RESEARCH ARTICLE

Study on extraction of thiophene from model gasoline with brønsted acidic ionic liquids

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Abstract Brønsted acidic ionic liquids (ILs), N-methylimidazole hydrogen sulfate ([HMIm]HSO$_4$) and N-methylpyrrolidone hydrogen sulfate ([HNMP]HSO$_4$), are synthesized and employed as extractants to extract thiophene from model gasoline (thiophene dissolved in n-octane). The effect of extraction temperature, extraction time and volume ratio of ILs to model gasoline on desulfurization rates is investigated. Then, the optimal desulfurization conditions are obtained: the ratio of ILs to model gasoline is 1:1, extraction temperature is 50°C for [HMIm]HSO$_4$ and 60°C for [HNMP]HSO$_4$, extraction time is 60 min. Meanwhile, the desulfurization rate of [HNMP]HSO$_4$ for model gasoline is 62.8%, which is higher than that of [HMIm]HSO$_4$ (55.5%) under optimal conditions. The reason is discussed on the basis of the interaction energy between thiophene and ILs at the B3LYP/6-311 ++ G(d,p) level. Furthermore, the total desulfurization rate of [HNMP]HSO$_4$ and [HMIm]HSO$_4$ reaches 96.4% and 94.4%, respectively, by multistage extraction. Finally, the used ILs can be reused by vacuum drying, and their desulfurization rates are not significantly decreased after recycling 7 times in single-stage desulfurization.

Keywords brønsted ionic liquids, model gasoline, thiophene, extraction, density functional theory

1 Introduction

In the past decade, deep desulfurization of fuel oils has attracted much attention with the development of the automobile industry worldwide because the combustion of sulfur compounds in gasoline and diesel fuel results in the emission of SO$_x$, which is a major cause of air pollution and acid rain. Thus, environmental legislations have been implemented to reduce the sulfur content in gasoline to less than 10 ppm by 2010 [1]. The conventional method of removal of sulfur compounds from fuel oils for industrial purposes is catalytic hydrodesulfurization (HDS). The HDS process is efficient to simple small molecular organic sulfides such as mercaptane, thioether, and so on. However, it is difficult to remove some aromatic sulfur compounds, such as thiophene and its derivatives. It also requires both high temperatures ($> 300°C$) and high pressures (> 4 MPa). Subsequently, non-hydrodesulfurization technology including adsorption [2], biodesulfurization [3], oxidation [4,5] and extractive desulfurization [6] sprang and developed.

Ionic liquids are organic salts with melting points around or below ambient temperature. Recently, more attention has been paid to ILs owing to their unique chemical and physical properties compared with conventional organic solvents, such as having negligible vapor pressure, high chemical and thermal stabilities, and excellent solubility [7]. ILs have been used as "green solvents" in a range of fundamental research and applications, including catalysis [8,9], synthesis [10,11], and separations [12,13]. Since 2001, Bösmann [14] reported the extractive desulfurization of diesel oil using a series of ILs for the first time; the extractive desulfurization process employing ILs has been extensively investigated [15–21]. The result shows that ILs have higher extraction rates and greater selectivity. All those studies mainly focus on fluorine-containing N-methylimidazole-based ILs or pyridinium-based ILs, Lewis acidic ILs and phosphate (sulfate) ester-based ILs [15–21]. In 2008, Liu [22] reported the extractive desulfurization of diesel oil using a series of brønsted acidic ILs. However, the chemical structures of brønsted acidic ILs are rather complex. As is well-known, effective ILs with lower costs for industrial application and higher extractive performance for extractive desulfurization process is essential.

In this paper, two brønsted acidic ILs, N-methy-

limidazole hydrogen sulfate ([HMIm]HSO$_4$) and *N*-methy-pyrrolidone hydrogen sulfate ([HNMP]HSO$_4$), which possess simple chemical structures and are synthesized in one step, are employed as extractants to extract thiophene from model gasoline, and the interaction energy between thiophene and ILs is calculated using the Gaussian 03 program.

