Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Stille couplings in water @RT

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Please do not adjust margins

Green Chemistry

Journal Name

ARTICLE

Highly Efficient I₂ Capture by Simple and Low-cost Deep Eutectic Solvents

Guofeng Li,[a] Chuanyu Yan,[a] Bobo Cao,[b] Jingyun Jiang,[a] Wancheng Zhao,[a] Jinfang Wang,[a] Tiancheng Mu*[a]

The efficient removal and storage of radioactive nuclear contamination including isotope of iodine (^{131}I) has attracted great concern especially after the explosion of Fukushima nuclear power plant. In this study, deep eutectic solvents (DESs) are proposed for the removal and storage of iodine (I_2). These DESs can be obtained by simply mixing two simple components (also cheap and biodegradable), which form liquids with melting points far below that of the individual components. A series of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) are selected for the preparation of DESs. The properties and I_2 capture efficiency of the prepared DESs have been investigated. The results indicate that some DESs have higher efficiencies for I_2 removal than previous reported materials. Among them, ChI-methylurea shows the best I_2 uptake efficiency with approximate 100% within 5 hours. Moreover, ChI-methylurea exhibits a good capability of I_2 storage with only 4.6% of the iodine evaporated after 10 hours' strong N_2 sweeping, which is also important since I_2 is easy to sublimate. Additional calculations also suggest that the high efficiency for I_2 capture by DESs mainly comes from the formation of halogen bonding (XB) between DESs and I_2. This work opens a new way for the application of DESs.

Introduction

For decades, the disposal of radioactive nuclear contamination has attracted great concern especially after an explosion at Fukushima nuclear power plant on 11 March 2011. Radiotoxic isotope of iodine (^{131}I) was released into the atmosphere and Pacific Ocean without any control.[1] The ^{131}I can also be generated as by-products during the fission of uranium and plutonium, and it is believed to cause thyroid cancer.[2-4] Thus, these radioactive contaminations need to be captured and stored away from the environment. Various materials, such as activated carbon[5], zeolite-like aluminosilicates[6-9], and metal–organic framework (MOF) materials[10-13] have been employed to remove iodine (I_2). Unfortunately, these materials are either of low removal efficiency or high cost.

Halogen bonding (XB)[14-23], a counterpart of hydrogen bonding (HB), is generally expressed as D···X–Y, in which X is the electrophilic halogen atom (e.g., F, Cl, Br, I); D is the electronegative group as the halogen bond acceptor (e.g., O, N, F, Cl, Br, I); and Y is any other atom (e.g., C, Cl, N). Simply, XB is an intermolecular electrostatic force between covalently-bonded halogens and electronegative species.[24] In our previous work[25], ionic liquids (ILs) have been used to efficiently capture and store I_2 thanks to the XB between I_2 and halides in ILs. Furthermore, the dynamics process of the I_2 capture were also investigated[26] to give some insights. However, the ILs are relatively expensive, difficult in preparation and purification, and the toxicity of imidazolium cations of these ILs is another discussable topic. Therefore, efficient and biofriendly materials to capture I_2 are still highly stressed for the environmental and economic considerations.

As the potential alternatives to replace conventional organic solvents as well as ILs, deep eutectic solvents (DESs) have become of growing interest both at academic and industrial levels.[27-29] These DESs can be obtained by simply mixing two safe components (also cheap and biodegradable), a combination of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), which form liquids with melting points far below that of the individual components, due to self-association.[30] One of the most widely used raw materials of these DESs is choline chloride (ChCl). ChCl is a very cheap, non-toxic and biodegradable material, which can be either extracted from biomass or readily synthesized from fossil reserves (million metric tons) through a very high atom economy process. In combination with safe HBDs such as urea, renewable polyols (e.g. glycerol) or renewable carboxylic acids (e.g. oxalic acids), ChCl is capable of rapidly forming a DES. DESs are considered as green solvents with the similar features of ILs: low volatility, wide liquid range, water compatible and non-flammable. Furthermore, their properties can be tuned by changing the molecular structure and ratio of the individual components.[28] Compared to the traditional ILs, the DESs are of low prices and easily prepared without any purification steps; moreover, they are non-toxic, biocompatible and

a. Department of Chemistry, Renmin University of China, Beijing 100872, China. E-mail: tcmu@ruc.edu.cn; tcmu@chem.ruc.edu.cn; Tel: +86 10 62514925
b. School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, P. R. China

Please do not adjust margins

biodegradable[31]. Due to the similarities with ILs[25, 26], the DESs may have the potentials to capture the I_2.

