desulfurization ability [20]. Therefore, only the scarcely-reported effect of water on the EDS performance of ILs with strong hydrophilic anions (particularly the favorable effect of water in the low water concentration range) was experimentally investigated with $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ as a representative.

Before studying the effect of water concentration on the EDS performance of $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$, the temperature of 55 °C, IL/model fuel mass ratio of 1:1, stirring time of 1 h and settling time of 1 h were firstly determined as a set of optimized conditions for EDS with $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ (see Supplementary Material S2 and Fig. S4). The effect of water concentration on the desulfurization performance of $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ was then experimentally studied under the optimized conditions.

As seen in Fig. 3, the desulfurization ratio gradually increases from 31.7% for neat $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ to 36.4% for $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ mixture with water content of 7.5 wt%, and then keeps nearly unchanged when rising the water content to 10.0 wt% ($D = 36.6\%$). Such an increase confirms that a certain amount of water within the range of [0, 10 wt%] has a promoted effect on the desulfurization ratio. With further increasing the water concentration from 10.0 wt% to 50.0 wt%, a gradual decrease in the desulfurization ratio is observed, which demonstrates the negative effect of water content higher than 10.0 wt% on the sulfur removal efficiency. Nevertheless, it still keeps at higher than 26.6% with water concentration of 50.0 wt%, which indicates its relatively stable desulfurization performance. The favorable effect of water concentration in the low water concentration range [0, 10 wt%] qualitatively validates the COSMO-RS prediction that a certain amount of water is acceptable and favorable for the desulfurization capacity (see Fig. S5 for the COSMO-RS predictions at 55 °C for $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ mixtures, Supplementary Material).

With respect to $W_{\text{fuel-in-IL}}$, a certain amount of model fuel ($0.052 \text{ g}\cdot\text{g}^{-1}$) is dissolved in the IL phase for EDS with neat IL, which is mainly owing to the dissolution of toluene [27]. Interestingly, $W_{\text{fuel-in-IL}}$ slightly drops with the rising of water concentration in the IL phase in the range of [0, 20.0 wt%], and almost keeps constant at $0.041 \text{ g}\cdot\text{g}^{-1}$ with water content in the range of [20.0 wt%, 50.0 wt%]. The decrease in $W_{\text{fuel-in-IL}}$ agrees well with the increasing selectivity of IL/ H_2O mixture to thiophene that was predicted by COSMO-RS. Although such a decrease is not remarkable, it is very favorable and promising as it indicates less loss of fuel in the EDS process. Moreover, as also illustrated in Fig. 3, the nitrogen content in the desulfurized fuel keeps nearly unchanged in a close range of

$1.65 \text{ mg}\cdot\text{kg}^{-1}$ – $1.79 \text{ mg}\cdot\text{kg}^{-1}$, which indicates that the presence of water in the EDS system has negligible influence on the solubility of IL in the fuel phase. For the water content in the desulfurized fuel, it remains in the range of $269 \text{ mg}\cdot\text{kg}^{-1}$ – $292 \text{ mg}\cdot\text{kg}^{-1}$ and seems to be independent on the water concentration in the IL.

Taking all these four aspects into account, a certain amount of water in the IL (<10 wt%) can enhance the desulfurization ratio and decrease the loss of fuel in the EDS process without causing contamination to the fuel. Such an effect of water was again validated through two sets of multistage extractions using neat $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ or $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ mixture with water concentration of 10 wt%, respectively. The comparison of multistage experiment also demonstrates that the promoted effect of water is not dependent on the sulfur content in model fuel. Besides, the sulfur-loaded IL/ H_2O mixture can be effectively regenerated and reused with EDS performance as high as that of fresh IL, which suggests that water in the mixture has no negative effect on the stability and reusability of the IL (see S3 and Figs. S6–S8, Supplementary Material).

3.3. Analysis of the effect of water on the EDS performance

In literature, the negative effect of water on the desulfurization ability of these ILs was generally explained by the strong hydrophilicity of IL and hydrophobicity of sulfur compounds. Water can thus play as anti-solvent in the EDS systems to repel the sulfur compounds from the vicinity of IL molecules, giving rise to decreasing extraction performance [19,20]. However, considering the strong hydrophilicity of $[\text{H}_2\text{PO}_4]^-$ and the different dependency of the desulfurization efficiency of $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ on water content, the only explanation for the effect of water from the hydrophilicity of IL is insufficient. To clarify the effect of water more clearly, an interpretation from the viscosity of IL, the solvent–solute interactions and the COSMO-RS based analysis was proposed.

