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Deep Eutectic Solvents: Green Solvents for Separation Applications

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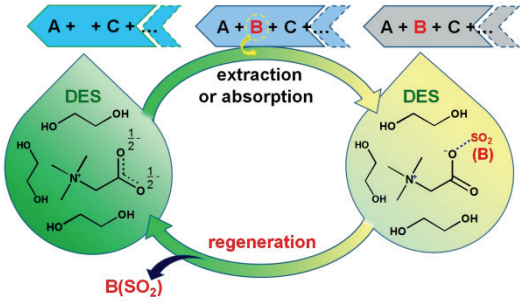
Abstract: Deep eutectic solvents (DESs) are regarded as a new class of green solvents because of their unique properties such as easy synthesis, low cost, environmental friendliness, low volatility, high dissolution power, high biodegradability, and feasibility of structural design. DESs have been widely applied for the separation of mixtures as alternatives to conventional solvents. A DES usually consists of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA). HBAs include amides, thiourea, amines, imidazole, azole, alcohols, acids and phenol. HBAs include quaternary ammonium salts, quaternary phosphonium salts, imidazolium-based salts, dication based salts, inner salts, and molecular imidazole and its analogues. Therefore, there are numerous DESs available for use in different applications. With an in-depth understanding of the common and novel properties of DESs, researchers have prepared and applied DESs to various types of separations. We first introduce the composition of DESs, including various HBDs and HBAs frequently used in the literature. Second, the properties of DESs, including phase diagrams, melting points, density, viscosity, and conductivity, are summarized. Third, recent applications of DESs in the separation of mixtures are reviewed, including the absorption of acidic gases (CO_2, SO_2 and H_2S), the extraction of bioactive compounds, extraction of sulfur- and nitrogen-containing compounds from fuel oils, extraction of phenolic compounds from oils, separation of mixtures of aromatic and aliphatic compounds, separation of alcohol and water mixtures, removal of glycerol from biodiesel, separation of alcohol and ester mixtures, removal of radioactive nuclear contaminants, and separation of isomer mixtures of benzene carboxylic acids. DESs are used in two ways for the separation of mixtures. (1) A DES prepared in advance is used as a solvent to separate a component from a mixture by selective dissolution or absorption of specific compound(s), such as the absorption of SO_2 using betaine+ethylene glycol DES. Here, DESs are used like traditional solvents. (2) A DES is formed *in situ* during the separation of mixtures by adding a HBA to a mixture containing one or more HBDs, such as the removal of phenol from an oil mixture using choline chloride, where a phenol+choline chloride DES is formed during the separation process and the formed DES does not dissolve in the oil phase. Although various DESs have been broadly developed for the separation of mixtures, research continues in the field of DESs, including analysis of the physicochemical properties of DES, especially during extraction or absorption, development of functional DESs for high-efficiency separations, development of efficient methods to regenerate DESs, and combined use of DESs with other techniques to improve separation processes. This article describes general trends in the development of DESs for separation and evaluates the problematic or challenging aspects of DESs in the separation of mixtures.



Key Words: Deep eutectic solvent; Separation of mixtures; Progress; Property; Hydrogen bond donor; Hydrogen bond acceptor

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低共熔溶剂：一种应用在混合物分离过程中的绿色溶剂

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摘要：低共熔溶剂(DESs)因具有合成容易、价格低廉、环境友好、挥发性低、溶解能力强、可生物降解、结构可设计等特点，被认为是一种绿色溶剂。近年来，研究者通过深入研究低共熔溶剂的性质，结合低共熔溶剂的特点，将其替代传统的有机溶剂，在混合物分离过程中开展了大量的研究工作，包括：酸性气体(如 CO_2、CO_2 和 H_2S)吸收、生物活性物质萃取、燃料油品中含硫和含氮化合物的脱除、油酚混合物分离、芳烃和脂肪烃混合物的分离、醇水混合物分离、生物柴油合成过程中甘油的脱除等。本文分析了低共熔溶剂的结构、性质和特点，综述了低共熔溶剂在分离领域的最新研究成果，探讨了低共熔溶剂在混合物分离应用中存在的问题，展望了低共熔溶剂的发展趋势。