In this study, a series of DESs including some new ones were synthesized and characterized, and some of them were selected for I_2 removal and storage. The I_2 removal efficiency of DESs was investigated by using solutions of I_2 in cyclohexane and analyzed by ultraviolet-visible (UV/vis) spectroscopy. For a better understanding on the I_2 capture by the DESs, a density functional theory (DFT) calculation on the interactions between the DESs and I_2 was performed.

Experimental

Materials

Choline bromide (ChBr) (98%), choline iodide (98%), tetrabutylammonium chloride (98%), tetramethylammonium chloride (98%), malonic acid (99%), 1,4-butanediol (99%), and D-(+)-glucose (98%) were purchased from TCI Shanghai. Urea (U) (99%), N-methylurea (MU) (98%), oxalic acid (99%), xylitol (98%), and choline chloride (ChCl) (99%) were obtained from J&K Chemical. Choline nitrate (99%), choline tetrafluoroborate (99%), choline hexafluorophosphate (99%), and choline perchlorate (99%) were purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China). Allyltrimethylammonium chloride (98%) was purchased from Energy Chemical. Ethylene glycol (99%), glycerol (99%) and I_2 were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the materials were used without further purification.

Synthesis and melting point measurements of the DESs

The HBDs and HBAs were mixed in around-bottomed flask in the desired molar ratio (from 1:1 to 1:4) and then was heated to between 50 °C and 120 °C with gentle stirring until a clear liquid formed. The melting point of the prepared DESs was measured using differential scanning calorimetry (DSC Q10, TA Instruments-Waters LLC). The samples were kept in a standard aluminum crucible and were conducted within a temperature range of 25 °C to 180 °C at a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

Iodine capturing experiments

UV/Vis spectra have been carried out with a sample pool with an optical length of 10 mm, within the wavelength range 280–700 nm, using the same solvent in the analyzed solution as a blank.[13] Two UV absorption peaks at 223 nm and 523 nm appear for I_2 in cyclohexane solution. However, due to the instrument or our sample pool, interference peaks appeared in the 200-300 nm. Therefore, the intensity of absorption peaks at λ = 523 nm is proportional with the quantity of I_2. The curve of calibration was obtained by six solutions (0.0001, 0.0002, 0.0003, 0.0004, 0.0005, 0.0006 mol/L) (Fig. S1). Each sample was measured at least three times and the absorbance was almost the same. Besides, calibration curve was measured again after the first time one month ago and the same calibration curve was obtained. It proves that the instrument is stable and the method is reliable. By measuring the

absorbance of I_2 after removal, corresponding concentration could be calculated according to the calibration curve and as a result, concentration change is validated during the iodine capturing and the I_2 removal efficiency would be obtained. It should be noted that I_2 in cyclohexane solution is the control and the background is cyclohexane solvent without I_2.

Computational methods

The geometry optimizations calculated using the B3LYP functional were carried out with Gaussian 09 package[32] using the 6-311++G(d,p) basis set, employing the counterpoise (CP) method for the Gaussian basis sets' superposition (BSSE)[33]. Around 10 different starting geometries were used to find the global minimum for each system (Fig. S2). The B3LYP/6-311++G(d,p) basis set, containing polarizable and diffuse functions, is considered can well describe the weak interactions in the binary systems, especially for halogen-bonded interactions and intermolecular H-bonded interactions. The interaction energy between the complete DES with radioiodine was obtained from DFT calculation at B3LYP/6-311++G(d,p) level. In this paper, interaction energy ΔE is defined as the zero-point energy difference between the DES with radioiodine complex, the sum of complete DES and iodine molecule. For the studied system ΔE can be evaluated by the following equation.

