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REVIEW

Ionic Liquids for SO₂ Capture: Development and Progress

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Removal of SO₂ from flue gas has attracted increasing interests under worldwide environmental pressure. In this paper, the recent progress of ionic liquids for SO₂ capture, including the absorption capacity, the desorption performance and the absorption mechanisms of guanidinium based ionic liquids, hydroxyl ammonium ionic liquids, imidazolium based ionic liquids and quaternary ammonium based ionic liquids, are reviewed. In addition, some strategies recently developed to enhance the absorption processes have been briefly introduced, such as ionic liquids mixtures, solidified ionic liquids and supported ionic liquids membranes. Moreover, the drawbacks for the industrial application of this technology have been proposed.

Keywords: Ionic liquids, SO₂, Absorption, Mechanism.

INTRODUCTION

Sulfur dioxide (SO₂), mainly emitted from the burning of fossil fuels, brings out severe air pollution such as acid rain. Thus SO₂-emitting industries worldwide are under pressure to reduce their sulfur emissions. The technologies for the capture of SO₂ have attracted increasing interests, among which flue gas desulfurization (FGD) is the most efficient way. The conventional Flue gas desulfurization technologies include wet scrubbing^{1,2} using calcium-based absorbents, dry scrubbing³ and absorption by aqueous amines. However, there are large amounts of non-renewable by products such as calcium sulfate⁴ and the consumption of water is huge during the wet scrubbing process. The dry scrubbing process is simple, but limited in industry due to the high ratio of Ca/S, low efficiency in removal of SO₂ and the high cost in recovery of desulfurizer. In addition, secondary pollution is the biggest problem to be solved for the absorption by aqueous amines, as the amines are easy to volatilize to flue gas with water.

Ionic liquids are molten organic salts consisting of large organic cations and inorganic or organic anion at ambient temperature. Due to the unique properties such as negligible vapour pressure, high thermal stability and excellent solvent power for a wide range of both organic and inorganic materials, ionic liquids have been considered environmental friendly solvents as water and supercritical CO₂. So far, ionic liquids have been widely used in organic synthesis⁵, extraction separation⁶, analytical chemistry⁷, biocatalysts and nanophase materials⁸.

In recent years, ionic liquids have been proposed to remove acid gases such as CO₂⁹, SO₂ and H₂S. Compared to the traditional industrial solvents, ionic liquids present significant advantages, especially in complex systems, as they could be tuned by appropriate selection of the structures of their cations and anions. In this work, ionic liquids used for SO₂ capture and separation from flue gas or mixed gas have been briefly summarized.

Ionic liquids used for SO₂ capture: Ionic liquids used for removal of SO₂ was first synthesized in 2004¹⁰, after which much attention has been drawn to the development of ionic liquids for removal of SO₂. According to cations, the ionic liquids can be classified as guanidinium based, hydroxyl ammonium, imidazolium based and quaternary ammonium based ionic liquids. The performance of absorption and desorption of SO₂ has been studied. In addition, some strategies to improve the performance have been developed, such as ionic liquids mixtures, solidified ionic liquids and supported ionic liquids membranes.

Guanidinium based ionic liquids: The first ionic liquids used for capture of SO₂ was synthesized by direct neutralization of 1,1,3,3-tetramethylguanidine (TMG) and lactic acid¹⁰. The solubility of SO₂ in the ionic liquids [TMG][LAC] (Fig. 1) was as high as 1.7 mol SO₂/mol ionic liquids at 40 °C and 120 KPa. However, when the ionic liquids ([TMG][LAC]) was used to remove SO₂ from the simulated flue gases, a mixture of N₂ and SO₂ with a SO₂ content of 8 % by volume, it exhibit a lower absorption capacity of 0.978 mol SO₂/mol ionic liquids

Fig. 1. Structure of ionic liquids [TMG][Lac]

at 40 °C, 101.325 KPa. The absorption capacity decreased with temperature increasing and the molar ratio of SO₂ to ionic liquids at 60 and 94 °C were only 0.775 and 0.512, respectively. However, this ionic liquids is limited in practice because of relatively low thermal stability, which results in that only a fraction of the absorbed gas could be thermally released before degradation of the ionic liquids occurs.