As seen in Fig. 4, the water concentration, especially in the region below 10 wt%, has a significant impact on the viscosity of $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$, which can be attributed to the weakened cation–anion interaction by water in aqueous IL [34,35]. For instance, the viscosity of neat $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ is $713.7 \text{ mm}^2\cdot\text{s}^{-1}$, while it sharply reduces to $53.2 \text{ mm}^2\cdot\text{s}^{-1}$ with water content of 10 wt% at 55 °C. Due to the remarkable decrease in viscosity, the cage-structures of $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]$ may be easily broke into much smaller clusters, resulting in more opportunity for the contact between the IL and sulfur compounds. Thus, it is favorable for the extraction performance to

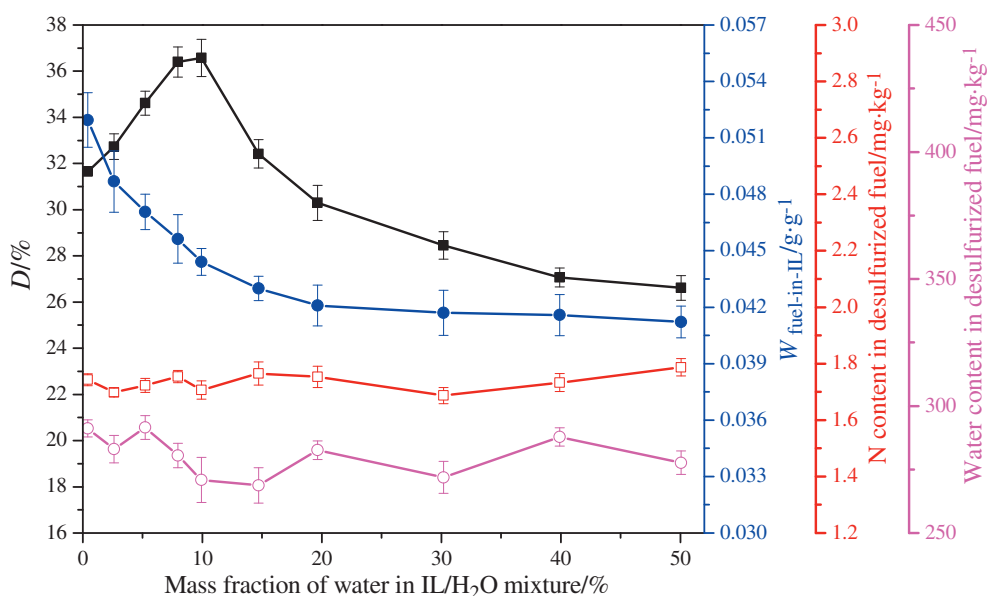


Fig. 3. Experimentally determined effect of water concentration in $[\text{C}_4\text{MIM}][\text{H}_2\text{PO}_4]/\text{H}_2\text{O}$ mixture on its EDS performance from four aspects. (■) D ; (●) $W_{\text{fuel-in-IL}}$; (□) N content in desulfurized fuel; (○) water content in desulfurized fuel.

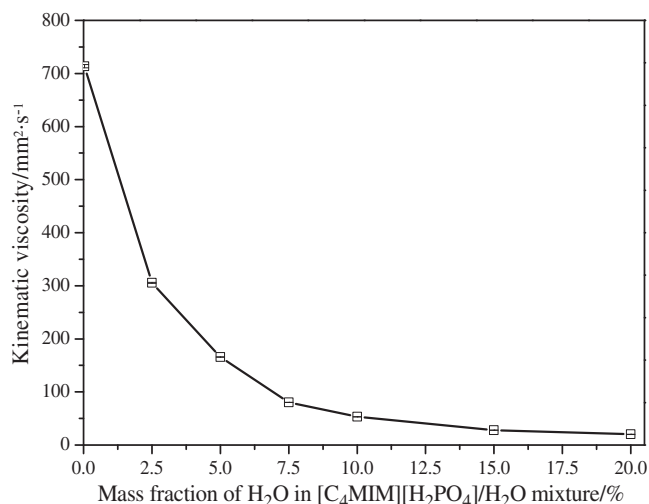


Fig. 4. Dependence of the kinematic viscosity of [C4MIM][H2PO4] on the water concentration.

introduce water to [C4MIM][H2PO4] in this respect. Nevertheless, with water content higher than 10 wt%, the decrease in viscosity is not remarkable. For the other ILs, such as [C2MIM][DEP] and [C6PY][BF4], adding water could also decrease their viscosity. But the dependency of viscosity on the water content for low-viscosity ILs is generally much weaker than that for high-viscosity ILs [34–36]. Since the viscosity of neat [C2MIM][DEP] (460 mPa·s at 21 °C) and [C6PY][BF4] (207.8 mm²·s⁻¹ at 20 °C) is much lower than [C4MIM][H2PO4] (5162.8 mm²·s⁻¹ at 25 °C, 713.7 mm²·s⁻¹ at 55 °C) [36], the rising in water content tends to have much weaker effect on their viscosity, suggesting less benefits to their extraction performance.