$$\Delta E = E_{(iodine+DES)} - (E_{(iodine)} + E_{(DES)})$$

Results and discussion

The DESs were synthesized from a simple combination of HBAs and HBDs with a certain molar ratio. The structures and abbreviations of raw materials (HBAs and HBDs) forming DESs and their melting points are shown in Table 1 and Fig. 1. It is noticeable that these eutectic mixtures bear melting points far below than that of the individual components, due to the hydrogen bonding[34] between HBAs and HBDs according to Fig. 1. In addition, the melting points of DES are also dependent upon the lattice energies of the HBAs and HBDs and the entropy changes arising from forming a liquid.[35]

Table 1 The combinations and melting points (T_m) of the DESs

HBA	HBD	n_{HBA} : n_{HBD}	T_m (°C)
ChCl	Urea	1:2	12[27]
ChCl	N-Methylurea	1:2	29[27]
ChCl	Ethylene Glycol	1:2	-66[36]
ChCl	Glycerol	1:2	-40[37]
ChCl	Oxalic acid	1:1	34[35]
ChCl	Malonic acid	1:1	10[35]
ChCl	Xylitol	1:1	Liquid at RT[a]
ChCl	Glucose	1:1	Liquid at RT
ChCl	1,4-Butanediol	1:4	Liquid at RT
ChBr	N-Methylurea	1:2	47
ChBr	Oxalic acid	1:1	Liquid at RT
ChBr	Malonic acid	1:1	Liquid at RT

ChI	N-Methylurea	1:2	91
ChI	Oxalic acid	1:1	52
ChI	Malonic acid	1:1	115
ChNO$_3$	N-Methylurea	1:2	40
ChPF$_6$	N-Methylurea	1:2	38
ChClO$_4$	N-Methylurea	1:2	59
ChBF$_4$	N-Methylurea	1:2	132
N(Me)$_4$Cl	Urea	1:2	60
N(Bu)$_4$Cl	Urea	1:2	118
AtMCh	Urea	1:2	54
[a]room temperature			

Hydrogen bond acceptor (HBA):
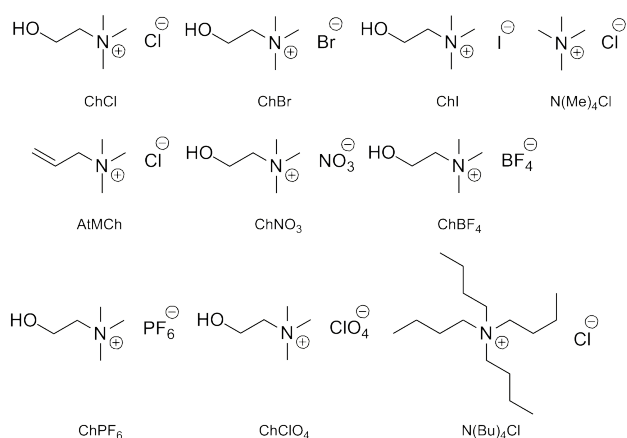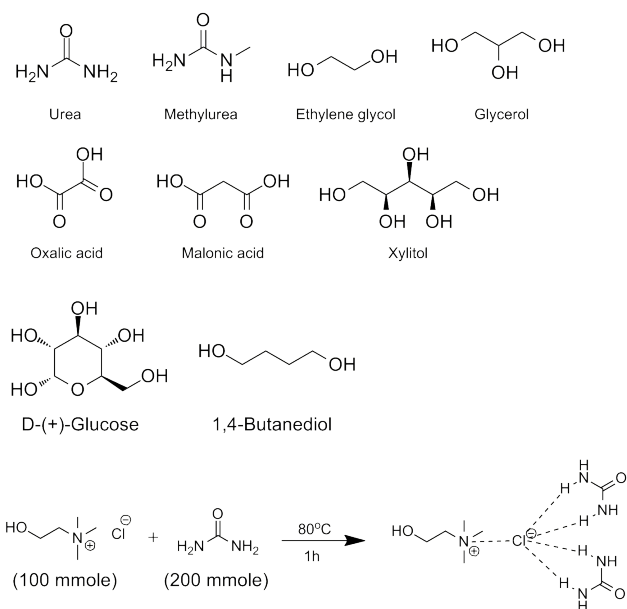

Hydrogen bond donor (HBD):

Fig. 1 Structures and abbreviations of raw materials forming DESs and hydrogen bonding in DESs.