The absorption of CO₂ by ionic liquids [TMG][Lac] was also studied in their work. The result showed that this ionic liquids present high selectivity towards SO₂, as the absorption capacity of CO₂ by the ionic liquid was very low (0.012 mol CO₂/mol ionic liquid). The selectivity of [TMG][Lac] towards CO₂ and SO₂ was also studied using molecular dynamics simulations¹¹. The simulation result showed that CO₂ has relatively poor interaction with the cations and the anions of the ionic liquids, while SO₂ has high interaction, especially with the [LAC] anion. Therefore, the ionic liquid [TMG][Lac] has a low absorption capacity towards CO₂, while the solubility of SO₂ is fairly high. This study lays the basic theory foundation for improvement of ionic liquids used for capture of SO₂. Prasad *et al.*¹² also studied the interaction between SO₂ and the ionic liquids [TMG][Lac] from first-principle calculations. The result indicated that the key factor on the solubility of SO₂ is the interaction between SO₂ and the anion in ionic liquids. So the relatively high solubility of SO₂ in [TMG][Lac] is attributable to the strong association of SO₂ with the anion [Lac].

Huang *et al.*¹³ prepared three new guanidinium based ionic liquids used for SO₂ capture. The ionic liquids, [TMGH][BF₄] and [TMGH][Tf₂N], were prepared by direct neutralization of TMG solution with aqueous fluoroboric acid and HBTa respectively, while the ionic liquids ([TMGB₂][BTA]) was synthesized by alkylated TMG solution. The ionic liquids were found to absorb a large amount of SO₂ gas corresponding to molar ratios of SO₂ to ionic liquids of 1.27, 1.18, respectively at 20 °C, 101.325 KPa. The SO₂ gas can be completely desorbed by heating to about 140 °C. However, when the ionic liquids were used to remove SO₂ from simulated flue gases (N₂ and SO₂ with a SO₂ molar content of 10 %), the absorption capacity was fairly low due to competing N₂ absorption.

Later, the strategy that hydroxyl group was grafted on the cations was proposed to improve the absorption performance of the ionic liquids¹⁴. A series of modified ionic liquids with alcohol-containing alkyl chains on the cations were synthesized and used for SO₂ capture. The ionic liquids ([TMGHPO][Tf₂N] and [TMGHPO₂][Tf₂N]) exhibited high solubility with a ratio of SO₂ to ionic liquids of 2.01, which illustrated that hydroxyl groups on the cations favour the absorption of SO₂. This result also indicated that the premier interaction was found between the cations of the ionic liquids and SO₂. However, when the

two ionic liquids were used to remove SO₂ from 10 % SO₂ gas (10 mole % in N₂), the absorption capability were still relatively low with the ratio of SO₂ to ionic liquids being 0.15 and 0.20 for [TMGHPO][Tf₂N] and [TMGHPO₂][Tf₂N], respectively.

It can be concluded that the guanidinium based ionic liquids have good performance in absorption of pure SO₂ gas and that the absorbed SO₂ can be released by heating or vacuum. However, the absorption capability of SO₂ from simulated flue gases is lower. Since the key interaction exists between the cations and SO₂, improvement can be made based on the cations.