关键词：低共熔溶剂；混合物分离；进展；特性；氢键受体；氢键供体

中图分类号：O645；TQ028

1 Introduction

In recent years, deep eutectic solvents (DESs) have been considered as green solvents, due to easy synthesis, structural designability and environmental friendliness. DESs have been applied in absorption and separation of mixtures. A deep eutectic is a eutectic mixture formed by compounds (usually both solids or one solid), where the eutectic temperature is considerably lower than would be predicted from the known enthalpies of fusion of the pure compounds using ideal solution theory. They usually result from strong hydrogen bond interactions. A DES has a variable composition that is close to the eutectic composition. For example, the temperature of eutectic mixtures of NaCl (m.p. 801 °C) and H_2O (m.p. 0 °C) is −21 °C, and that of choline chloride (ChCl, m.p. 303 °C) and urea (m.p. 134 °C) is 12 °C. For a long time, eutectic mixtures are studied in the inorganic research field. Up to 2003, Abbott *et al.* [1] found that quaternary ammonium salts (QASs) and amides could form liquid eutectic mixtures, called DESs, which extended DESs to the organic salt research field, broadly extending their applications.

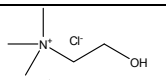
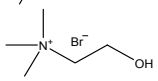
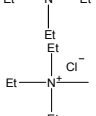
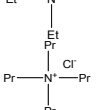
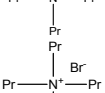
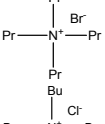
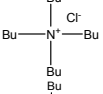
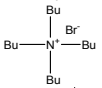
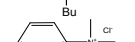
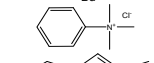
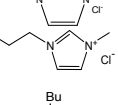
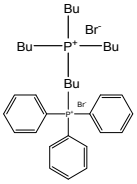
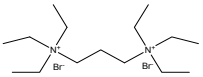
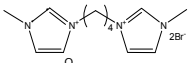
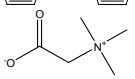
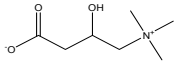
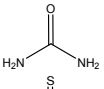
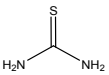
DESs reported recently in the literature are mainly composed of QASs, quaternary phosphonium salts (as hydrogen bond acceptor, HBA) and carboxylic acids, amides, alcohols (as hydrogen bond donor, HBD). Because they share many characteristics and properties with ionic liquids (ILs), a kind of green solvents, DESs are now widely acknowledged as a new class of IL analogs [1]. Compared with ILs, DESs are cheaper, easier to prepare, lower toxicity and more environmentally friendly. Hence, DESs are also considered as green solvents and have been applied in the absorption and separation of mixtures. This article reviews the recent development of DESs in absorption of acidic gases from gas mixtures, extraction of bioactive compounds, metal ions or oxides, phenols from oils and aromatic compounds from oils, desulfurization of fuels, separation of the isomers of benzene carboxylic acids (BCAs) and alcohol-ester mixtures, purifying biodiesel, and so on.

Dr. WU Weize, born in 1967, obtained his bachelor at Dalian University of Technology in 1989. Then, he worked and studied at Institute of Coal Chemistry, CAS, where he received his Ph.D. In 2002, he moved to Institute of Chemistry, CAS as an associate professor. From 2004 to 2006, he worked as a Research Fellow at the University of Nottingham, UK. In 2006, he came to Beijing University of Chemical Technology, where he is currently Professor of Chemical Engineering. His research focuses on coal conversion to chemicals, biomass conversion to chemicals, purification of flue gas, applications of DESs, ILs and SCFs in separations. He has authored more than 160 peer-reviewed papers and 18 patents.

2 Compositions of DESs

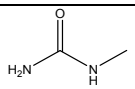
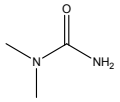
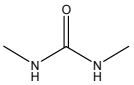
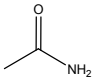
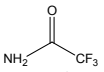
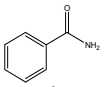
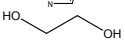
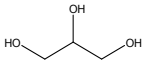
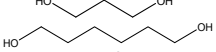
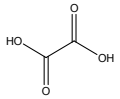
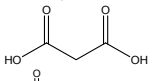
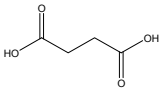
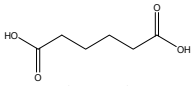
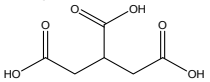
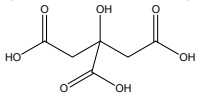
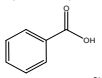
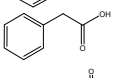
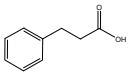
As discussed above, a DES is composed of an HBA and an HBD. Hence we summarize main HBAs and HBDs in Table 1. HBAs can be classified as QASs, imidazolium-based salts, quaternary phosphonium salts, dication based salts, inner salts, and molecular imidazole and its analogs. HBAs can be classified as water, urea, thiourea, amides, indole, azole, alcohols, acids, and phenol. Except water, ethylene glycol (EG) and glycerol (Gly), these HBAs and HBDs are usually solid at room temperature, as shown in Table 1. Normally, except water, these HBAs and HBDs have low volatility because of their ionicity or strong polarity. When an HBA and an HBD are mixed and formed a DES, the volatility of the DES become low due to the hydrogen bonding between HBA and HBD. Some HBAs and HBDs are biodegradable, like ChCl, choline bromide