For deep understanding the solvent properties of the as-synthesised DESs and the interactions between DESs and I$_2$, the solvatochromic parameters of the DESs were measured according to the literature[38-41]. The detailed method and procedure for these experiments were given in ESI. However, no obvious relation between the solvatochromic parameters (Table S1) and the I$_2$ capture kinetic and capacity could be found.

Typically the sorption kinetics was investigated by using I$_2$ dissolved in cyclohexane and analyzed by UV-vis spectroscopy. It should be noted that some of the DESs used in I$_2$ capture experiment have melting points higher than room temperature, which is not a matter because the I$_2$ capture experiments were carried out by putting the DES in the solution of I$_2$ in cyclohexane. The pictures showing the visual colour change after adsorption of I$_2$ with various DESs (C$_i$ = 0.01M, t = 24h and at room temperature) are given in Fig. S3. The I$_2$ kinetic adsorption (Fig. 2) was firstly analyzed by using seven methylurea-based DESs with different HBAs (the same cation with different anions (Cl$^-$, Br$^-$, I$^-$, PF$_6^-$, NO$_3^-$, BF$_4^-$, ClO$_4^-$)) and their visual colour change after 24h was shown in Fig. S3a. As shown in Fig. 2, the seven DESs exhibit different absorption efficiency of I$_2$. Among them, three DESs exhibit high efficiency (>80%) in 5 hours, especially ChI-methylurea with nearly 100% of I$_2$ removal from the stating solution. The I$_2$ capture efficiency of ChI-methylurea is much higher than the best MOF materials (48h)[13], which is one of the most efficient I$_2$ capture materials[25]. However, the methylurea-based DESs with different HBAs (ChPF$_6$, ChNO$_3$, ChBF$_4$ and ChClO$_4$) are of almost no absorption for iodine. Since there is a relatively strong force which is called halogen bonding between a halogen ion and iodine molecule, so the absorption efficiency of DESs with halogen ion is much higher than those with other anions. Besides, we also found that the ChI-Oxalic acid and ChI-Malonic acid could absorb all of the iodine from the stating solution in 24 hours (Fig. S3d).
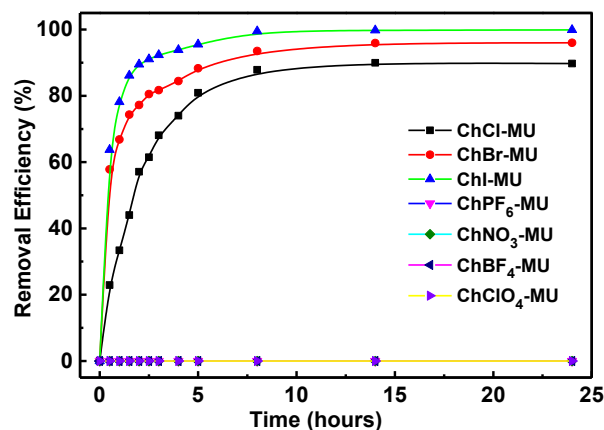

Fig. 2 I$_2$ removal kinetics of methylurea (MU)-based DESs with different HBAs (different anions with the same cation) at room temperature (volume of I$_2$ in cyclohexane = 5 ml, concentration = 0.01 mol/L, amount of DESs = 0.1 g).