Hydroxy ammonium ionic liquids: Hydroxy ammonium ionic liquids are basically prepared by neutralization of organic amine with different organic acids. Yuan *et al.*¹⁵ synthesized a series of hydroxy ammonium ionic liquids (Fig. 2), which present a high solubility of SO₂. Among these ionic liquids, 2-hydroxyethyl ammonium exhibited the highest absorption capacity with a value of 1.04 mol SO₂/mol ionic liquids. The absorbed SO₂ could be released under vacuum or by heating and the ionic liquids can be recycled for 4 times with a recovery larger than 90 %. The absorption capability of these ionic liquids showed close association both with the cations and the anions. The study showed that the effect of cations on the solubilities of SO₂ followed the sequence: 2-hydroxyethylammonium > tri-(2-hydroxyethyl) ammonium > 2-(2-hydroxyethoxy) ammonium, while the effect of anions is lactate > acetate > formate.

R₁, R₂, R₃: H or HO-CH₂-CH₂- or HO-CH₂-CH₂-O-CH₂-CH₂-
R: H, CH₃ and CH₃-CH(OH)-

Fig. 2. Structure of the hydroxy ammonium ionic liquids

Compared with guanidinium based ionic liquids, hydroxy ammonium ionic liquids show a relatively lower absorption capability for SO₂. However, the decomposition temperature of the hydroxy ammonium ionic liquids is mostly higher than that of guanidinium based ionic liquids, meaningly that the hydroxy ammonium ionic liquids have higher thermal-stability.

Imidazolium based ionic liquids: Imidazolium based ionic liquids are based on the imidazole ring and have attract much attention due to their unique properties. The imidazolium based ionic liquids, [BMIM][BTA] and [BMIM][BF₄], were firstly used for SO₂ capture¹². The ionic liquids can physically absorb large amounts of SO₂ with a capacity of 1.1-1.6 mol SO₂/mol ionic liquids and the SO₂ can be completely desorbed by heating to about 140 °C. However, the absorption capability of SO₂ from the simulated flue gases is similarly low.

Jessica *et al.*¹⁶ measured the solubility of SO₂ in the ionic liquids [HMIM][Tf₂N] and [HMPY][Tf₂N]. The result suggested that the solubility in [HMIM][Tf₂N] was extremely high and that the absorption capacity can be as high as 1.6 mol

SO₂/mol ionic liquids at 25 °C and 3.44 atm. Additionally, the Henry's law constants were also calculated in their work. Compared to that of CO₂, there was over an order of magnitude decrease in the Henry's law constants for SO₂. This result illustrated that these ionic liquids present high selective towards SO₂.

A series of imidazolium based ionic liquids with halide anions, such as [BMIM][Cl], [BMIM][Ac], [BMIM][BF₄], [BMIM][PF₆] and [BMIM][MeSO₄], were also prepared for SO₂ capture and the effect of different anions was also investigated¹⁷. These ionic liquids exhibited high solubility within the range of 1.91–2.22 mol SO₂/mol ionic liquids at 50 °C and the solubility followed the order: Br > Cl > I. However, the SO₂ absorbed by [BMIM][Cl] and [BMIM][Ac] couldn't be completely released when heated. It is due to the strong interaction between SO₂ and the relative strong basic anions such as [Ac].

In order to improve the absorption capability of ionic liquids with a less basic anion, the cations were functionalized with ether groups, considering that SO₂ could interact with oxygen atoms in the ether groups. The ionic liquids, ether-functionalized imidazolium methanesulfonates (Fig. 3), were found to have pretty high SO₂ solubility with a value of at least 2 moles SO₂/mol ionic liquids at 30 °C and 1 atm¹⁸. The SO₂ can be readily and completely desorbed by heating at 100 °C in a N₂ flow and the ionic liquids can be reused for 5 times without loss of absorption capability.

Fig. 3. Structure of ionic liquids [EMIM][MeSO₃]

Another strategy to improve the absorption capacity is to increase the number of interaction sites between the ionic liquids and SO₂. Two azole-based ionic liquids, [P₆₆₆₁₄][Tetz] and [P₆₆₆₁₄][Im], were prepared by neutralization of tetrazole (Tetz) or imidazole (Im) and solution of phosphonium hydroxide in ethanol¹⁹. The molar ratios of SO₂ to ionic liquids for [P₆₆₆₁₄][Tetz] and [P₆₆₆₁₄][Im] decreased from 3.72 to 1.54 and 4.80 to 2.07, respectively, as the pressure decreased from 1.0 to 0.1 atm. The ionic liquids, [P₆₆₆₁₄][Tetz], can be reused for 28 times.

