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Extraction process of sulfur compounds from fuels with protic ionic liquids

Zhuo Li, [a,b] **Jinggang Xu,*** [a] **Dan Li,** [c] **Changping Li,*** [c]

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Sulfur compounds in fuels are hazardous to the environment and have a great challenge. In this study, series of protic ionic liquids (PILs) were designed, such as N,N-dimethyl-N-cyanoethyl ammonium butyrate($[DMAPN]^+[Bu]^-$), N,N-dimethyl-N-cyanoethyl ammonium propionate($[DMAPN]^+[Pr]^-$), N,N-dimethyl-N-cyanoethyl ammonium acetate($[DMAPN]^+[Ac]^-$), N,N-dimethyl-N-cyanoethyl ammonium formate($[DMAPN]^+[Fo]^-$), N,N-dimethyl-N-(2-(2-hydroxyethoxy))ammonium propionate($[DMEE]^+[Pr]^-$), N,N-dimethyl-N-hydroxyethyl ammonium propionate ($[DMEA]^+[Pr]^-$), N,N-dimethyl-N-hydroxyethyl ammonium acetate($[DMEA]^+[Ac]^-$), N,N-dimethyl-N-hydroxyethyl ammonium formate($[DMEA]^+[Fo]^-$), N,N-dimethyl -N-butyl ammonium acetate($[DMBA]^+[Ac]^-$), N-methyl-N-hydroxyethyl ammonium propionate ($[MEA]^+[Pr]^-$), N-methyl-N-hydroxyethyl ammonium acetate ($[MEA]^+[Ac]^-$). And their extraction desulfurization capability was evaluated. Through the selection, two PILs were chosen to optimize the desulfurization process. Results showed that benzothiophene (BT) and thiophene (T) can be removed by PILs effectively. Both cations and anions have influence on extraction efficiencies. However, cations have greater influence on the desulfurization process. In optimal conditions, extraction efficiency can be more than 80% with one cycle. After 6～8 cycles, the removal efficiency could reach up to 99.5%. It is worth noting that PILs could be recycled by simple vacuum distillation. After 4 times of recycling, the desulfurization efficiency change slightly. Finally, mechanism study shows that hydrogen bonding interaction between the sulfur atom and the active hydrogen of PILs accounts for the high desulfurization efficiency. This green process would provide a new route for extraction desulfurization of fuels.

1.Introduction

In recent years, with the increase of motor vehicles, automobile exhausts especially sulfur content in fuels, has become a major source of air pollution. Acid rain resulting from the automobile exhaust has become more and more serious, which not only causes damage to buildings and soils, but also hazardous to the environment. [1,2] Therefore, most countries put forward the strict regulations on the sulfur emission. According to the Directive of the European Union, the total sulfur contents in gasoline or diesel fuels in Europe should not exceed 10 ppm after 2010. [3] So, considerable attention has been given to deep desulfurization of fuels to eliminate its hazardous influence on the environment. [4] Hydrodesulfurization(HDS) is a conventional 'gold' method widely adopted for the removal of sulfur contents in petroleum refineries. [5] In HDS process, sulfur compounds can react with hydrogen and be converted into hydrogen sulfide or corresponding hydrocarbons. Although HDS is efficient in removing mercaptans, sulfides, and sulfur from fuels, it is less effective for the removal of sulfur containing compounds with larger steric hidrance, such as thiophene and its derivatives. [6,7] The harsh operating conditions and high costs of HDS hinders its application in the deep removal of thiophene based sulfur contents. Another disadvantage of HDS is the easy olefin saturation and the notable decrease of octane number of gasoline after treatment.[8] Therefore, non-hydrodesulfurization technology has attracted great attention. Some new desulfurization process have been developed in recent years, such as oxidative process, [9,10] adsorption, [11,12] biological process, [13,14] extraction, [15,16] and oxidation coupling with extraction, [17,18] etc.

Extraction desulfurization process is based on the principle of organic sulfides and hydrocarbons have different solubility in the solvent. However, traditional extractants applied for desulfurization process are volatile organic solvents, which pollute the environment seriously because of their strong volatile and high toxic properties. Therefore, the development of the new green and efficient extractants can be of great importance to remove sulfur compounds from fuels effectively.