In order to uncover the capture mechanism of radioiodine by DES, computational studies applying DFT have been performed. The structures formed by interaction between iodine molecule and isolated DESs were optimized and shown in Fig. S2. The DFT

Green Chemistry Accepted Manuscript

calculations (Fig. S2 and Table 2) strongly verify experimental I_2 capture results. As we all know, the higher the interaction energy between DESs and I_2 is, the more efficiently the DESs absorb I_2. For example, the interaction energy between I_2 and methylurea with ChI, ChCl, ChBF$_4$ is -379.23, -357.38 and -290.50 KJ/mol, respectively (Tabel 2). It is in line with the order of the absorption of iodine (Fig. 2). Besides, the I_2 removal efficiency of methylurea-based DESs with various halogen ions is also different, for example, ChI>ChCl. It is because that the electrostatic interaction between choline and Cl$^-$ (-1317.64 KJ/mol) is stronger than choline with I$^-$ (-868.84 KJ/mol) (Table 2), thus weakens the halogen bonding between Cl$^-$ and I_2 and finally leads to the lower removal efficiency.

Table 2   Computed sum of electronic and zero-point energies between DES and I_2

DES+I_2	$^a\triangle E$(A.U.)	$\triangle E$(KJ/mol)
ChCl-urea + I_2	-0.1289	-338.55
ChCl-methylurea + I_2	-0.1361	-357.38
ChCl/glycerol + I_2	-0.1140	-299.19
ChI-methylurea + I_2	-0.1444	-379.23
ChBF$_4$-methylurea + I_2	-0.1106	-290.50
N(Bu)$_4$Cl-urea + I_2	-0.1301	-341.54

^{a}The $\triangle E$ refers to the interaction energy between DES and I_2. It is calculated using the equation $\Delta E = E_{(iodine+DES)} - (E_{(iodine)} + E_{(DES)})$.

Besides the effects of HBAs on the capture efficiency, we are intended to find the effect of the HBDs on the I_2 capture efficiency. Fig. 2 showed that for all methylurea based DESs, ChI-methylurea has the highest removal efficiency. Thus, it is reasonable to investigate the efficiency of ChI based DESs for understanding the effects of HBDs on I_2 capture. However, most of the ChI based DESs are solid at room temperature, and they are more difficult for preparation than ChCl based DESs. Besides that, the ChCl based DESs have high efficiency for I_2 capture, too. Therefore, in this study, a series of choline-based DESs were chosen as removal agents to examine the effect of the functionalization through 9 different HBDs (Fig. 3). There is different absorption efficiency of iodine for ChCl-based DESs and their visual colour change after 24 h was shown in Fig. S3b. ChCl-methylurea has the best I_2 adsorption efficiency with 90% of initial I_2 removed after 24 hours and others follow. For example, the I_2 adsorption efficiency of ChCl-ethylene glycol, ChCl-urea, ChCl-glycerol, ChCl-oxalic acid is 80%, 67%, 56% and 40%, respectively.
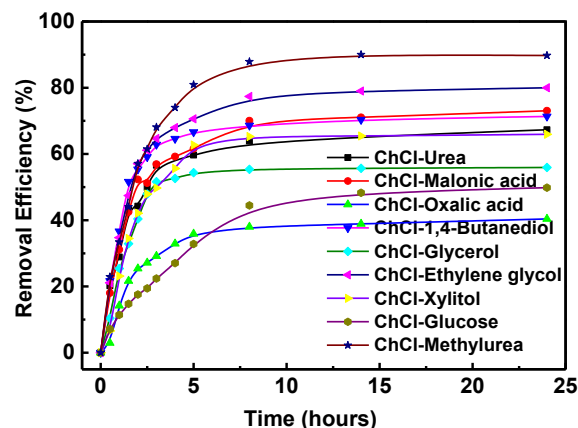

Fig. 3 I_2 removal kinetics of ChCl-based DESs with different HBDs at room temperature (volume of I_2 in cyclohexane = 5 ml, concentration = 0.01 mol/L, amount of DESs = 0.1 g).

This difference may arise from that different hydrogen bonding between chloridion and HBDs leads to the different interactions (halogen bond) between chloridion and I_2. In Table 2, the interaction energies between I_2 and choline with methylurea, urea and glycerol are -357.38, -338.55 and -299.19 KJ/mol, respectively. It perfectly fits for the order of iodine capture (Fig. 3). In addition, the I_2 removal efficiency of ChCl-methylurea is better than ChCl-urea. This promising result highlights the fact that methylurea is a better electron donor, forming strong charge-transfer complexes with iodine[13].

