RSC Advances

PAPER



Cite this: RSC Adv., 2015, 5, 15892

Received 11th December 2014 Accepted 21st January 2015

DOI: 10.1039/c4ra16186f

www.rsc.org/advances

1. Introduction

In recent years, with the increase of motor vehicles, automobile exhausts and especially the sulfur content in fuels have become a major source of air pollution. Acid rain resulting from automobile exhausts has become a more and more serious problem, which not only causes damage to buildings and soils, but is also hazardous to the environment.^{1,2} Therefore, most countries put forward strict regulations on sulfur emission. According to the Directive of the European Union, the total sulfur content in gasoline or diesel fuels in Europe should not exceed 10 ppm after 2010.³ So, considerable attention has been given to the deep desulfurization of fuels to eliminate their 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 the HDS process,

Extraction process of sulfur compounds from fuels with protic ionic liquids[†]

Zhuo Li,^{ab} Jinggang Xu,^{*a} Dan Li^c and Changping Li^{*c}

Sulfur compounds in fuels are hazardous to the environment and present a great challenge. In this study, a series of protic ionic liquids (PILs) was designed, such as N,N-dimethyl-N-cyanoethyl ammonium butyrate ([DMAPN]⁺[Bu]⁻), N,N-dimethyl-N-cyanoethyl ammonium propionate ([DMAPN]⁺[Pr]⁻), N,N-dimethyl-Ncyanoethyl 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,Ndimethyl-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]⁻), and N-methyl-N-hydroxyethyl ammonium acetate ([MEA]⁺[Ac]⁻), and their extraction desulfurization capability was evaluated. Through selection, two PILs were chosen to optimize the desulfurization process. The results showed that benzothiophene (BT) and thiophene (T) can be removed using PILs effectively. Both cations and anions have an influence on the extraction efficiencies. However, cations have a greater influence on the desulfurization process. Under optimal conditions, the extraction efficiency can be higher than 80% for one cycle. After 6-8 cycles, the removal efficiency could reach up to 99.5%. It is worth noting that the PILs could be recycled via simple vacuum distillation. After 4 times of recycling, the desulfurization efficiency changed slightly. Finally, a mechanistic study shows that hydrogen bonding interactions between the sulfur atom and active hydrogen of the PILs account for the high desulfurization efficiency. This green process would provide a new route for the extraction desulfurization of fuels.

> sulfur compounds can react with hydrogen and be converted into hydrogen sulfide and the 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 a larger steric hindrance, such as thiophene and its derivatives.^{6,7} The harsh operating conditions and high costs of HDS hinder its application in the deep removal of thiophene-based sulfur contents. Another disadvantage of HDS is the easy olefin saturation and the notable decrease in the octane number of gasoline after treatment.⁸ Therefore, non-hydrodesulfurization technologies have attracted great attention. Some new desulfurization processes have been developed in recent years, such as oxidative,^{9,10} adsorption,^{11,12} biological,^{13,14} extraction,^{15,16} and oxidative coupling with extraction processes,^{17,18} etc.

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



View Article Online

View Journal | View Issue

^eCollege of Resources and Environment, Northeast Agricultural University, Harbin, China. E-mail: jinggangxu@126.com

^bSchool of Science, Dalian Ocean University, Dalian, China

^cDepartment of Chemical Engineering, Dalian University, Dalian, China. E-mail: changpingli@dicp.ac.cn

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra16186f

Paper

Ionic liquids (ILs) are usually composed completely of ions with melting points lower than 100 °C.^{19,20} Compared with traditional organic solvents, they have unique properties such as high thermal and chemical stabilities, a 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 distillation and dissolution in other phases during the desulfurization process can be avoided, as ILs have a good extraction capability for aromatic sulfur compounds, and do not dissolve in fuels. So, the extraction desulfurization based on ILs has become a hot topic in recent years.^{26–30} However, the high costs and high viscosities of commonly used imidazolium based ILs hinder their application in the desulfurization process.