Ionic liquids (ILs) are usually composed of ions completely with melting point less than 100 ℃. [19,20] Compared with traditional organic solvents, it has unique properties such as high thermal and chemical stability, negligible vapor pressure, high ionic conductivity, non-flammability and a tunable solvation capacity. [21-25] With the above special properties, the loss of ILs resulting from the distillation and dissolution in other phase during desulfurization process can be avoided. As ILs have good extraction capability for aromatic sulfur compounds, and do not dissolve in fuels. So extraction desulfurization based on ILs has become a hot topic in recent years. [26-30] However, the high cost and high viscosity of commonly used imidazolium based ILs hinders its application in desulfurization process.

Amine based protic ionic liquids (PILs) is a new type of ones, which can be designed according to our own demand through proton exchange between BrØnsted acid and BrØnsted base. [31] PILs not only have excellent physical and chemical properties of traditional ionic liquids, it also has its own unique properties, such as cheap raw materials, simple synthesis process, wide range of viscosity (10 mPa.s～650 mPa.s), simple recycling process with vacuum distillation. Most important, PILs are mainly composed of non-toxic, biodegradable materials. Therefore, PILs exhibit special environmentally friendly and biocompatible properties compared with traditional ILs. [31-35] In our previous research, two PILs namely $[DMEE]^+[Pr]^-$ and $[DMAPN]^+[Pr]^-$ were attempted for removing DBT from fuels. And higher desulfurization efficiency was got. [36]

With the above preliminary research, more systematical research is exerted for the removal of organic sulfur from fuels. In this study, series of amine based PILs were designed and synthesized, such as $[DMAPN]^+[Bu]^-$, $[DMAPN]^+[Pr]^-$, $[DMAPN]^+[Ac]^-$, $[DMAPN]^+[Fo]^-$, $[DMEE]^+[Pr]^-$, $[DMEA]^+[Pr]^-$, $[DMEA]^+[Ac]^-$, $[DMEA]^+[Fo]^-$, $[DMBA]^+[Ac]^-$, $[MEA]^+[Pr]^-$, $[MEA]^+[Ac]^-$, which contains cyano group, hydroxyl group and ether group. And their extraction capability for benzothiophene (BT) and thiophene (T) in fuels was also probed. Some factors that affect desulfurization efficiency were investigated, such as the type of PILs, extraction time, rotation speed, PILs dosage, initial sulfur concentration, etc. to determine the optimal conditions for desulfurization process. And the recycling of PILs was realized successfully. Finally, extraction mechanisms were also studied systematically with quantitative ^1H NMR and FT-IR.

2. Experimentals

2.1 Preparation of PILs

Synthesis process was carried out under an inert atmosphere (N_2). Raw materials were purified before use. Amine was placed in a 250 mL round-bottomed flask equipped with a stirrer and cooled using an ice bath for 30 min. Acid was added dropwise using a dropping funnel. Care must be taken to keep the reaction mixture cool because the reaction is very exothermic. After the addition was completed, the mixture was stirred for 24 h. After this period, PILs were removed from the reaction flask and stored under N_2 until use for further experiments. Synthesis process of $[DMAPN]^+[Pr]^-$ was taken as an example of synthesis process. 3-Dimethylaminopropionitrile (49.08 g, 0.5 mol) was placed in a 250 mL round-bottomed flask equipped with a stirrer and cooled using an ice bath for 30 min. Propionic acid (37.04 g, 0.5 mol) was added dropwise using a dropping funnel. After the addition was completed, the mixture was stirred for 24 h. Then $[DMAPN]^+[Pr]^-$ can be got. The structures of PILs are shown in Fig.1. The purity of ILs was confirmed using ^1H NMR, which was listed in Fig.S1 of supporting information. $[DMAPN]^+[Pr]^-$: ^1H NMR ($CDCl_3$) δ 11.55 (m, 1H); δ 2.77 (t, 2H); δ 2.60 (dd, 2H); δ 2.36 (s, 6H); δ 2.31 (q, 2H); δ 1.12 (t, 3H).