Table 1 The simplified names, structures and melting points of HBAs and HBDs of DESs often used in the literature.

	Name	Simplified name	Melting point/°C	Structure
HBAs	choline chloride	ChCl	303 [2]	
	choline bromide	ChBr	287–289 [a]	
	tetramethylammonium chloride	TMAC	420 [a]	
	tetraethylammonium chloride	TEAC	39 [3]	
	triethylmethylammonium chloride	TEMAC	282 [3]	
	tetrapropylammonium chloride	TPAC	241 [3]	
	tetrapropylammonium bromide	TPAB	270 [4]	
	tetrabutylammonium chloride	TBAC	85 [5]	
	tetrabutylammonium bromide	TBAB	104 [6]	
	benzyltrimethylammonium chloride	BTMAC	243 [a]	
	1-ethyl-3-methylimidazolium chloride	EMIMCl	87 [7]	
	1-butyl-3-methylimidazolium chloride	BMIMCl	41 [8]	
	tetrabutylphosphonium bromide	TBPB	99–101 [a]	
	methyltriphenylphosphonium bromide	MTPPB	234 [9]	
	N,*N*,*N*',*N*',*N*'-hexaethyl-propane-1,3-diammonium dibromide	HPDBr	85 [10]	
	1,4-bis[*N*-(*N*'-methylimidazolium)]butane dibromide	$[C_3(MIM)_2][Br]_2$	139 [11]	
	betaine	Bet	293 [12]	
	L-carnitine	L-car	196–198 [13]	
	imidazole	IM	90 [14]	
	2-methylimidazole	2-MI	144–146 [15]	
HBDs	water	H_2O	0 [16]	
	urea	–	134 [2]	
	thiourea	Thi	175 [7]	

to be continued

continued Table 1

Name	Simplified name	Melting point/°C	Structure
1-methyl urea	MU	93 [7]	
1,1-dimethyl urea	1,1-DMU	102 [7]	
1,3-dimethyl urea	1,3-DMU	180 [7]	
acetamide	AA	80 [7]	
2,2,2-trifluoroacetamide	TFA	72 [7]	
benzamide	BA	129 [7]	
caprolactam	CPL	69 [14]	
indole	In	130 [3]	
1,2,4-triazole	Tri	119–121 [a]	
ethylene glycol	EG	−12.9 [7]	
glycerol	Gly	17.8 [7]	
1,6-hexanediol	1,6-Hex	42 [7]	
oxalic acid	OA	190 [2]	
malonic acid	MA	135 [2]	
succinic acid	SA	185 [2]	
adipic acid	AA	153 [7]	
tricarballylic acid	TCA	159 [7]	
citric acid	CA	149 [7]	
benzoic acid	BA	122 [7]	
phenylacetic acid	PAA	77 [2]	
phenylpropionic acid	PPA	48 [2]	
phenol	PhOH	41 [11]	

[a] data from Scifinder at https://scifinder.cas.org.

bromide (ChBr), betaine (Bet), L-carnitine (L-car), water, urea, EG, Gly, oxalic acid (OA), malonic acid (MA), succinic acid (SA), and citric acid (CA), because they are biomaterials or are from biomass.

3 Properties of DESs

This article focuses on the following properties of DESs: phase diagram, melting point, density, viscosity, and conductivity, which are introduced as follows.

Fig. 1 shows a typical phase diagram of two components with a eutectic point (EP) and DES. It shows that the eutectic point temperature is much lower than those of substances A and B, which may be selected from Table 1. Using Table 1, one can select an HBD and an HBA to compose a DES that can satisfy a purpose.