2 Experimental section

2.1 Materials

N-methylimidazole (purity, ⩾ 98%) was purchased from the Zhejiang Linhai Kaile Chemical Plant and *N*-methypyrrolidone (analytical grade) was purchased from Tianjin Weichen Chemical Reagent Technology & Trade Co., Ltd. Sulfuric acid (purity, ⩾ 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. *n*-octane (chemical grade) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Thiophene (⩾ 99%) was purchased from Alfa Aesar.

2.2 Preparation of [HMIm]HSO$_4$ and [HNMP]HSO$_4$

The typical synthetic processes of [HMIm]HSO$_4$ are briefly described as follows. 1.0 mol *N*-methyl imidazole was weighed and dropped into a 250 mL three-neck flask, then 1.0 mol sulfuric acid was added dropwise into the 250 mL three-neck flask with a dropping funnel under magnetic stirring at room temperature, and a massive white smoke appeared in the instillment process. The mixture became a sticky light yellow transparent liquid after stirring at 80°C for 4 h. The resultant liquid ([HMIm]HSO$_4$) was washed three times with ether and ethyl acetate, respectively, then it was dried in vacuum to remove the ether and ethyl acetate. The typical synthetic process of [HNMP]HSO$_4$ was similar to that of [HMIm]HSO$_4$ mentioned above.

The structures of two ILs, as shown in Fig. 1, have been identified by FT-IR, and the FT-IR data are as follows. [HMIm]HSO$_4$: 3421.2 (s), 3141.4 (s), 2963.9 (m), 2870.7 (m), 2607.7 (m), 1624.4 (w), 1182.7 (s), 1022.1 (s), 869.2 (s), 581.6 (s). [HNMP]HSO$_4$: 3455.6 (m), 2951.2 (s), 1688.7 (s), 1494.4 (s), 1398.0 (w), 1310.4 (m), 1222.9 (s), 1165.0 (s), 1038.9 (m), 872.8 (s), 582.0 (s).
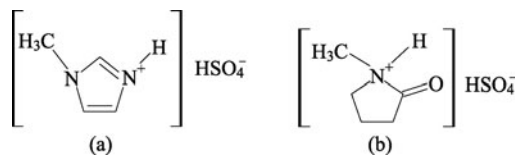

Fig. 1 Chemical structures of the brønsted acidic ILs: (a) *N*-methyl-imidazole hydrogen sulfate ([HMIm]HSO$_4$) and (b) *N*-methyl-pyrrolidone hydrogen sulfate ([HNMP]HSO$_4$)

2.3 Preparation of model gasoline

The model gasoline was composed of thiophene and *n*-octane. 0.6342 g thiophene was weighed accurately and added into a 250 mL volumetric flask, then *n*-octane was added into the above volumetric flask until the volume was determined to be at 250 mL. It showed that the concentration of thiophene was 2.5368 g/L in model gasoline.

2.4 Extractive desulfurization process

All of the extractive desulfurization experiments were conducted in a 20 mL stoppered test tube. ILs were added to the model gasoline and vibrated for a certain time at different temperatures to reach extraction equilibrium. Then they were settled for 5 min to obtain phase splitting.

2.5 Analysis of sulfur content

The upper phase (*n*-octane) was withdrawn and analyzed for sulfur content by a GC-flame ionization detector (GC-FID) and SE-54 capillary column (30 m×0.32 mm× 1.0 μm film thickness). Analysis conditions were as follows: injection port temperature, 180°C; detector temperature, 180°C; oven temperature, 80°C.

3 Results and discussion

3.1 Effects of different ILs and volume ratios of ILs to model gasoline on desulfurization rates

When the optimized extraction conditions were kept at a temperature of 50°C and extraction time of 60 min for [HMIm]HSO$_4$, and a temperature of 60°C and extraction time of 60 min for [HNMP]HSO$_4$, a series of experiments varied with volume ratios of ILs to model gasoline were carried out in order to investigate the effect volume ratios of ILs to model gasoline on the removal of thiophene, just as shown in Fig. 2.