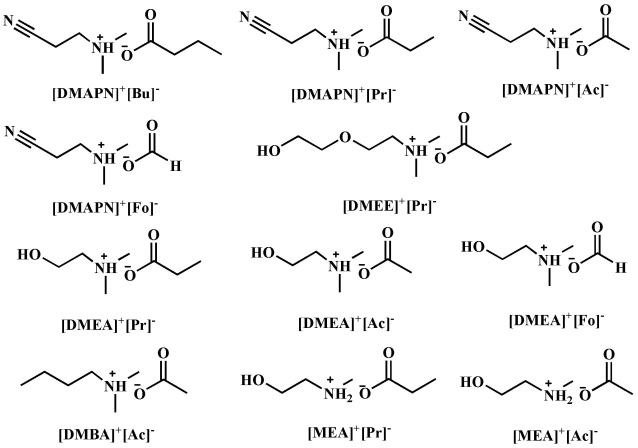

Fig.1 Structures of PILs

2.2 Extraction process

BT or T was dissolved in n-octane as model oil. The sulfur content of the model oil was 1600 ppm. Extraction process was performed in the self-made devices at 25 ℃. The reactants contained 1 g of IL and 1 g of model oil. The mixture was stirred at room temperature for 30 min except as otherwise defined. The ratio of reactants was adjusted according to the different conditions. All experiments in this study were carried out in duplicate to determine its reproducibility, and the experimental errors were within 3%.

2.3 Analytical methods

The sulfur content of the model oil was measured by the gas chromatograph(GC). The chromatogram conditions are listed as follows: chromatogram column, HP-5; injection volume, 0.6 μL; carrier gas (N_2), 210 mL/min; H_2, 35 mL/min; air, 350 mL/min; flux, 1.6 mL/min, at constant flow mode; inlet temperature, 300 ℃; detector temperature, 300 ℃; and column temperature(BT), heating from 120 ℃ to 150 ℃ with 15 ℃/min increase, 150 ℃ to 160 ℃ with 2 ℃/min increase, 160 ℃ to 250 ℃ with 25 ℃/min increase; column temperature(T), heating from 60 ℃, stay 2 min, to 100 ℃ with 10 ℃/min increase, 100 ℃ to 250 ℃ with 25 ℃/min increase. The concentration of T and BT were measured with an internal standard method, using hexadecane as the internal standard solvent. The concentration of hexadecane was 2000 ppm. The analysis of the standard curve is shown in Fig.S2 and Fig.S3 of the Supporting Information. The correlation coefficient achieved 0.99992 and 0.99993.

3.Results and disccussions

3.1 Selection of PILs

The designable property makes the diversity of PILs. So the proper chosen of PILs is very important for the desulfurization process. The selection of PILs was shown in Fig. 2. From the results, the structures of cations and anions both influence the desulfurization process. However, cations have greater influence on the desulfurization process. The extraction sequence for cations are listed as follow: $[DMAPN]^+[Pr]^-$ > $[DMEE]^+[Pr]^-$ >

$[DMEA]^+[Pr]^-$ > $[MEA]^+[Pr]^-$, while for anions: $[DMAPN]^+[Bu]^-$ > $[DMAPN]^+[Pr]^-$ > $[DMAPN]^+[Ac]^-$ > $[DMAPN]^+[Fo]^-$. Among all the PILs, $[DMAPN]^+[Bu]^-$ gets the highest extraction desulfurization efficiency, and the extraction efficiency can reach up to 62.5% for BT and 59.9% for T. Taken all factors into account, $[DMAPN]^+[Pr]^-$ and $[DMEA]^+[Pr]^-$ were chosen as the representative of PILs to optimize the extraction desulfurization process.

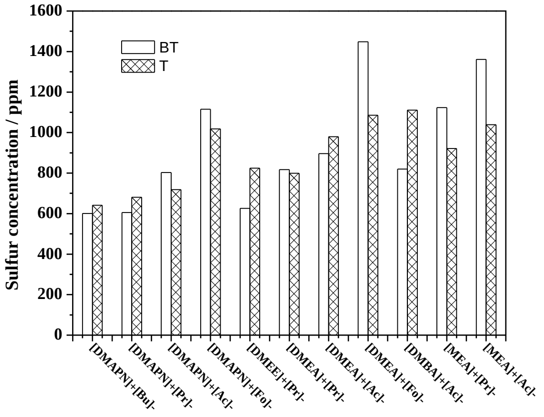

Fig.2 Effect of PILs types on extraction efficiency

3.2 Optimization of the extraction parameters

To optimize the desulfurization process, some factors influencing extraction, such as effect of extraction time, rotation speed, phase ratio and initial concentration, were investigated.