ChCl is frequently used as an HBA in the literature. ChCl (m.p. 303 °C) and urea (134 °C) can form a DES at a mole ratio of 1 : 2 with a eutectic point of 12 °C [2]. Choline fluoride, choline nitrate, ChCl and choline tetrafluoroborate also can form DESs with urea at mole ratios of 1 : 2 with EP temperatures of 1 °C, 4 °C, 12 °C, 67 °C, respectively [2]. The order of EP temperature, $F^- > NO_3^- > Cl^- > BF_4^-$, suggests some correlation with hydrogen bond strength. Abbott *et al.* [2] studied the EP temperatures of ChCl with oxalic acid (190 °C), malonic acid (135 °C), and succinic acid (185 °C), and found they were 34 °C, 10 °C, and 71 °C, respectively, all occurring at a mole ratio of 1 : 1, which suggests that EP temperature has not related with the length of alkyl in dicarboxylic acid as HBD.

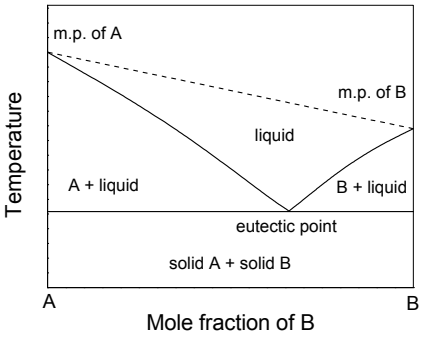


Fig. 1 Two-component *T-x* phase diagram with a eutectic point and DES (liquid).

The eutectic points occurring at a mole ratio of 1 : 1 suggests a 1 : 1 complex between the acid and chloride ion, or bridging acids between neighboring chloride ions.

Our research group studied the phase diagrams of ChCl with phenol, *o*-cresol, and 2,3-xylenol [17]. The EP temperatures of ChCl with phenol, *o*-cresol, and 2,3-xylenol are −20 °C, −23 °C, and 17 °C, at a ChCl : HBD mole ratio of 1 : 3. Phenolic compounds can serve as HBD to interact with chloride anions, but produce different lattice energies of DES, resulting in different freezing points.

Table 2 shows densities, viscosities, and conductivities of selected DESs and compared with those of two ILs. It can be seen that the densities of DESs formed by QASs and quaternary phosphonium salts with HBDs are usually greater than that of water [18]. The densities of DESs are influenced by both HBAs and HBDs as shown in Table 2. For a DES, its density decreases with increasing temperature, which is similar to ordinary solvents. Most DESs have higher viscosities than ILs, but ChCl+EG DES is lower. The conductivities of DESs are lower than ILs, due to the dilution of HBDs that are not electrically conductive.

4 Applications of DESs

The ionic nature and relatively high polarity of DESs make them have very low volatility for absorption of a gas from mixed gases, and high solubility for polar compounds and not for nonpolar compounds. Hence, the applications of DESs in absorption and separation are reviewed in this article on the following aspects: absorption of acidic gases, extraction of bioactive compounds, extraction of sulfur compounds and nitrogen compounds from fuel oils, extraction of phenolic compounds in oils, separation of aromatics and aliphatics

Table 2 Density, viscosity and conductivity of selected DESs.