First, we can observe that the general trend of desulfurization rates is decreased with the increments of the volume ratios of ILs to model gasoline. It should be pointed out that the desulfurization rates are significantly decreased with decreasing volume ratios of ILs to model gasoline ranging from 1:0.5 to 1:3, then decrease indistinctly when decreasing volume ratios of ILs to model gasoline from 1:3 to 1:5. The main reason for these phenomena is probably that ILs and model gasoline cannot mix sufficiently, which results in the decrease of desulfurization rates.

Second, it should be also noted that the desulfurization rates of [HNMP]HSO$_4$ are higher than those of [HMIm]HSO$_4$ at the conditions of the same volume ratios of ILs to model gasoline. This indicates that the extraction capacity of [HNMP]HSO$_4$ is higher than that of [HMIm]HSO$_4$. The
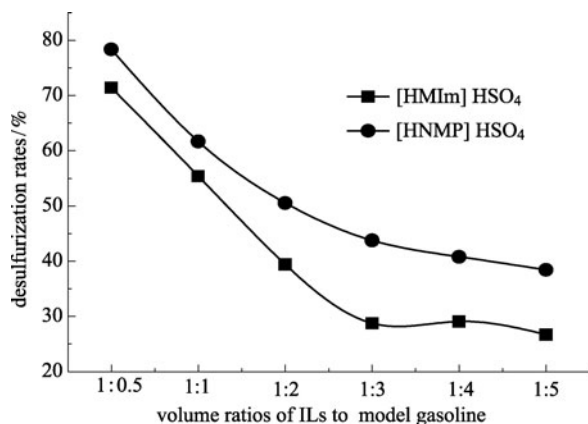
Fig. 2 Effects of volume ratios of ILs to model gasoline on desulfurization rates at the optimized conditions for [HMIm]HSO$_4$: extraction temperature, 50°C; extraction time, 60 min; [HNMP] HSO$_4$: temperature 60°C; extraction time, 60 min

result is ascribed to the difference in the cation characteristics of both ILs, which results in the different extractive mechanisms. The mechanism of the extraction of aromatic sulfur compounds for imidazole-based ILs can be explained as a possible π-π interaction between aromatic sulfur compounds and the imidazole rings of ILs. Meanwhile, the formation of liquid clathrate is due to the interaction between the ionic liquids and aromatics through π-π interaction, which has been expatiated by Holbrey [23] in 2003. However, the N-methylpyrrolidone molecule

contains a pyrrolidone active group with an electron acceptor function, and the thiophene is an electron donor molecule according to the $4n + 2$ rule, therefore, the mechanism of the extraction of aromatic sulfur compounds for [HNMP]HSO$_4$ can be explained as the formation of charge transfer complexes (CTC) between the electron acceptor (pyrrolidone) and π-donors (thiophene) [24,25].