As shown in Fig. 4, urea-based DESs with different HBAs (ChCl, N(Me)$_4$Cl, AtMCh and N(Bu)$_4$Cl) exhibit different absorption efficiency of iodine and their visual colour change after 24h was shown in Fig. S3c. Among the DESs, N(Me)$_4$Cl-urea is the worst candidate for iodine removal in cyclohexane, with only 45% of I_2 removed from the stating solution after 24 hours. It is better for ChCl-urea and AtMCh-urea, with I_2 capturing efficiency 67% and 85%, respectively. The best removal capacity is reached for N(Bu)$_4$Cl-urea with a maximal efficiency of nearly 100%. It is much better than the reported best metal–organic framework (MOF) (48h)[13]. The I_2 removal efficiency of previously reported materials was presented in Table S2, from which we can conclude that DESs exhibit a relative higher efficiency than MOF MIL-101-NH$_2$ and ionic liquids.
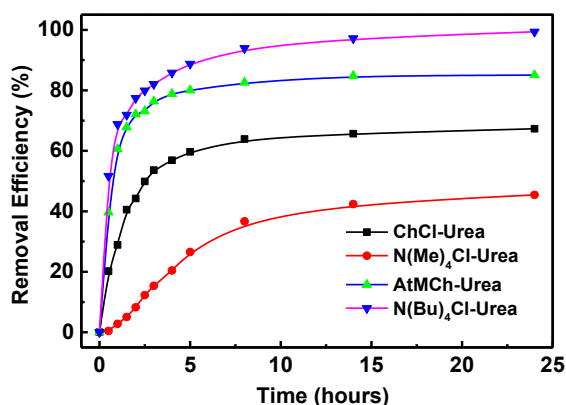
Fig. 4 I_2 removal kinetics of urea-based DESs with different HBAs (different cations with the same anion) at room temperature (volume of I_2 in cyclohexane = 5 ml, concentration = 0.01 mol/L, amount of DESs = 0.1 g).

From the structure of the urea-based DESs, we could see that the larger the volume of the cation is, the more efficiently the DESs remove the iodine. It may be because that the larger volume of the cation weakens the electrostatic force between chloride and ammonium ion, thus making the halogen bond force stronger between chlorine and the iodine molecules and as a result, leading to a higher I_2 removal efficiency.

Besides the capture efficiency, the total I_2 capture capacity of the DESs could be used as a parameter to evaluate the performance of the DESs for I_2 capture. Therefore, the capture capacity of ChI-methylurea and ChCl-urea was measured. The detailed procedure for the measurement was presented in ESI too. The experimental result showed that the capture capacity could reach 0.99 g I_2/ g DES (1.19 mol I_2/ mol DES) and 0.48 g I_2/ g DES (0.38 mol I_2/ mol DES) for ChI-methylurea and ChCl-urea, resprctively at room temperature and is relatively higher than or at least comparable to other reported materials. The capture capacity results also coincide with the DFT calculation results (Table 2) and I_2 removal efficiency experimental results (Fig. 2).

Apart from the I_2 removal, it is also highly essential to store I_2 within a relatively small space since I_2 is easy to sublimate. Although various organic solvents can dissolve I_2 well, they are flammable, toxic, and highly volatile. While the DESs are non-toxic, non-flammable and non-volatile, thus, they are a good choice to store I_2. The nitrogen sweeping experiment was carried out to examine the ability of the DESs to keep volatile iodine for a long time (Fig. S4): put the platinum plate containing DES or DES/I_2 sample in the thermal gravimetric analysis (TGA) instrument and set the nitrogen gas flow at 40 ml min^{-1}, temperature at 30 °C for 15 hours. According to Fig. S5, only 4.6% of the iodine in ChI-methylurea evaporated after 10 hours. It is much better than the powdered iodine (69%) and the [Bmim][Br] (11%, the best I_2 storage ionic liquids)[25]. Besides, the N(Bu)$_4$Cl-urea and ChI-malonic acid are also good candidates for storing I_2 given remained mass of iodine 90.1% and 89.5%, respectively. The N$_2$ sweeping experiment simulates and

exaggerates the real atmosphere of I_2 storage in air. In other words, if the I_2 could be reliable storage under the N$_2$ sweeping conditions, then it could be more reliable storage under ambient conditions.