DES HBA/HBD	HBA : HBD mole ratio	ρ/(g·cm^{-3}) (T/°C)	ν/(mPa·s) (T/°C)	σ/(mS·cm^{-1}) (T/°C)	Ref.
ChCl/urea	1 : 2	1.25(25)	750(25)	0.75(25)	2
ChCl/EG	1 : 2	1.12(25)	37(25)	1.12(25)	1
ChCl/glycerol	1 : 2	1.18(25)	259(25)	1.18(25)	1
ChCl/2,2,2-trifluoroacetamide	1 : 2.5	1.342(25)	77(40)	–	1
ChCl/imidozole	3 : 7	–	15(70)	12(60)	6
ChCl/phenol	1 : 3	1.095(20)	58.8(20)	2.38(20)	17
ChCl/phenol	1 : 3	1.092(25)	44.6(25)	3.14(25)	17
ChCl/phenol	1 : 3	1.089(30)	35.2(30)	3.88(30)	17
ChCl/phenol	1 : 3	1.086(35)	28.2(35)	4.77(35)	17
ChCl/phenol	1 : 3	1.083(40)	23.1(40)	5.76(40)	17
ChCl/phenol	1 : 3	1.080(45)	19.2(45)	6.77(45)	17
ChCl/*o*-cresol	1 : 3	1.071(25)	77.6(25)	1.21(25)	17
ChCl/1,4-butylene glycol	1 : 3	1.06(20)	140(20)	1.63(20)	19
MTPPB/EG	1 : 4	1.23(25)	109.8(25)	0.788(25)	19
MTPPB/Gly	1 : 1.75	1.29(25)	887.1(45)	0.165(25)	19
MTPPB/2,2,2 Trifluoroacetamide	1 : 8	1.39(25)	136.5(25)	0.848(25)	19
BTMAC/EG	1 : 3	–	201.9(55)	0.485(55)	19
BTMAC/Gly	1 : 5	–	553.7(55)	0.163(55)	19
[Bmim][BF_4]		1.14(25)	115(25)	3.5(25)	7
[Bmim][$(CF_3CO_2)_2N$]		1.43(25)	69(25)	3.9(25)	7

mixtures, separation of alcohols and water mixtures, removal of glycerol from biodiesel and other separations.

4.1 Absorption of acidic gases

4.1.1 SO_2 absorption

Sulfur dioxide (SO_2) present in flue gas is formed by burning fossil fuels with high contents of S-contained compounds. It is one of the dominant air pollutants threatening human health and the environment. While SO_2 is also a kind of chemical materials used for the making of sulfur, sulfuric acid, wine processing, and so on. Currently, flue gas desulfurization (FGD) is widely used in industry to control SO_2 emission by limestone as an absorbent. But the absorbents cannot be recycled and a huge amount of wastewater is generated, from which useful SO_2 is not recovered. Hence, it is necessary to develop renewable and efficient absorbents for removal and recovery of SO_2.

Han *et al.* [20] found that ChCl and glycerol can form a series of DESs that could quickly absorb SO_2 and the absorbed SO_2 easily desorbed. The DES with a ChCl : Gly mole ratio of 1 : 1 shows the best SO_2 absorption capacity of 0.678 $g \cdot g^{-1}$ at conditions of 20.0 °C, and 0.1 MPa of SO_2. The absorbed SO_2 in the DES could be recovered at 50.0 °C under an N_2 flow and the DES could be regenerated. While NMR results indicate that the interaction between SO_2 and DES is physical, which suggests that the DES cannot be used for the removal of SO_2 with low concentrations. In 2015, Sun *et al.* [21] also synthesized four ChCl based DESs and measured their absorption capacity of SO_2 and the results indicated that ChCl+thiourea DES showed the highest absorption capacity of 2.96 $mol \cdot mol^{-1}$ at 20 °C and 0.1 MPa of SO_2.

Duan *et al.* [22] synthesized DESs from tetrabutylammonium bromide (TBAB) and caprolactam and used them to absorb SO_2 in a mixed gas. They found that the DES with 1 : 1 mole ratio showed the highest SO_2 absorption capacity. At 25.0 °C and 0.1 MPa of SO_2, SO_2 absorption capacity can reach a mole fraction of 0.680 and the absorbed SO_2 can be recovered at a pressure of 10.1 kPa and a temperature of 110.0 °C. The DES can be reused for several times. Liu's group [14] also used caprolactam to synthesize a series of DESs. Their studies indicate that the solubilities of pure SO_2 of 0.1 MPa in caprolactam+ethanamide DES and caprolactam/imidazole are 0.497 $g \cdot g^{-1}$ and 0.624 $g \cdot g^{-1}$, respectively, at 30.0 °C. The results indicate that the absorption of SO_2 is physical. At the same time, the same group [23] synthesized ethanolamine+KSCN DESs and found that the DES with ethanolamine : KSCN mole ratio of 3 : 1 could absorb 0.588 $g \cdot g^{-1}$ DES at 20.0 °C and pure SO_2.

Dai *et al.* [24] synthesized DESs formed by 1-ethyl-3-methylimidazolium chloride (EMIMCl) and EG with different mole ratios and used them to capture SO_2. The results indicated that the SO_2 absorption capacity increased with the content of EMIMCl, and the DES with EMIMCl : EG mole ratio of 2 : 1 could capture 1.15 $g \cdot g^{-1}$ at 20 °C and 0.1 MPa of SO_2.