Fig. 3 shows the effect of extraction time on extraction efficiency. The sulfur content in fuels was reduced tremendously with the increase of time at the very beginning. However, after 10 min, extraction equilibrium can be reached. The lower viscosity of PILs would probably account for this fast equilibrium. This shorter extraction equilirium time is very beneficial for its future industrial applications. However, 30 min was chosen as extraction time in the following study to guarantee a sufficient equilibrium.

Effect of rotation speed was another factor to affect extraction process, which was shown in Fig. 4. The result indicates that the rotation speed has no influence on extraction desulfurization efficiency. The main reason for this is that the low viscosity of the two PILs is beneficial for the mass transfer during the extraction process. As the mass transfer can be very important for energy consumption, it will promote the application of ILs. In this research, 800 rpm was selected in the following experiments.

During the extraction process, the concentration gradient is the driving force for extraction. Therefore, ionic liquids dosage is an important factor. The result was shown in Fig. 5. From the result, larger ionic liquids dosage would be favorable for the desulfurization process. When the phase ratio of $[DMAPN]^+[Pr]^-$ to fuels reaches 4:1, the extraction efficiency can achieve 88.5% for BT and 84.7% for T. When the phase ratio of $[DMEA]^+[Pr]^-$ to fuels comes to 4:1, the extraction efficiency can achieve 81.9% for BT and 77.4% for T. Its extraction efficiency is much higher than the traditional ionic liquids. Considering economic efficiency, the mass ratio of PILs to fuels was chosen as 1:1 in the following experiments.

Initial concentration of sulfur compounds is also a factor that influences partition coefficients of sulfur. The result was shown in Fig. 6. It can be seen that the partition coefficients increase and then decrease with the increase of the initial sulfur concentration. And extraction efficiencies by $[DMAPN]^+[Pr]^-$ are higher than that of $[DMEA]^+[Pr]^-$. All factors taken into account, 1600 ppm is chosen as the initial concentration of fuels.