Furthermore, we investigated the fundamental nature of the interaction between thiophene and ILs [HMIm]HSO$_4$ and [HNMP]HSO$_4$ using the Gaussian 03 program at the B3LYP/6–311 ++ G(d,p) level. The optimized structures of thiophene, [HMIm]$^+$, and [HNMP]$^+$, are shown in Fig. 3. It can be observed that the thiophene molecule has a symmetric structure and all atoms are in the same plane, then this shows that the thiophene molecule possesses an aromatic structure. Meanwhile, the [HMIm]$^+$ cation with a plane five-membered ring structure shows aromatic characterization, and the [HNMP]$^+$ cation has a three-dimensional structure. It indicates that the interaction ability of thiophene and [HMIm]$^+$ is different from the one of thiophene and [HNMP]$^+$. Then, we investigate the interaction energy of T-[HMIm]$^+$ and T-[HNMP]$^+$ (T = thiophene), shown in Figs. 4(a) and (b), respectively. The optimized structure of T-[HMIm]$^+$ in Fig. 4(a) shows that the thiophene is located beside the aromatic ring of the [HMIm]$^+$ cation, furthermore, its aromatic ring is perpendicular to the aromatic ring of the [HMIm]$^+$ cation, which is correspondent with the literature [26]. Otherwise, as for the T-[HNMP]$^+$ complex in Fig. 4(b), thiophene is located
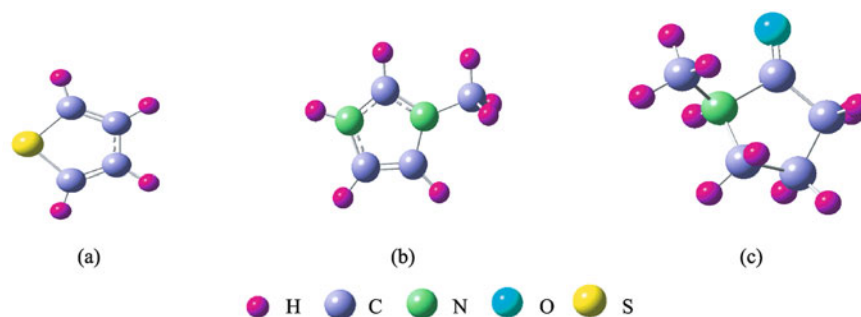

Fig. 3 Optimized structures of thiophene (a), [HMIm]$^+$ (b) and [HNMP]$^+$ (c)
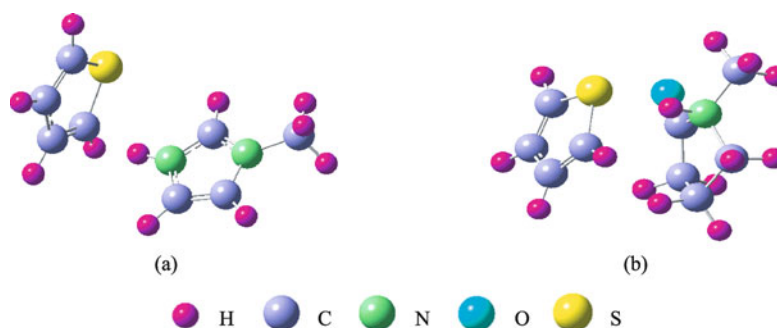

Fig. 4 Optimized structures of T-[HMIm]$^+$ (a) and T-[HNMP]$^+$ (b)

beside the ring of the [HNMP]$^+$ cation as well, but its aromatic ring is parallel to the ring of the cation.

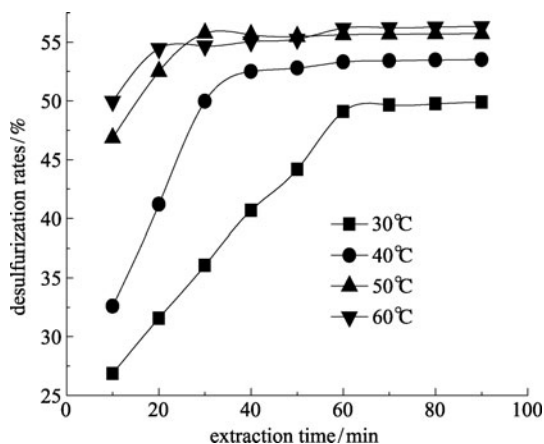**Fig. 5** Effects of extraction time and temperature on the desulfurization rates of [HMIm]HSO$_4$ when the volume ratio of IL to model gasoline is 1:1

Then, the interaction energies between thiophene and the cation of ILs are calculated according to the Eq. (1) [26].