Furthermore, we took ChCl-urea as an example for investigation the reusability/recyclability of DESs. The experiment was carried out by TGA and the detailed procedure for the experiment was given in ESI. The experimental results showed that I_2 could be removed from ChCl-urea at 120 °C in 3 hours, which proved that the DESs are reusable for I_2 capture.

Conclusions

In conclusion, a series of DESs have been synthesized and were employed to capture and store I_2. The results show that some of the DESs have higher efficiency than the previously reported materials. Besides that, the DESs are more environmental friendly and cheaper, and could be easily prepared and without any purification. Among them, ChI-methylurea shows the best I_2 adsorption efficiency with approximative 100% after only 5 hours. Moreover, ChI-methylurea exhibits a good capability of I_2 storage with only 4.6% of the I_2 evaporated after 10 hours N$_2$ sweeping, which is also important since I_2 is easy to sublimate. Primary calculations suggested that the high effciency for I_2 capture by DESs mainly comes from the formation of halogen bonding between DESs and I_2. We could counclude that the DESs are very promising materials for large-scale industrial radioiodine removal in the future, and we will have a further investigation on it.

Acknowledgements

Notes and references

1   K. Kosaka, M. Asami, N. Kobashigawa, K. Ohkubo, H. Terada, N. Kishida and M. Akiba, *Water Res.*, 2012, **46**, 4397-4404.
2   F. C. Kupper, M. C. Feiters, B. Olofsson, T. Kaiho, S. Yanagida, M. B. Zimmermann, L. J. Carpenter, G. W. Luther, 3rd, Z. Lu, M. Jonsson and L. Kloo, *Angew. Chem., Int. Ed.*, 2011, **50**, 11598-11620.
3   E. Ostroumova, A. Rozhko, M. Hatch, K. Furukawa, O. Polyanskaya, R. J. McConnell, E. Nadyrov, S. Petrenko, G. Romanov, V. Yauseyenka, V. Drozdovitch, V. Minenko, A. Prokopovich, I. Savasteeva, L. B. Zablotska, K. Mabuchi and A. V. Brenner, *Environ. Health Perspect.*, 2013, **121**, 865-871.
4   J. P. Bleuer, Y. I. Averkin and T. Abelin, *Environ. Health Perspect.*, 1997, **105**, 1483-1486.
5   T. Kubota, S. Fukutani, T. Ohta and Y. Mahara, *J. Radioanal. Nucl. Chem.*, 2012, **296**, 981-984.
6   K. W. Chapman, P. J. Chupas and T. M. Nenoff, *J. Am. Chem. Soc.*, 2010, **132**, 8897-8899.
7   D. F. Sava, M. A. Rodriguez, K. W. Chapman, P. J. Chupas, J. A. Greathouse, P. S. Crozier and T. M. Nenoff, *J. Am. Chem. Soc.*, 2011, **133**, 12398-12401.
8   T. D. Bennett, P. J. Saines, D. A. Keen, J. C. Tan and A. K. Cheetham, *Chem. Eur. J.*, 2013, **19**, 7049-7055.
9   P. S. Huang, C. H. Kuo, C. C. Hsieh and Y. C. Horng, *Chem.*

Commun., 2012, **48**, 3227-3229.

10   H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 2004, **126**, 15844-15851.

11   B. F. Abrahams, M. Moylan, S. D. Orchard and R. Robson, *Angew. Chem., Int. Ed.*, 2003, **42**, 1848-1851.

12   Z. J. Zhang, W. Shi, Z. Niu, H. H. Li, B. Zhao, P. Cheng, D. Z. Liao and S. P. Yan, *Chem. Commun.*, 2011, **47**, 6425-6427.