The above synthesized DESs can absorb high-concentration SO_2 with high absorption capacities due to the physical interaction between the DESs and SO_2. While the SO_2 concentrations in flue gas is much low, such as 0.2% (volume fraction). Therefore, it is necessary to develop functional DESs that can interact chemically with SO_2 and can capture SO_2 in flue gas with high absorption capacities.

Based on the mechanism of SO_2 absorption mechanism by functional ILs, our research group [25] designed and synthesized two kinds of functional DESs based inner salts, Bet and L-car as HBA and EG as HBD. Our results indicated that the SO_2 absorption capacities of L-car+EG DES and Bet+EG DES with a mole ratio of 1:3 were 0.820 $mol \cdot mol^{-1}$ and 0.332 $mol \cdot mol^{-1}$, respectively, at 40.0 °C and 0.002 MPa of SO_2. The results of FT-IR, ^1H NMR and ^{13}C NMR showed that $–COO^-$ on Bet or L-car had a strong chemical interaction with SO_2, as shown in Fig. 2. Because water is also an environmentally benign solvent and exists in flue gas, two kinds of functional DESs based Bet and L-car as HBA and H_2O as HBD were synthesized to capture SO_2 with low concentrations, showing high absorption capacities of SO_2 [26].

Since imidazole analogs have a base N atom that can interact with acidic SO_2 and capture low-concentration SO_2, imidazole (Im), 2-methylimidazole (2-MI), 2-ethylimidazole (2-Et), and 2-propylimidazole (2-Pr) were chosen as HBAs and Gly as HBD to prepare four DESs [27]. All the DESs show high thermostability. For instance, Im+Gly DES has a weight loss of 0.047% at 100 °C by sweeping N_2 for 6 h. The available absorption of 0.2% (volume fraction) SO_2 in Im+Gly DES was high, up to 0.634 $mol \cdot mol^{-1}$ (0.161 $g \cdot g^{-1}$) with $n_{Im} : n_{Gly} = 1 : 2$ at 40 °C.

Deng *et al.* [28] prepared several DESs using Tri and ChCl to capture SO_2. The DES of ChCl and Tri with a mole ratio of 1 : 3 can absorb 0.33% SO_2 with an absorption capacity of 0.116 $g \cdot g^{-1}$ at 30 °C.

In our previous work [29], we have found that if the pK_a of an acid is larger than that of sulfurous acid, the IL synthesized from the acid as an anion is a functional IL and can chemically absorb SO_2 with a large absorption capacity. Then we synthesized a functional absorbent, sodium lactate (NaLa). NaLa was dissolved in water and formed NaLa+H_2O DES or NaLa aqueous solution, which is environmentally benign and stable. NaLa+H_2O DES with equal mass can absorb 0.130 $g \cdot g^{-1}$ at an SO_2 concentration of 2.5% (volume fraction) and 40 °C.

4.1.2 CO_2 absorption

CO_2 is one of greenhouse gases and mainly emitted from the burning of fossil fuels. The most efficient way to reduce the

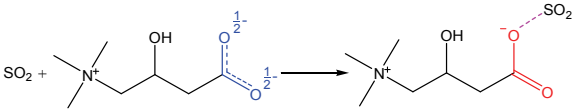


Fig. 2 The proposed mechanism of SO_2 absorption by L-car+EG DES.

emission of CO_2 is CO_2 capture after the burning of fuels, which needs efficient absorbents.