Since the thermal stability of some ionic liquids is low, the degradation of the ionic liquids may occur during the desorption processes of SO₂ at high temperatures. For the purpose of improving thermal stability, several novel ionic liquids were prepared and used to separate SO₂ from the simulated flue gases²⁰. The ionic liquids were stable below 150 °C without any loss of weight. The effect of the cations on the SO₂ absorption capacity followed the order: [N₂₂₂₂] > [BMIM] ≈ [HMIM] > [TMG] > [MEA]. The absorption capacity of [BMIM][Lac] was 0.807 mol SO₂/mol ionic liquids at 40 °C and the ionic liquids could be recycled for 5 times without obvious loss of capacity.

In summary, much work has been done on the development of iminazolium based ionic liquids. Efforts have been made to improve the absorption capacity of the ionic liquids as well as thermal stability.

Quaternary ammonium based ionic liquids: Guo *et al.*²¹ synthesized a series of caprolactam tetrabutyl ammonium bromide ([CPL][TBAB]) ionic liquids and the solubility of SO₂ was measured. The absorption capacity of SO₂ in the ionic liquids at 35 °C and 101.325KPa can be as high as 1.84 mol/mol ionic liquids. The ionic liquids can be reused for 6 times with a high efficiency of desorption (99 %). A mixture of ionic liquids [CPL][TBAB] and sodium humate (HA-Na) solution was also used to remove SO₂ from flue gas²². The result showed that the maximum absorption efficiency of SO₂ approached almost 95 %, allowing this mixed solution to be used repeatedly for 5 recycles at 25 °C and atmospheric pressure.

Fig. 4. Structure of ionic liquids [CPL][TBAB]

Ionic liquids mixtures: Ionic liquids have attracted extensive interests from the research community and are considered to be of potential use in flue gas desulfurization processes. However, currently available ionic liquids are all expensive. In addition, the high viscosity of ionic liquids induces the low heat and mass transfer performance in SO₂ absorption processes. These two factors limit the industrial application of ionic liquids in flue gas desulfurization processes. So, it is necessary to develop ionic liquids with low viscosity and low cost as well as high SO₂ absorption capacity and absorption rate. A new strategy to solve this problem is to blend ionic liquids with water or other organic solvent to form hybrid absorbents, which has been adopted in CO₂ capture^{23–26}.

The solubility of SO₂ in [CPL][TBAB] was measured and the ionic liquids exhibited a high affinity for SO₂. However, the viscosity of the ionic liquids is high, which makes the mass and heat transfer difficult. So the mixture of [CPL][TBAB] and water was designed to remove SO₂, as the viscosity decreased with the water content increased²⁷. Two phases appeared when SO₂ was introduced into the mixture. The SO₂ was concentrated in the lower phase and the absorption capacity can be as high as 52.29 g/100 g solution. After the two phases were separated, the absorbed SO₂ can be released by heating under reduced pressure.

Three hydroxyl ammonium dicarboxylate ionic liquids were also used to absorb SO₂ with DMEA²⁸. The hybrid solvents exhibited very low viscosity, which was beneficial to

the transfer of SO₂ absorption. The solubility of SO₂ increased with the DMEA content increased, but the desorption became difficult. So there existed optimal DMEA / ionic liquids molar ratio. Due to the low viscosity, the SO₂ can be absorbed by the mixture very rapidly. After the two layers were separated, the SO₂ can also be released from the lower layer by heating under reduced pressure.