13   C. Falaise, C. Volkringer, J. Facqueur, T. Bousquet, L. Gasnot and T. Loiseau, *Chem. Commun.*, 2013, **49**, 10320-10322.

14   P. Murray-Rust and W. D. S. Motherwell, *J. Am. Chem. Soc.*, 1979, **101**, 4374-4376.

15   N. Ramasubbu, R. Parthasarathy and P. Murray-Rust, *J. Am. Chem. Soc.*, 1986, **108**, 4308-4314.

16   Q. Li, X. Xu, T. Liu, B. Jing, W. Li, J. Cheng, B. Gong and J. Sun, *Phys. Chem. Chem. Phys.*, 2010, **12**, 6837.

17   C. B. Aakeroy, M. Baldrighi, J. Desper, P. Metrangolo and G. Resnati, *Chem. Eur. J.*, 2013, **19**, 16240-16247.

18   H. S. El-Sheshtawy, B. S. Bassil, K. I. Assaf, U. Kortz and W. M. Nau, *J. Am. Chem. Soc.*, 2012, **134**, 19935-19941.

19   J. P. M. Lommerse, A. J. Stone, R. Taylor and F. H. Allen, *J. Am. Chem. Soc.*, 1996, **118**, 3108-3116.

20   P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, *Angew. Chem., Int. Ed.*, 2008, **47**, 6114-6127.

21   M. G. Sarwar, B. Dragisic, E. Dimitrijevic and M. S. Taylor, *Chem. Eur. J.*, 2013, **19**, 2050-2058.

22   C. Walbaum, M. Richter, U. Sachs, I. Pantenburg, S. Riedel, A. V. Mudring and G. Meyer, *Angew. Chem., Int. Ed.*, 2013, **52**, 12732-12735.

23   Q. Li, Q. Lin, W. Li, J. Cheng, B. Gong and J. Suo, *ChemPhysChem*, 2008, **9**, 2265-2269.

24   S. V. Rosokha, C. L. Stern and J. T. Ritzert, *Chem. Eur. J.*, 2013, **19**, 8774-8788.

25   C. Yan and T. Mu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5071-5075.

26   Y. Chen, C. Yan, W. Zhao, Z. Liu and T. Mu, *RSC Adv.*, 2014, **4**, 55417-55429.

27   A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003,70-71.

28   Q. Zhang, K. De Oliveira Vigier, S. Royer and F. Jerome, *Chem. Soc. Rev.*, 2012, **41**, 7108-7146.

29   E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.*, 2014, **114**, 11060-11082.

30   D. J. G. P. van Osch, L. F. Zubeir, A. van den Bruinhorst, M. A. A. Rocha and M. C. Kroon, *Green Chem.*, 2015, **17**, 4518-4521.

31   M. Francisco, A. van den Bruinhorst and M. C. Kroon, *Angew. Chem., Int. Ed.*, 2013, **52**, 3074-3085.

32   S.-H. Liu, H. Fu, Y.-M. Cheng, K.-L. Wu, S.-T. Ho, Y. Chi and P.-T. Chou, *J. Phys. Chem. C*, 2012, **116**, 16338-16345.

33   S. F. Boys and F. Bernardi, *Mol. Phys.*, 2002, **100**, 65.

34   N. Azizi, S. Dezfooli, M. Khajeh and M. M. Hashemi, *J. Mol. Liq.*, 2013, **186**, 76-80.

35   A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142-9147.

36   K. A. Shahbaz, F. S. Mjalli, M. A. Hashim and I. M. Al Nashef, *J. Appl. Sci.*, 2010, **10**, 3349–3354.

37   M. Hayyan, F. S. Mjalli, M. A. Hashim and I. M. Al Nashef, *Fuel Process. Technol.*, 2010, **91**, 116–120.

38   E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253-3260.

39   M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377-383.

40   P. G. Jessop, D. A. Jessop, D. Fu and L. Phan, *Green Chem.*, 2012, **14**, 1245.

41   L. K. Hauru, M. Hummel, A. W. King, I. Kilpelainen and H. Sixta, *Biomacromolecules*, 2012, **13**, 2896-2905.

Green Chemistry Accepted Manuscript