$$\Delta E = E_{\text{T-cation}} - (E_{\text{T}} + E_{\text{cation}}), \qquad (1)$$

where E_{T} and E_{cation} are the individual energies of thiophene and cations ([HMIm]$^+$ or [HNMP]$^+$). $E_{\text{T-cation}}$ is the energy of T-[HMIm]$^+$ or T-[HNMP]$^+$, and we should point out that all of them are calculated by the Gaussian 03 program mentioned above. ΔE denotes the interaction energy between thiophene and the cation of ILs. On the basis of the optimized structures of thiophene and cations in Figs. 3 and 4, the calculated interaction energy of T-[HMIm]$^+$ is 38.86 kJ/mol, which is lower than that (42.24 kJ/mol) of T-[HNMP]$^+$. This indicates that the interaction force between thiophene and [HNMP]HSO$_4$ is larger than that of thiophene and [HMIm]HSO$_4$. The result is consistent with the experiment results shown in Fig. 2. It indicates that the extraction capacity of [HNMP]HSO$_4$ is higher than that of [HMIm]HSO$_4$ at the same volume ratios of ILs to model gasoline.

3.2 Influences of extraction time and temperature on the desulfurization rates

Figures 5 and 6 show the effects of extraction time and temperature on desulfurization rates of [HMIm]HSO$_4$ and [HNMP]HSO$_4$ at different temperatures from 30°C to 70°C, respectively. It can be observed that extraction temperature and time have a strong influence on desulfurization rates of [HMIm]HSO$_4$ and [HNMP] HSO$_4$. First of all, we can observe that the desulfurization rates of both ILs increase with the increment of extraction temperature, obviously. As for this phenomenon, the

reason seems to be that when the extraction temperature increases, the viscosity of ILs is reduced, thus, the mobility of ILs increases. Therefore, the desulfurization rates of ILs increase with the increment of extraction temperature owing to the good mixing of ILs and the oil phase under the vibrating conditions. It also can be seen that the desulfurization rates of the two ILs change slightly until the temperature is high enough. The reason is that the extraction capacity of ILs is up to saturation. Finally, the appropriate extraction temperatures and extraction times for both ILs are selected as extraction temperature, 50°C, extraction time, 60 min for [HMIm] HSO$_4$ and extraction temperature, 60°C, extraction time, 60 min for [HNMP] HSO$_4$, when we take into account the desulfurization rates and operating costs.
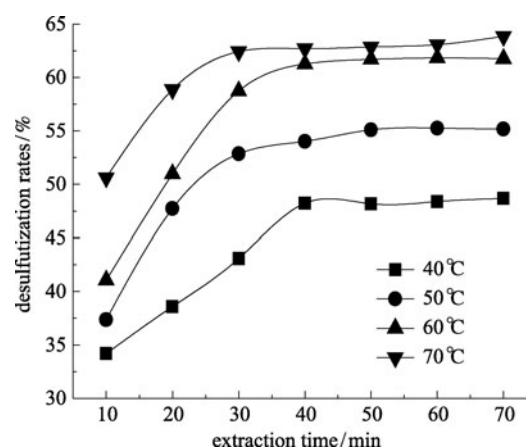

Fig. 6 Effects of extraction time and temperature on the desulfurization rates with [HNMP]HSO$_4$ when the volume ratio of IL to model gasoline is 1:1