Recently, another eutectic mixture has caused wide interest. The eutectic ionic liquids are made up of organic quaternary ammonium salts and low molecular weight amides. These eutectic ionic liquids exhibit significant properties such as low viscosity and high solubility. Five amide-thiocyanates eutectic ionic liquids, acetamide-KSCN (3:1), caprolactam (CPL)-KSCN (3:1), acetamide-NH₄SCN (3:1), CPL-NH₄SCN (3:1) and urea-NH₄SCN (3:2), were prepared for SO₂ capture²⁹. The solubility of SO₂ in these ionic liquids was quite high and the absorption capacity of acetamide-KSCN (3:1) could reach 5.17 mol SO₂ / mol ionic liquids at 20 °C and 1 atm. The absorbed SO₂ can be easily released at 70 °C under vacuum and the ionic liquids can be reused for at least 5 times without any loss of absorption capacity.

Solidified ionic liquids: Ionic liquids have been widely used in flue gas desulfurization, but the high viscosity could be operational drawback as well as a cause for slow sorption rate because of relatively small gas-liquid interface and slow diffusion rate of gas molecules in viscous media. ionic liquids are solidified as ionic polymers or porous silica supported ionic liquids so as to enlarge the gas-liquid interface.

To improve the absorption capacity and rate, crosslinked porous particles based on the ionic copolymer of 1,1,3,3-tetra-methylguanidine acrylate and N,N-methylenebisacrylamide were prepared³⁰. The particles demonstrated high absorption capacity for SO₂, 0.26 g SO₂ per g P(TMGA-co-MBA) and high absorption rate. The absorbed SO₂ can be released by heating under vacuum and the SO₂ absorption properties kept unchanged during the SO₂ absorption/desorption cycles.

[TMG][Lac] was immobilized into porous silica particles by a simple impregnation-vaporization method. The [TMG][Lac] supported particles present large specific surface area and high absorption capacity for SO₂³¹. The result showed that the absorption capacity increased from 0.61 g SO₂/g [TMG][Lac] at 30 °C to about 0.88 g SO₂/g [TMG][Lac] at 20 °C for [TMG][Lac]-SiO₂ 1/1 and from 0.67 to 0.95 for [TMG][Lac] 0.5/1. The solid ionic liquids particles can be recycled for several times without loss of absorption capability. In addition, the silica supported ionic liquids exhibit good mechanical strength and thermal stability. So the ionic liquids particles are expected to be widely used in flue gas desulfurization.

Supported ionic liquids membranes: The supported liquid membranes (SLMs) are porous materials whose pores are filled with liquids. Supported ionic liquids membranes (SILMs) are developed for SO₂ absorption or separation, as the nonvolatility and incredible stability of ionic liquids enable the membrane separation process to avoid the loss of the supported liquid.

The permeability of SO₂ in five imidazolium based ionic liquids supported on the polyethersulfone microfiltration membranes was measured at 25-45 °C and atmospheric

pressure³². The SO₂ selectivity using supported ionic liquids membranes was 9-19 times that of CO₂. So the supported ionic liquids membranes are expected to have widely application in recovery of SO₂ from flue gas or gas mixtures.

Two kinds of supported ionic liquids membranes used for SO₂ separation were prepared using porous membranes made of PVDF with hydrophobic materials. The membranes were soaked in the ionic liquids [MIM][ace] and [BIM][ace]³³. The permeabilities of air, CO₂, 10 vol. % SO₂-air were obtained. The permeability of air was one order of magnitude lower than that of CO₂ and it was also lower than that of the mixture of air and 10 vol. % SO₂. The supported ionic liquids membranes made of hydrophilic PVDF and [BIM][ace] showed the highest permeability and are expected to be used in SO₂ separation processes.

In order to enhance the selectivity, α-D-glucose penta-acetate (GPA) was impregnated in supported ionic liquids membranes and used for the separation of CO₂ and SO₂ or separation of SO₂ from flue gas stream³⁴. It was found that selectivities of CO₂/N₂ and SO₂/N₂ were obviously improved compared with supported ionic liquids membranes without GPA. So the supported ionic liquids membranes with GPA are expected to have a potential application for the separation of CO₂ and SO₂ from a flue gas stream.