Amine based protic ionic liquids (PILs) are a new type of ILs, which can be designed according to our own demand through proton exchange between Brønsted acid and Brønsted base.³¹ PILs not only have the excellent physical and chemical properties of traditional ionic liquids, they also have their own unique properties, such as cheap raw materials, a simple synthesis process, wide range of viscosities (10–650 mPa s), and a simple recycling process with vacuum distillation. Most importantly, 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 probed for removing DBT from fuels, and a higher desulfurization efficiency was achieved.³⁶

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

2. Experimental

2.1 Preparation of PILs

The synthesis process was carried out under an inert atmosphere (N_2). Raw materials were purified before use. The 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, the PILs were removed from the reaction flask and stored under N_2 until use for further experiments. The synthesis process of $[DMAPN]^+[Pr]^-$ was taken as an example for describing the 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, $[DMAPN]^+[Pr]^-$ was obtained. The structures of the PILs are shown in Fig. 1. The purity of the ILs was confirmed using 1H NMR spectroscopy, which is listed in Fig. S1 of the ESI.† $[DMAPN]^+[Pr]^-: ^1H NMR (CDCl_3) \delta 11.55 (m, 1H); \delta 2.77 (t, 2H); \delta 2.60 (dd, 2H); \delta 2.36 (s, 6H); \delta 2.31 (q, 2H); \delta 1.12 ppm (t, 3H).$

2.2 Extraction process

BT or T was dissolved in *n*-octane as a model oil. The sulfur content of the model oil was 1600 ppm. The extraction process was performed in the self-made devices at 25 °C. 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 μ L; carrier gas (N₂), 210 mL min⁻¹; H₂, 35 mL min⁻¹; air, 350 mL min⁻¹; flux, 1.6 mL min⁻¹, at constant flow mode; inlet temperature, 300 °C; detector temperature, 300 °C; and column temperature (BT), heating from 120 °C to 150 °C with 15 °C min⁻¹ increase, 150 °C to 160 °C with 2 °C min⁻¹ increase, 160 °C to 250 °C with 25 °C min⁻¹ increase; column temperature (T), heating from 60 °C, stay 2 min, to 100 °C with 10 °C min⁻¹ increase, 100 °C to 250 °C with 25 °C min⁻¹ increase. The concentration of T and BT were measured with an internal



Fig. 1 Structures of the PILs.

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 S3 of the ESI.† The correlation coefficients achieved were 0.99992 and 0.99993.

3. Results and discussions

3.1 Selection of PILs

The designable nature of the structuresmakes a diversity of PILs possible. So, the proper choice of PIL is very important for the desulfurization process. The selection of PILs is shown in Fig. 2. As derived from the results, the structures of the cations and anions both influence the desulfurization process. However, the cations have a greater influence on the desulfurization process. The extraction sequence for the cations is listed as follows: $[DMAPN]^+[Pr]^- > [DMEE]^+[Pr]^- > [DMAPN]^+[Pr]^- > [DMAPN]^+[Pr]^- > [DMAPN]^+[Pr]^- > [DMAPN]^+[Ac]^- > [DMAPN]^+[Fo]^-. Among all PILs, [DMAPN]^+[Bu]^- has the highest extraction desulfurization efficiency, and the extraction efficiency can reach up to 62.5% for BT and 59.9% for T. Taking all factors into account, <math>[DMAPN]^+[Pr]^-$ and $[DMEA]^+[Pr]^-$ were chosen as representative PILs to optimize the extraction desulfurization process.

3.2 Optimization of the extraction parameters

To optimize the desulfurization process, some factors influencing the 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 the extraction efficiency. The sulfur content in fuels was reduced tremendously with the increase in time at the very beginning. However, after 10 min, the extraction equilibrium could be reached. The lower viscosity of the PILs probably accounts for this fast equilibrium. The shorter extraction equilibrium time is very beneficial for future industrial applications. However, 30 min was chosen as the extraction time in the following study to guarantee a sufficient equilibrium.

The effect of rotation speed was another factor to affect the extraction process, which is shown in Fig. 4. The result indicates





that the rotation speed has no influence on the 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 the energy consumption, it will promote the application of ILs. In this research, 800 rpm was selected for the following experiments.

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

The initial concentration of the sulfur compounds is also a factor that influences the partition coefficients of sulfur. The result is shown in Fig. 6. It can be seen that the partition coefficients increase and then decrease with the increase in initial



Fig. 2 Effect of PIL types on the extraction efficiency.