3.3 Deep desulfurization properties of two ILs

To study the deep desulfurization properties of ILs, the desulfurization performance during the multi-stage extraction of two ILs are studied in Fig. 7. The first extraction process is carried out by taking equivalent volume model gasoline and IL and vibrating 60 min under the optimized extraction temperature 50°C for [HMIm] HSO$_4$ and 60°C for [HNMP] HSO$_4$. Then, the second extraction performance is investigated by adding fresh ionic liquids with equivalent volume into model gasoline, which are separated from the first extraction. As shown in Fig. 7, the sulfur contents of model gasoline have already been reduced to 0.1408 g/L for [HMIm]HSO$_4$ and 0.0916 g/L for [HNMP]HSO$_4$ after the fifth extraction, and the total percentage of desulfurization of [HMIm]HSO$_4$ and [HNMP]HSO$_4$ is 94.4% and 96.4%, respectively. We also find that the desulfurization rates do not have significant increment after the fifth extraction. Maybe, by then it has reached the extraction limit of ILs in the desulfurization of model gasoline.
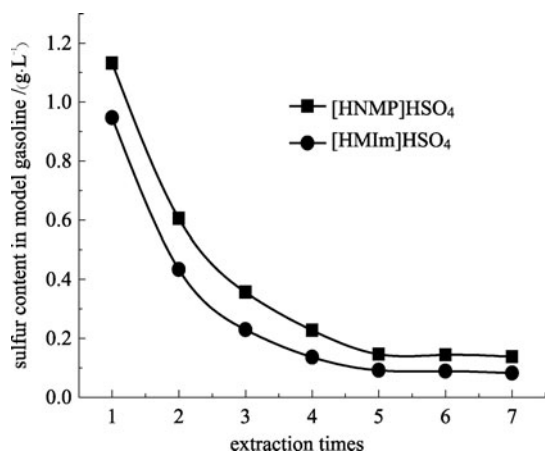
Fig. 7 Deep desulfurization properties of ILs

3.4 Regeneration and recycling property of two ILs

The regeneration and recycling of ILs are important for the industrial application of ILs-extraction. Removal of sulfur compounds from an IL can be performed by three methods: heating the IL to remove the sulfur compounds [15], re-extraction of sulfur compounds with the low-boiling hydrocarbons pentane or hexane [16], and precipitating the sulfur compounds through a water dilution process [17,19]. In this work, the regeneration of ILs is obtained by heating the ILs to remove thiophene. The used ionic liquids are dried under vacuum at 60°C for 2 h. As shown in Fig. 8, it can be seen that ILs just have a slight loss of extraction capability after being utilized over 7 times.
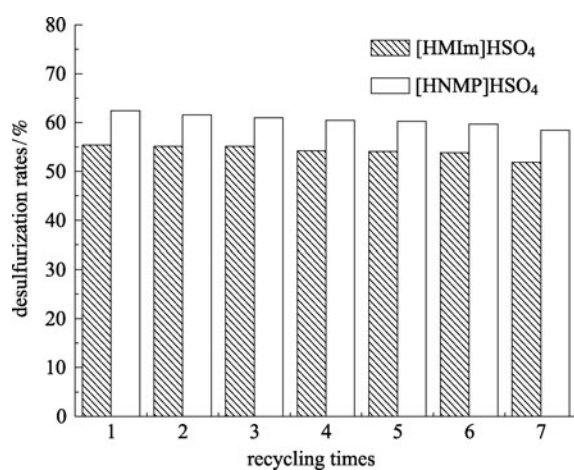

Fig. 8 Recycling of two ILs

4 Conclusions

1) The optimal desulfurization conditions of [HNMP]HSO$_4$ and [HMIm]HSO$_4$ have been obtained: the extraction temperature is 60°C and 50°C, respectively, extraction time is 60 min, and volume ratio of ILs to model gasoline is 1:1.

2) The effect of volume ratios of ILs to model gasoline on desulfurization rates shows that the extraction performance of [HNMP]HSO$_4$ is better than that of [HMIm] HSO$_4$. Furthermore, the result can be confirmed by the fact that the interaction energy for T-[HMIm]$^+$ (38.86 kJ/mol) is lower than that of T-[HNMP]$^+$ (42.24 kJ/mol), obtained using the Gaussian 03 program.

3) The desulfurization performances of two ILs during multi-stage extraction indicate that the extraction performance of [HNMP]HSO$_4$ is better than that of [HMIm] HSO$_4$. Furthermore, the total desulfurization rate of [HNMP]HSO$_4$ and [HMIm]HSO$_4$ reaches 96.4% and 94.4% by five extraction stages, respectively.

4) The used ionic liquids are dried for regeneration under vacuum at 60°C for 2 h, and the two ILs just have a slight loss of extraction capability after being utilized over 7 times.

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