Mechanism of SO₂ absorption by ionic liquids: In order to design more effective ionic liquids for industrial application, it is necessary to get a clear understanding of the mechanism of the SO₂ absorption processes. The mechanism has been extensively discussed using detection means such as FT-IR, NMR and UV. The mechanism of absorption by some ionic liquids having been studied so far is presented in Table-1.

TABLE-1
MECHANISM OF SO₂ ABSORPTION
IN DIFFERENT IONIC LIQUIDS

Ionic liquids	Mechanism
[TMG][Lac] ¹⁰	Physical and chemical absorption
[HMIM][Tf ₂ N]	Physical ¹⁶ or Chemical ³⁵ absorption
[HMPY][Tf ₂ N] ¹⁶	Physical absorption
[TMG][BF ₄] ¹²	Physical absorption
[TMG][BTA] ¹²	Physical absorption
[BMIM][BF ₄] ¹²	Physical absorption
[BMIM][BTA] ¹²	Physical absorption
[TMGB ₃][BTA] ¹²	Physical absorption
Hydroxyl ammonium ILs ¹⁵	Physical and chemical absorption
[TMGHPO][BF ₄] ¹⁴	Physical absorption
[TMGHPO2][BF ₄] ¹⁴	Physical absorption
[P ₆₆₆₁₄][Tetz] ¹⁹	Chemical absorption
[P ₆₆₆₁₄][Im] ¹⁹	Chemical absorption
[TMGHH][Tf ₂ N] ³⁰	Physical absorption
[TMGHH][Lac] ³⁶	Physical absorption and chemical absorption
[BMIM][Ac] ³⁵	Chemical absorption
[BMIM][MeSO ₄] ³⁵	Chemical absorption
[EMIM][C(CN) ₃] ³⁷	Physical absorption
[EMIM][SCN] ²⁷	Chemical absorption
[Acetamide][KSCN] ²⁷	Physical absorption
[CPL][KSCN] ²⁷	Physical absorption
[Acetamide][NH ₄ SCN] ²⁷	Physical absorption
[CPL][NH ₄ SCN] ²⁷	Physical absorption
[Urea][NH ₄ SCN] ²⁷	Physical absorption

Physical and chemical absorption: The absorption processes of SO₂ by ionic liquids [TMG][Lac] were discussed under different pressures by Wu *et al.*¹⁰. It was considered to be chemical absorption lower than 100 KPa and both physical and chemical absorption higher than 120 KPa. The mechanism of chemical absorption process is showed in Fig. 5. It was considered that SO₂ reacts with the NH₂ group on the cation, while the O atom on S=O probably forms intramolecular hydrogen bond with the H atom of the amine.

Fig. 5. Reaction between the ionic liquids [TMG][Lac] and SO₂

The absorption of SO₂ by hydroxyl ammonium ionic liquids were also considered to be both physical and chemical absorption processes¹⁵. The mechanism was considered that the SO₂ molecule attacks the -NH group in the cations of the ionic liquids and forms the N-S bond and that simultaneously the carboxylate is turned to carboxylic acid (Fig. 6).

Fig. 6. Reaction between hydroxyl ammonium ionic liquids and SO₂

Physical absorption: Anderson *et al.*¹⁶ studied the solubility of SO₂ in [HMIM][Tf₂N] and [HMPY][Tf₂N]. The high solubility was considered to be based on physical sorption processes. The absorption processes by amide-thiocyanates eutectic ionic liquids are also found to be physical processes. But the mechanism of the interaction between ionic liquids and SO₂ have not been discussed²⁷.