The effect of water concentration on the interactions between solvent or solvent mixture (in this case neat [C4MIM][H2PO4] or [C4MIM][H2PO4]/H2O mixture) and solute (in this case thiophene) was experimentally evaluated by UV–Vis spectroscopy. It should be noted that several experimental techniques, such as nuclear magnetic resonance (NMR) [37], Fourier transform infrared spectroscopy (FT-IR) [38] and ultraviolet–visible (UV–Vis) spectra [28,39] can be employed for this purpose. Here, the UV–Vis approach was selected as it can directly adopt the same aqueous IL solution as the reference blank, with no requirement of extra solvent to dilute the mixture for sample preparation. Thus, the UV–Vis approach appears to be more suitable for analyzing the effect of water concentration.

As seen in Fig. 5, a clear absorption band of thiophene can be observed in all solvents including heptane, neat IL and IL/H2O mixtures with different water concentration. Compared with the broad absorption peak of thiophene at 231.0 nm in heptane, its absorption band in the neat IL and in the aqueous IL solutions becomes narrow and shifts to 245.2 nm–250.0 nm (Table S2, Supplementary Material). All these facts verify the existence of interactions between the IL or IL/H2O mixture and thiophene [28, 39]. In the IL/H2O mixtures with water content below 10 wt%, the adsorption spectra of thiophene are very similar with slight difference in the red shift of the maximal adsorption. Especially, the adsorption peaks of thiophene in the aqueous IL solutions with water concentration of 5.0 wt%, 7.5 wt% and 10 wt% are at the same position (248.4 nm). It suggests that the solvent–thiophene interactions do not change significantly with water content less than 10 wt%. Similar conclusion was also drawn by the molecular dynamic simulation of desulfurization with aqueous IL systems [40]. Combined with the benefits of the greatly decreased viscosity, the promoted effect of water on the EDS performance of [C4MIM][H2PO4] with water content below 10 wt% can be thus interpreted.

With further rising in water concentration (higher than 10 wt%), the adsorption band of thiophene gradually increases and shifts leftwards, indicating the declining tendency of solvent–thiophene interaction in

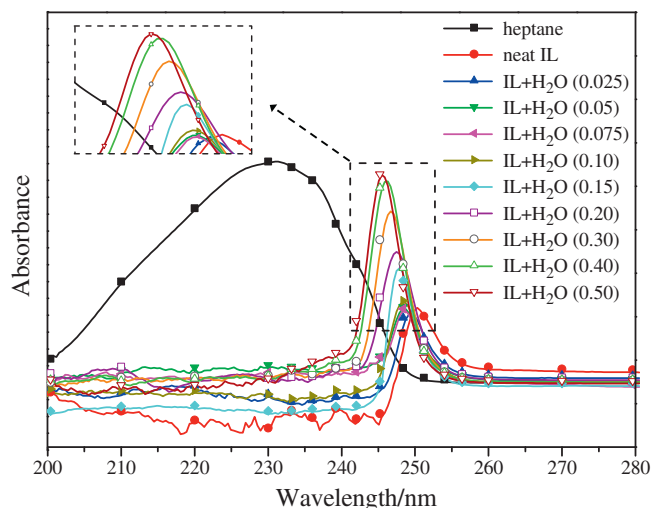


Fig. 5. UV–Vis spectra of thiophene in heptane, neat [C4MIM][H2PO4] and [C4MIM][H2PO4]/H2O mixtures of different water concentration.

the IL/H2O mixtures [39]. This can account for the depressed EDS performance for IL/H2O mixtures with water content from 10 wt% to 50 wt% considering the much less benefits from the decreased viscosity in this range. Nevertheless, in the IL/H2O mixtures with water concentration of 50 wt%, thiophene still presents a narrowed adsorption spectrum with an obvious shift to 245.2 nm. It demonstrates that strong solvent–thiophene interaction still exists, which contributes to the relatively stable extraction performance [28,39].