Fig. 4 Effect of rotation speed on the extraction efficiency.



Fig. 5 Effect of mass ratio on the extraction efficiency.

sulfur concentration, and the extraction efficiencies of $[DMAPN]^+[Pr]^-$ are higher than those of $[DMEA]^+[Pr]^-$. All factors taken into account, 1600 ppm was chosen as the initial concentration of sulfur in the fuels.

3.3 Multiple extraction cycles

Efficient desulfurization was achieved within 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 deep desulfurization, multiple extraction cycles were conducted and investigated, which is shown in Fig. 7. After 6–8 extraction cycles, deep desulfurization was realized with an extraction efficiency of more than 99.5%. The sulfur content of fuels can be reduced below 7.8 ppm, which cannot be achieved solely by the extraction process with traditional ILs.

3.4 Repeated use and recycling of used PILs

To see if the PILs have become saturated, repeated use of the used PILs for the extraction desulfurization was investigated. As shown in Fig. 8, the PILs became saturated and their extraction capability was lost after five repeated uses. So, the recycling and reuse of PILs can be of great necessity from both economic and



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



Fig. 7 Effect of multiple extraction cycles on desulfurization efficiency.

environmental aspects. In our specific case, the used PILs, namely [DMAPN]⁺[Pr]⁻ and [DMEA]⁺[Pr]⁻, both have lower boiling points. This results in the development of a new recycling method by vacuum distillation. Then, the recycled PILs were used in a further extraction process, as shown in Fig. 9. It can be found that the extraction efficiencies are very stable after four times of recycling. So, this result is very significant for future industrial applications and the facile recycling of PILs. Furthermore, the structures of the PILs do not change, as shown in Fig. 10. As can be seen from the above study, the PILs can be recycled and reused easily and efficiently.

3.5 Extraction mechanisms

Although the extraction mechanism is always challengeable, it is very important for understanding the extraction process. So, quantitative ¹H NMR and FT-IR spectroscopy were used for mechanistic studies, and the spectra are shown in Fig. 11 and 12. In this part, [DMAPN]⁺[Pr]⁻ was taken as an example to systematically probe the extraction mechanisms. Fig. 11 shows the ¹H NMR results of different molar ratios between [DMAPN]⁺[Pr]⁻ and thiophene (T). It can be seen that hydrogen bonding interactions exist between the active hydrogen of the PIL and the sulfur atom of T. These hydrogen bonding



Fig. 8 Effect of repeated use of PILs



Fig. 9 Extraction performance of recycled PILs.



Fig. 10 1 H NMR spectra of pure and recycled PILs. (a) Pure [DMAPN]^{+}[Pr]^{-}. (b) Recycled [DMAPN]^{+}[Pr]^{-}. (c) Pure [DMEA]^{+}[Pr]^{-}. (d) Recycled [DMEA]^{+}[Pr]^{-}.



140 15.5 15.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 4.5 8.0 7.5 7.0 4.5 6.0 5.5 5.0 4.5 4.0 5.5 5.0 2.5 2.0 1.5 1.0 0.5 f: (grad)

Fig. 11 1 H NMR of different molar ratios ([DMAPN]⁺[Pr]⁻/T). (a) 1 : 0 (b) 1 : 0.1 (c) 1 : 0.5 (d) 1 : 1 (e) 0 : 1.

interactions will result in the reinforcement of the sulfur atom's electron withdrawing ability for the α -H and β -H in the ring of T, which will lead to a decrease in the T ring electron density and



Fig. 12 FT-IR of different molar ratios (T/[DMAPN]⁺[Pr]⁻). (a) 1:0 (b) 1:1 (c) 0.5:1 (d) 0.1:1 (e) 0:1.

its corresponding hydrogen nucleus electron density. The vibrating magnetic field strength decreases and the chemical shift values increase. With the increase in T, the phase ratio of PIL/T from 1:0.1 to 1:1 increases, and the hydrogen atom signals such as α -H (7.2981 ppm) and β -H (7.0920 ppm) both obviously move to a lower field, namely to 7.3606, 7.3472, and 7.3286 ppm for α -H and to 7.1284, 7.1230, and 7.1080 ppm for β -H. At the same time, with increasing thiophene ratio, the active hydrogen of [DMAPN]⁺[Pr]⁻ also shifts to the higher field. As can be seen from the above analysis, the driving force of the extraction process is probably the hydrogen bonding interactions.