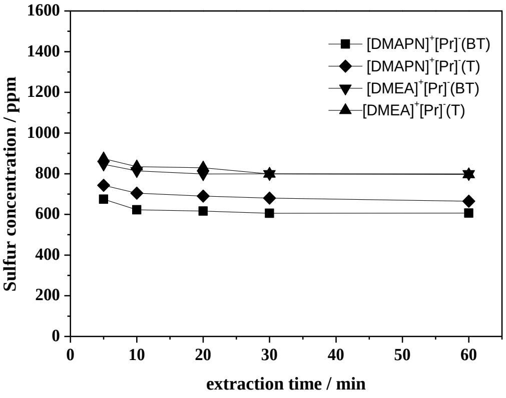

Fig.3 Effect of extraction time on extraction efficiency

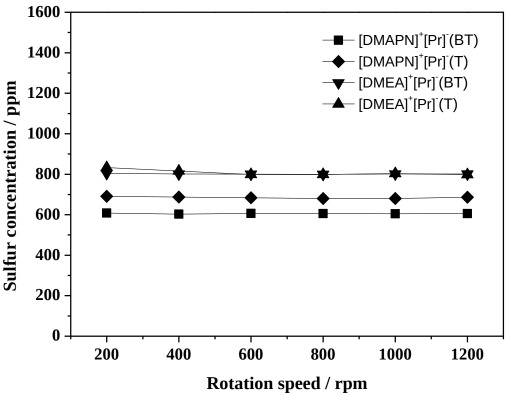

Fig.4 Effect of rotation speed on extraction efficiency

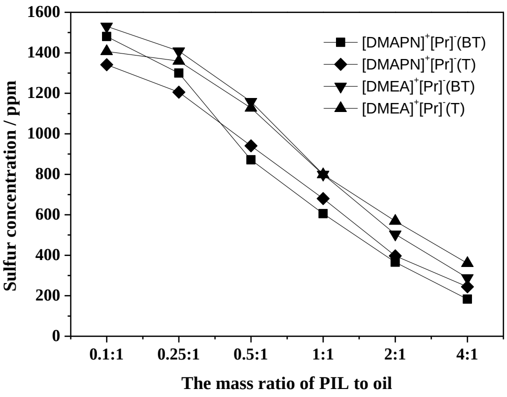

Fig.5 Effect of mass ratio on extraction efficiency

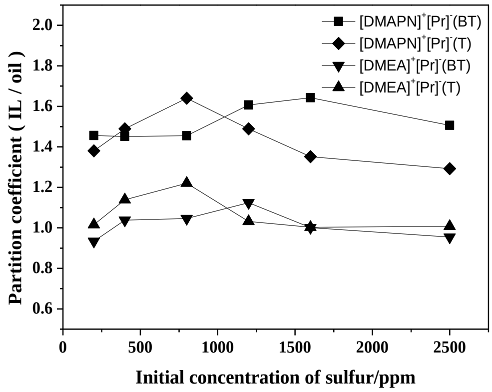

Fig.6 Effect of initial concentration of sulfur on extraction efficiency

3.3 Extraction with multiple times

Efficient desulfurization was got with one cycle; however, deep desulfurization is always our goal. The sulfur content in fuels should be less than 10 ppm to meet the Euro V standards. To achieve the deep desulfurization process, multiple extraction cycles were investigated, which was shown in Fig. 7. After 6～8 extraction cycles, deep desulfurization was realized with extraction efficiency more than 99.5%. The sulfur content of fuels can be reduced below 7.8 ppm, which cannot be achieved only by the extraction process with traditional ILs.

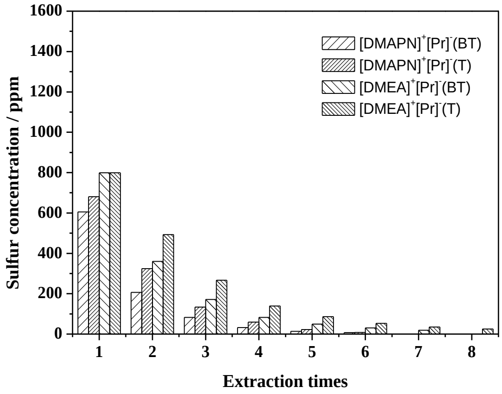

Fig.7 Multiple extraction times on desulfurization efficiency

3.4 Repeated use and recycling of used PILs

To see if PILs have become saturated, repeated use of the used PILs for extraction desulfurization was done. From Fig. 8, PILs became saturated and its extraction capability was lost after five times of repeated use. So the recycling and reuse of PILs can be of great necessity from both economic and environmental aspects. In our specific case, the used PILs, namely, [DMAPN]$^+$[Pr]$^-$ and [DMEA]$^+$[Pr]$^-$, both have lower boiling points. This results in the new recycling methods by vacuum distillation. Then the recycled PILs will be used for further extraction process listed in Fig. 9. It can be found that the extraction efficiencies are very stable after four times of recycling. So it is very significant for its future industrial application for the facile recycling of PILs. Furthermore, the structure of PILs do not change as shown in Fig.10. From the above study, the PILs can be recycled and reused easily and efficiently.