The other three aspects of EDS performance, i.e., the effect of water content on the solubility of fuel components in the IL phase, the solubility of IL and the water content in the desulfurized fuel phase were analyzed by the COSMO-RS theory. Fig. 6 presents the σ profiles of the IL (cation and anion) and the other compounds in the studied EDS system. As seen, water has a very broad σ -profile with two pronounced peaks around $-1.6 \text{ e} \cdot \text{nm}^{-2}$ and $+1.5 \text{ e} \cdot \text{nm}^{-2}$, which reflects its excellent ability to act as a donor as well as an acceptor for hydrogen-bond. Compared with water, the anion $[\text{H}_2\text{PO}_4]^-$ has even stronger hydrogen-bond donor and hydrogen-bond acceptor ability, which can also be indicated by its high HB-acc3 of 36.028 and HB-don3 of 4.973 from the quantitative point of view (correspondingly the HB-acc3 and HB-don3 of water is 5.693 and 3.851). Combining with the visible hydrogen-

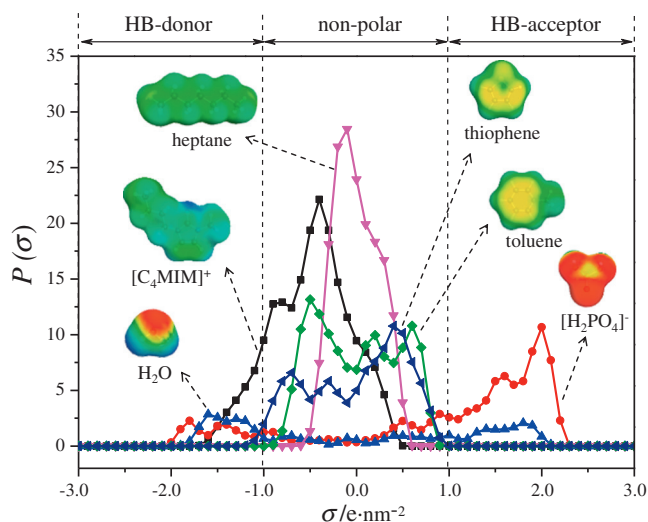


Fig. 6. σ -Profiles and COSMO-cavities of the cation and anion of [C4MIM][H2PO4], and the other compounds in the EDS system.

bond donor ability of the cation $[C_4MIM]^+$, the strong polarity and hydrophilicity of the IL $[C_4MIM][H_2PO_4]$ can be verified [30,31].

On the contrary, the σ profiles of the fuel components locate almost fully in the nonpolar region, indicating their strong hydrophobic character. Among them, heptane has the least polarity and the strongest hydrophobicity, which are reflected in the narrow distribution of its σ profile around $0\text{ e}\cdot\text{nm}^{-2}$. Accordingly, the hydrophobicity of the fuel components follows the ranking of heptane > toluene > thiophene. The ranking of their hydrophobicity can be quantitatively suggested by the activity coefficient of them in water (in natural logarithmic): heptane (13.17) > toluene (9.01) > thiophene (7.44) [31,32].

Due to the strong hydrophilicity of $[C_4MIM][H_2PO_4]$, the water and IL in the EDS process would favorably form an aqueous IL phase rather than dissolve in the strongly hydrophobic fuel phase. Therefore, the water content and the solubility of IL in the desulfurized fuel phase remains stable. On the other hand, as described by Jiang *et al.*, the water in the IL phase has repellent effect on the dissolution of hydrophobic fuel compounds [20]. In this case, the stronger repellent effect of water on heptane and toluene (particularly heptane) can account for the decreased solubility of fuel in the aqueous IL phase, which agrees reasonably with the tendencies of COSMO-RS predicted S_1 and S_2 (Figs. 1 and 2). While for thiophene, which is of very low content in the system and exists strong interactions with IL molecule, the effect of water is complex and may still contribute to a promoted sulfur removal efficiency [37,40].

4. Conclusions

The effect of water on the EDS performance of ILs was evaluated by COSMO-RS and experimental approach. The COSMO-RS predictions suggest that the effect of water on the EDS performance of ILs depends on the anion character to some extent while it is less dependent on the cation alkyl chain length, and indicate a favorable effect of water in the small concentration range for ILs with strong hydrophilic anions. In the experiments with a representative IL $[C_4MIM][H_2PO_4]$, the promoted desulfurization ratio, the decreased solubility of fuel in the IL, the unchanged solubility of the IL and water content in the desulfurized fuel were demonstrated with water concentration below 10 wt%, which basically verify the COSMO-RS predictions. Such an effect of water was reasonably interpreted from the viscosity of IL, solvent–solute interactions and COSMO-RS based polarity analysis. This work could provide a basis for studying the effect of water during the selection of ILs for EDS and other similar systems in future research.

Supplementary Material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.cjche.2016.08.029>.

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