To confirm the hydrogen bonding interaction mechanism, characterization with FT-IR spectroscopy was also carried out, which is shown in Fig. 12. The hydrogen bonds affect the C–S–C stretching vibration of thiophene to a certain extent.³⁷ So, the C–S–C stretching vibration is taken as an example and was observed at wavenumbers between 1000 and 1100 cm⁻¹. As 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 to 1075 cm^{-1} for 0.1 : 1. This phenomenon results from the formation of hydrogen bonds between [DMAPN]⁺[Pr]⁻ and thiophene. Therefore, it can be concluded that the hydrogen bond formation between the active hydrogen of the PIL and the sulfur atom of thiophene accounts for the higher extraction efficiency.

For the ¹H NMR results of different molar ratios between $[DMAPN]^{+}[Pr]^{-}$ and BT, we refer to Fig. S4 in the ESI.[†] The same trends were also obtained in the ¹H NMR spectra. So, we can draw the conclusion that hydrogen bonding is the main driving force for this specific extraction desulfurization process.

4. Conclusions

A series of protic ionic liquids was designed and synthesized. Their extraction desulfurization capability was estimated. Through selection, two typical PILs were chosen as typical examples to optimize the extraction desulfurization process. The results show that BT and T can be effectively removed using PILs. Both cations and anions have an influence on the extraction. However, the cations have a greater influence on the desulfurization process. The sequence is: $[DMAPN]^+[Pr]^- >$ $[DMEE]^+[Pr]^- > [DMEA]^+[Pr]^- > [MEA]^+[Pr]^-$, while for anions it is: $[DMAPN]^+[Bu]^- > [DMAPN]^+[Pr]^- > [DMAPN]^+[Ac]^- >$ [DMAPN]⁺[Fo]⁻. Moreover, the extraction process was optimized. Under optimal conditions, the extraction efficiency could be higher than 80% for only one cycle. After 6-8 cycles, the sulfur content of fuel could be decreased below 7.8 ppm and the removal efficiency could reach up to 99.5%. The deep desulfurization process was realized successfully. It is worth mentioning that the PILs could be successfully recycled via simple vacuum distillation, 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 the PILs changed slightly. Finally, through the systematic research on the extraction mechanism, it was found that the hydrogen bond formation between the sulfur atom of BT/T and the active hydrogen of the PILs accounts for the high desulfurization efficiency. This novel green process would provide a new route for the extraction desulfurization of fuels. Further research on this work is still ongoing in our laboratory.

Acknowledgements

We would like to thank the National Natural Science Foundation of China (Grant no. 21176033 and 21306016) for financial support of this project.

Notes and references

- 1 L. Z. Zhai, Q. Zhong, C. He and J. Wang, *J. Hazard. Mater.*, 2010, 177, 807.
- 2 W. D. Liang, S. Zhang, H. F. Li and G. D. Zhang, *Fuel Process. Technol.*, 2013, **109**, 27.
- 3 B. Wang, J. P. Zhu and H. Z. Ma, *J. Hazard. Mater.*, 2009, **164**, 256.
- 4 C. J. Zou, P. W. Zhao, J. Ge, Y. B. Qin and P. Y. Luo, *Fuel*, 2013, **104**, 635.
- 5 S. Brunet, D. Mey, G. Pérot, C. Bouchy and F. Diehl, *Appl. Catal.*, *A*, 2005, **278**, 143.
- 6 A. Seeberger and A. Jess, Green Chem., 2010, 12, 602.
- 7 M. Francisco, A. Arce and A. Soto, *Fluid Phase Equilib.*, 2010, **294**, 39.
- 8 X. L. Ma, L. Sun and C. S. Song, Catal. Today, 2002, 77, 107.
- 9 W. S. Zhu, Y. X. Ding, H. M. Li, J. Qin, Y. H. Chao, J. Xiong, Y. H. Xu and H. Liu, *RSC Adv.*, 2013, **3**, 3893.
- 10 W. S. Zhu, G. P. Zhu, H. M. Li, Y. H. Chao, Y. H. Chang, G. Y. Chen and C. R. Han, *J. Mol. Catal. A: Chem.*, 2011, 347, 8.
- 11 H. Song, X. Wan, M. Dai, J. J. Zhang, F. Li and H. L. Song, *Fuel Process. Technol.*, 2013, **116**, 52.
- 12 Z. Barnea, T. Sachs, M. Chidambaraml and Y. Sasson, J. Hazard. Mater., 2013, 244, 495.