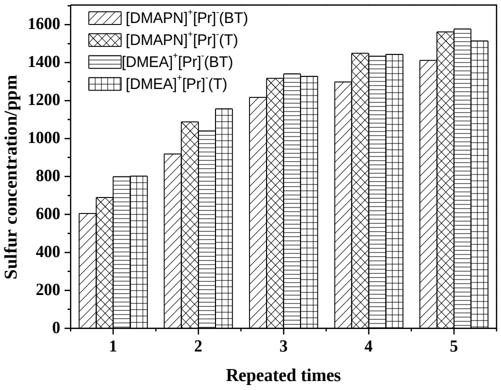

Fig.8 Effect of repeated use of PILs

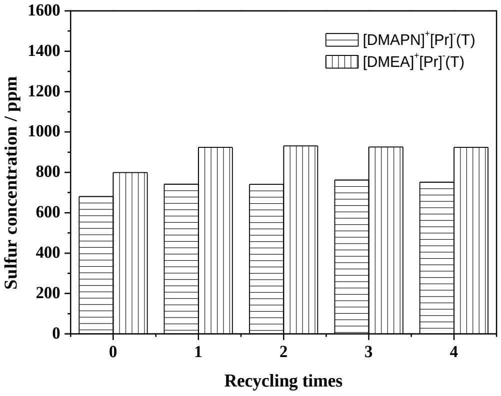

Fig.9 Extraction performance with recycled PILs

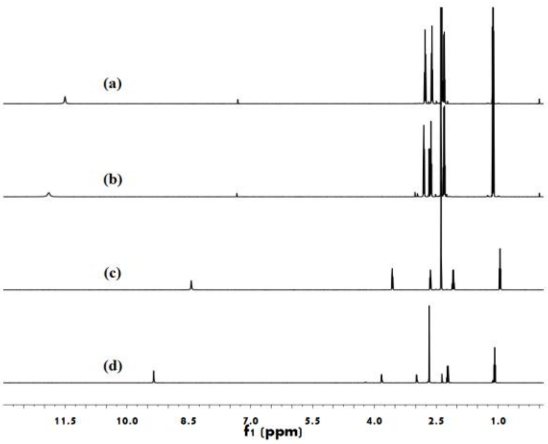

Fig.10 ^{1}H NMR of pure and recycled PILs

(a) Pure [DMAPN]$^+$[Pr]$^-$ (b) Recycled [DMAPN]$^+$[Pr]$^-$
(c) Pure [DMEA]$^+$[Pr]$^-$ (d) Recycled [DMEA]$^+$[Pr]$^-$

3.5 Extraction mechanisms

Although the extraction mechanism is always challengeable, it is very important for revealment of the extraction process. So quantitative ^{1}H NMR and FT-IR were used for the mechanism studies, which was shown in Fig.11 and Fig.12. In this part, [DMAPN]$^+$[Pr]$^-$ was taken as an example to probe the extraction mechanisms systematically. Fig. 11 shows the ^{1}H NMR results of different molar ratio between [DMAPN]$^+$[Pr]$^-$ and thiophene (T). It can be seen that the hydrogen bonding interaction between the active hydrogen of PIL and sulfur atom of T. This hydrogen bonding interaction will result in the reinforcement of sulfur atom's electron withdrawing ability for α-H and β-H in the ring of T, which will lead to the decrease of the T ring electron density and its corresponding hydrogen nucleus electron density. And the vibrating magnetic field strength decrease and chemical shift value increase. With the increase of T, the phase ratio of PIL/T from 1:0.1 to 1:1, the hydrogen atoms such as α-H (7.2981 ppm) and β-H (7.0920 ppm) both move to the lower field intensity obviously, namely (7.3606 ppm, 7.3472 ppm, 7.3286 ppm) for α-H and (7.1284 ppm, 7.1230 ppm, 7.1080 ppm) for β-H, respectively. At the same time, with the increase of thiophene ratio, the active hydrogen of [DMAPN]$^+$[Pr]$^-$ also shifts to the higher field. From the above analysis, the driven force of the extraction process would probably be the hydrogen bonding interaction.

To confirm the hydrogen bonding interaction mechanism, characterization with FT-IR was also carried out, which was shown in Fig.12. Hydrogen bond affects the C-S-C stretching vibration of thiophene to a certain extent.[37] So, C-S-C stretching vibration is taken as a probe. It is observed at wavenumbers between 1000 cm^{-1} and 1100 cm^{-1}. Seen from Fig.12, the C-S-C vibration of pure thiophene is observed at 1079 cm^{-1}, which shifts to 1076 cm^{-1} for T:[DMAPN]$^+$[Pr]$^-$ (1:1 and 0.5:1) and 1075 cm^{-1} for 0.1:1. This phenomenon results from the formation of the hydrogen bond between [DMAPN]$^+$[Pr]$^-$ and thiophene. Therefore, it can be concluded that the hydrogen bond formed between active hydrogen of PIL and sulfur atom of thiophene accounts for the higher extraction efficiency.