The absorption processes by ionic liquids [TMGH][Tf₂N], [TMGHPO][Tf₂N] and [TMGPO₂][Tf₂N] *etc* had been analyzed. It was concluded that no new chemical bonds appeared during the absorption process according to the Raman and UV spectra. The primer interaction was suggested to be vander Waals type of bonding between the delocalized π bonding systems in the cations and SO₂. The physical absorption processes were explained using the local structure in ionic liquids. Due to the polarity of SO₂ molecule, the void space originally available in ionic liquids could be taken up much more easily by SO₂. Since the molecular radius of SO₂ is larger than the cavities in ionic liquids, the volume of ionic liquids increased significantly during gas absorption^{13,14}.

Chemical absorption: Shiflett *et al.*³⁵ studied the chemical absorption by ionic liquids [Bmim][Ac], [Bmim][MeSO₄], [Hmim][Tf₂N] systematically. The pressure-temperature-composition (PTx) data was measured and analyzed using an equation-of-state model. Then, excess thermodynamic functions and Henry's constants obtained from the PTx data were used to classify whether the absorption is physical or chemical type. According to the excess Gibbs, enthalpy functions and the magnitude of the Henry's constants, the absorption processes were considered to be chemical absorption processes.

Conclusion

In summary, much work has been done on the synthesis and characterization of ionic liquids used for removal of SO₂ as well as the mechanism of the absorption processes. Different kinds of ionic liquids have been prepared and some of them exhibit high absorption capacity for SO₂. In addition, several strategies have been proposed to improve the performance of ionic liquids, such as solid ionic liquids, supported ionic liquids membranes and ionic liquids mixtures. However, the technology has not been widely used in industry due to the high cost of ionic liquids, complexity of flue gas and other factors. So there is still much work to be done:

(1) It is of great necessary to find a way to reduce the high cost of ionic liquids.

(2) Considering flue gas in practice is about 110-160 °C, high thermal-stable ionic liquids are expected to be developed and the performance of SO₂ absorption to be studied systematically.

(3) Many ionic liquids so far exhibit high absorption capability for pure SO₂, but low absorption capacity for SO₂ from the simulated flue gases. So the effect of other gases in flue gas on the performance of ionic liquids needs to be investigated so as to design more effective ionic liquids.

(4) There is not a common or clear understanding of the mechanism of the sorption of SO₂ by ionic liquids.

REFERENCES

- G. Al-Enezi, H. Ettouney, H. El-Dessouky and N. Fawzi, *Ind. Eng. Chem. Res.*, **40**, 1434 (2001).
- H.-J. Ryu, J.R. Grace and C.J. Lim, *Energy Fuels*, **20**, 1621 (2006).
- X. Ma, T. Kaneko, T. Tashimo, T. Yoshida and K. Kato, *Chem. Eng. Sci.*, **55**, 4643 (2000).
- L. Philip and M.A. Deshusses, *Environ. Sci. Technol.*, **37**, 1978 (2003).
- T. Welton, *Chem. Rev.*, **99**, 2071 (1999).
- B. Tang, W. Bi, M. Tian and K.H. Row, *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.*, **904**, 1 (2012).
- S. Pandey, *Anal. Chim. Acta*, **556**, 38 (2006).
- Z. Yang and W. Pan, *Enzym. Microb. Technol.*, **37**, 19 (2005).
- M. Hasib-ur-Rahman, M. Siaz and F. Larachi, *Chem. Eng. Process.*, **49**, 313 (2010).
- W. Wu, B. Han, H. Gao, Z. Liu, T. Jiang and J. Huang, *Angew. Chem. Int. Ed.*, **43**, 2415 (2004).
- Y. Wang, H. Pan, H. Li and C. Wang, *J. Phys. Chem.*, **111**, 10461 (2007).
- B. Ram Prasad and S. Senapati, *J. Phys. Chem.*, **113**, 4739 (2009).
- J. Huang, A. Riisager, P. Wasserscheid and R. Fehrmann, *Chem. Commun.*, **38**, 4027 (2006).
- J. Huang, A. Riisager, R.W. Berg and R. Fehrmann, *J. Mol. Catal. A*, **279**, 170 (2008).
- X.L. Yuan, S.J. Zhang and X.M. Lu, *J. Chem. Eng. Data*, **52**, 596 (2007).
- J.L. Anderson, J.N.K. Dixon, E.J. Maginn and J.F. Brennecke, *J. Phys. Chem.*, **110**, 15059 (2006).
- K.Y. Lee, C.S. Kim, H. Kim, M. Cheong, D.K. Mukherjee and K.-D. Jung, *Bull. Korean Chem. Soc.*, **31**, 1937 (2010).