- 13 A. Stanislaus, A. Marafi and M. S. Rana, *Catal. Today*, 2010, **153**, 1.
- 14 M. Mukhopadhyaya, R. Chowdhury and P. Bhattacharya, *AIChE J.*, 2007, **53**, 2188.
- 15 Y. S. Chi, C. P. Li, Q. Z. Jiao, Q. S. Liu, P. F. Yan, X. M. Liu and U. Welz-Biermann, *Green Chem.*, 2011, 13, 1224.
- 16 C. D. Wilfred, C. F. Kiat, Z. Man, M. A. Bustam, M. I. M. Mutalib and C. Z. Phak, *Fuel Process. Technol.*, 2012, 93, 85.
- 17 D. S. Zhao, R. Liu, J. L. Wang and B. Y. Liu, *Energy Fuels*, 2008, 22, 1100.
- 18 H. Y. Lü, W. Z. Ren, H. Y. Wang, Y. Wang, W. Chen and Z. H. Suo, *Appl. Catal.*, A, 2013, 453, 376.
- 19 R. D. Rogers and K. R. Seddon, Science, 2003, 302, 792.
- 20 H. Weingärtner, Angew. Chem., Int. Ed., 2008, 47, 654.
- 21 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- 22 P. S. Kulkarni and C. A. M. Afonsoac, *Green Chem.*, 2010, **12**, 1139.
- 23 R. Ferraz, L. C. Branco, I. M. Marrucho, J. M. M. Araújo,
 L. P. N. Rebelo, M. N. da Ponte, C. Prudêncio,
 J. P. Noronha and Ž. Petrovski, *Med. Chem. Commun.*, 2012,
 3, 494.
- 24 H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal.*, *A*, 2010, **373**, 1.
- 25 A. Dharaskar Swapnil, Res. J. Chem. Sci., 2012, 2, 80.
- 26 Y. X. Ding, W. S. Zhu, H. M. Li, W. Jiang, M. Zhang, Y. Q. Duan and Y. H. Chang, *Green Chem.*, 2011, 13, 1210.
- 27 G. R. Yu, X. Li, X. X. Liu, C. Asumana and X. C. Chen, *Ind. Eng. Chem. Res.*, 2011, **50**, 2236.
- 28 A. R. Hansmeier, G. W. Meindersma and A. B. de Haan, *Green Chem.*, 2011, **13**, 1907.
- 29 U. Domanska and M. Wlazlo, Fuel, 2014, 134, 114.
- 30 K. Kędra-Królik, M. Fabrice and J. N. Jaubert, *Ind. Eng. Chem. Res.*, 2011, **50**, 2296.
- 31 T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
- 32 T. L. Greaves, A. Weerawardena, I. Krodkiewska and C. J. Drummond, *J. Phys. Chem. B*, 2008, **112**, 896.
- 33 B. Nuthakki, T. L. Greaves, I. Krodkiewska,
 A. Weerawardena, M. I. Burgar, R. J. Mulder and
 C. J. Drummond, *Aust. J. Chem.*, 2007, 60, 21.
- 34 Y. S. Chi, Z. D. Zhang, C. P. Li, Q. S. Liu, P. F. Yan and U. Welz-Biermann, *Green Chem.*, 2011, **13**, 666.
- 35 X. F. Sun, S. Y. Liu, A. Khan, C. Zhao, C. Y. Yan and T. C. Mu, *New J. Chem.*, 2014, 38, 3449.
- 36 Z. Li, C. P. Li, Y. S. Chi, A. L. Wang, Z. D. Zhang, H. X. Li, Q. S. Liu and U. Welz-Biermann, *Energy Fuels*, 2012, 26, 3723.
- 37 A. A. Mashkovsky, A. A. Nabiullin and S. E. Odinokov, J. Chem. Soc., Faraday Trans., 1983, **79**, 951.