As for the ^{1}H NMR results of different molar ratio between [DMAPN]$^+$[Pr]$^-$ to BT, it can referred to Fig.S4 in supporting information. The same trends can also be obtained. So it can be safely drawn the conclusion that hydrogen bond is the main driven force for this specific extraction desulfurization process.

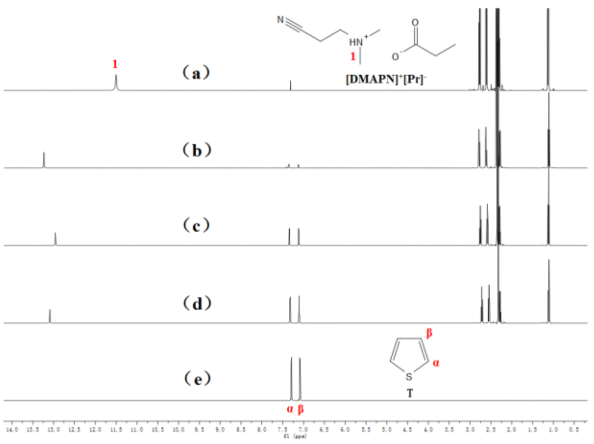

Fig.11 ^{1}H NMR of different molar ratio ([DMAPN]$^+$[Pr]$^-$/T)

(a) 1:0 (b) 1:0.1 (c) 1:0.5 (d) 1:1 (e) 0:1

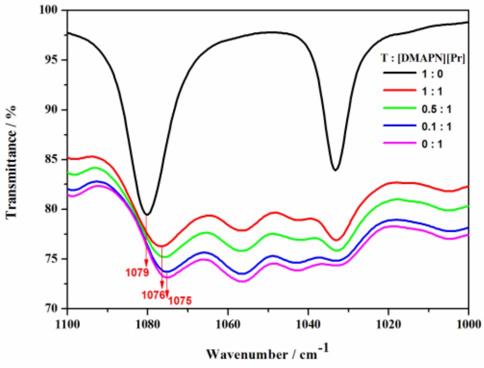

Fig.12 FT-IR of different molar ratio (T/[DMAPN]$^+$[Pr]$^-$)

(a) 1:0 (b) 1:1 (c) 0.5:1 (d) 0.1:1 (e) 0:1

4. Conclusions

Series of protic ionic liquids were designed and synthesized. And their extraction desulfurization capability was estimated. Through the selection, two typical PILs were chosen as typical ones to optimize the extraction desulfurization process. Results show that BT and T can be removed by PILs effectively. Both cations and anions have influence on extraction. However, cations have greater influence on the desulfurization process. The sequence is: [DMAPN]$^+$[Pr]$^-$ > [DMEE]$^+$[Pr]$^-$ > [DMEA]$^+$[Pr]$^-$ > [MEA]$^+$[Pr]$^-$, while for anions: [DMAPN]$^+$[Bu]$^-$ > [DMAPN]$^+$[Pr]$^-$ > [DMAPN]$^+$[Ac]$^-$ > [DMAPN]$^+$[Fo]$^-$. Moreover, the extraction process was optimized. In optimal conditions, extraction efficiency can be more than 80% with only one cycle. After 6～8 cycles, the sulfur content of fuel can be decreased blow 7.8 ppm and the removal efficiency could reach up to 99.5%. Deep desulfurization process can be realized successfully. It is worth mentioning that PILs could be recycled by simple vacuum distillation successfully, which can be of great significance for the recycling of the used ILs in the industrialization process. After 4 times of recycling, the desulfurization efficiency of PILs changed slightly. Finally, through the systematically research on extraction mechanism, hydrogen bonds formed between the sulfur atom of BT/T and the active hydrogen of PILs accounts for the high desulfurization efficiency. This novel green process would provide a new route for extraction desulfurization of fuels. Further research on this work is still going on in our laboratory.

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Notes and references

[a] *College of Resources and Environment, Northeast Agricultural University, Harbin, China*
E-mail:jinggangxu@126.com
[b] *School of Science, Dalian Ocean University, Dalian, China*
[c] *Department of Chemical Engineering, Dalian University, Dalian, China*
E-mail: changpingli@dicp.ac.cn

* To whom correspondence should be addressed

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