18. S.Y. Hong, J. Im, J. Palgunadi, S.D. Lee, J.S. Lee, H.S. Kim, M. Cheong and K.-D. Jung, *Energy Environ. Sci.*, **4**, 1802 (2011).
19. C. Wang, G. Cui, X. Luo, Y. Xu, H. Li and S. Dai, *J. Am. Chem. Soc.*, **133**, 11916 (2011).
20. S. Tian, Y. Hou, W. Wu, S. Ren and C. Zhang, *RSC Adv.*, **3**, 3572 (2013).
21. B. Guo, E. Duan, A. Ren, Y. Wang and H. Liu, *J. Chem. Eng. Data*, **55**, 1398 (2010).
22. Y. Zhao and G. Hu, *RSC Adv.*, **3**, 2234 (2013).
23. Z. Feng, F. Cheng-Gang, W. You-Ting, W. Yuan-Tao, L. Ai-Min and Z. Zhi-Bing, *J. Chem. Eng.*, **160**, 691 (2010).
24. D. Camper, J.E. Bara, D.L. Gin and R.D. Noble, *Ind. Eng. Chem. Res.*, **47**, 8496 (2008).
25. B.R. Mellein and J.F. Brennecke, *J. Phys. Chem.*, **111**, 4837 (2007).
26. M.M. Taib and T. Murugesan, *J. Chem. Eng.*, **181**, 56 (2012).
27. B. Liu, F. Wei, J. Zhao and Y. Wang, *RSC Adv.*, **3**, 2470 (2013).
28. E. Duan, B. Guo, M. Zhang, Y. Guan, H. Sun and J. Han, *J. Hazard. Mater.*, **194**, 48 (2011).
29. K. Huang, J.-F. Lu, Y.-T. Wu, X.-B. Hu and Z.-B. Zhang, *Chem. Eng. J.* **36**, 215 (2013).
30. L. Wu, D. An, J. Dong, Z. Zhang, B.-G. Li and S. Zhu, *Macromol. Rapid Commun.*, **27**, 1949 (2006).
31. Z. Zhang, L. Wu, J. Dong, B.-G. Li and S. Zhu, *Ind. Eng. Chem.*, **48**, 2142 (2009).
32. Y.-Y. Jiang, Z. Zhou, Z. Jiao, L. Li, Y.-T. Wu and Z.-B. Zhang, *J. Phys. Chem.*, **111**, 5058 (2007).
33. P. Luis, L.A. Neves, C.A.M. Afonso, I.M. Coelho, J.G. Crespo, A. Garea and A. Irabien, *Desalination*, **245**, 485 (2009).
34. X.-B. Hu, Y.-X. Li, K. Huang, S.-L. Ma, H. Yu, Y.-T. Wu and Z.-B. Zhang, *Green Chem.*, **14**, 1440 (2012).
35. M.B. Shiflett and A. Yokozeki, *Ind. Eng. Chem. Res.*, **49**, 1370 (2010).
36. G. Yu and X. Chen, *J. Phys. Chem. B*, **115**, 3466 (2011).
37. C. Wang, J. Zheng, G. Cui, X. Luo, Y. Guo and H. Li, *Chem. Commun.*, **49**, 1166 (2013).