In 2008, Han *et al.* [30] studied the solubility of CO_2 in ChCl+urea DESs at temperatures from 40.0 °C to 60.0 °C and CO_2 pressures up to 13 MPa. The DES with ChCl : urea mole ratio of 1 : 2 shows the highest absorption capacity. The enthalpies of CO_2 absorption in the DESs are minor, indicating that the absorption process is exothermic. In 2013, Leron and Li [31] also used ChCl to form DESs with Gly at a ChCl : Gly mole ratio of 1 : 2, and measured the solubility of CO_2 in the DESs at temperatures from 30.0 to 70.0 °C and CO_2 pressures up to 6.3 MPa. At 30.0 °C and 1.22 MPa of CO_2 pressure, the solubility of CO_2 is 4.0% (mass fraction). Li *et al.* [32] measured CO_2 solubility in DESs formed by ChCl with different HBDs, EG, Gly and malonic acid. Francisco *et al.* [33] synthesized environmentally benign DESs of ChCl and lactic acid with a mole ratio of 1 : 2. At 30 °C and 1.655 MPa of CO_2 pressure, the DES with ChCl : lactic acid mole ratio of 1 : 2 can absorb 0.71% (*w*), which is much lower than that of ChCl+urea DESs. While ChCl+lactic acid DESs are much more stable than ChCl+urea DESs. Deng *et al.* [34] measured the solubility of CO_2 in ChCl+levulinic acid DESs and ChCl+furfuryl alcohol DESs, and calculated the dissolution Gibbs free energy, enthalpy, and entropy. Deng *et al.* [35] synthesized three kinds of guaiacol-based DESs and measured CO_2 solubility in the DESs at temperatures from 20–50 °C and pressures up to 600 kPa. The absorption of CO_2 by the above DESs is physical and follows Henry's law.

Sze *et al.* [36] synthesized DESs formed by ChCl, Gly and 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN) with mole ratios around 1 : 2 : 6, and measured CO_2 solubility in the DESs, indicating that the solubility can reach about 10 $g \cdot g^{-1}$ at 0.1 MPa of CO_2. Due to the volatility of monoethanolamine (MEA), Ali *et al.* [37] synthesized ChCl+MEA DESs and measured CO_2 solubility in the DESs, and a DES with ChCl:MEA mole ratio of 1:6 could absorb 0.075 $g \cdot g^{-1}$ at 25 °C and 1.0 MPa CO_2.

In 2016, Choi *et al.* [38] synthesized a kind of DESs using ethylenediamine as HBD for capture CO_2. They found that a DES by monoethanolamine hydrochloride and ethylenediamine with a mole ratio of 1 : 3 can capture 33.7% (*w*) CO_2 at 30 °C, 25.2% CO_2 just in 2.5 min. The result indicated that the DES used had very fast absorption rate and good reusability.

4.1.3 H_2S absorption

In 2011, Duan *et al.* [39] designed and synthesized a series of DESs by caprolactam and tetrabutyl ammonium bromide. The solubilities of H_2S in the DESs were measured at 30.0–90.0 °C and atmospheric pressure, and the solubility of H_2S in a DES with 1 : 1 mole ratio was 5.40% at 30 °C and was reused. The authors reported that there were no chemical interaction between DESs and H_2S and only physical interaction. The results suggest that the solubility of H_2S decreases with the decrease of the partial pressure of H_2S, following Henry's law.

4.2 Extraction of bioactive compounds

Recently, DESs have been gaining increasing interest as sustainable and safe solvents due to their green and efficient extraction of natural products from biomass potential applications in the pharmaceutical and biochemical industries.

Choi *et al.* [40] synthesized natural deep eutectic solvents (NADES) composed of natural compounds and investigated the extraction of phenolic compounds of diverse polarity using NADES. They demonstrated that the extractability of both polar and less polar metabolites was greater with NADES than conventional solvents. Most major phenolic compounds like safflower were recovered from NADES with a yield between 75% and 97%. The NADES are of sustainability, biodegradability, and their high solubilization power of both polar and nonpolar compounds and regarded as green solvents for extraction of bioactive compounds from natural sources.

In 2016, the same group [41] used lactic acid+glucose NADESs and 1,2-propanediol+ChCl NADESs to extract anthocyanins in flower petals of Catharanthus roseus. The two kinds of NADESs presented a similar extraction power for anthocyanins as conventional organic solvents. These NADESs are possible alternatives to existing organic solvents in health-related areas such as food, pharmaceuticals and cosmetics.

In 2015, Wang *et al.* [42] synthesized four kinds of ChCl-based DESs to extract bovine serum albumin (BSA), and optimal ChCl+glycerol DES with a mole ratio of 1 : 1 was selected as the suitable extraction solvent. 98.16% of the BSA could be extracted into the DES-rich phase in a single-step extraction. A high extraction efficiency of 94.4% was achieved, and the conditions were also applied to the extraction of trypsin. Importantly, BSA was not changed during the extraction process. The formation of DES-protein aggregates plays a significant role in the separation process.

Due to the high viscosity of DESs mixed with extracted substances, which may influence the extraction capacity and stabilizing ability of the target compounds, ultrasound-assistance method was employed in extraction with DESs, called UAE. Lee *et al.* [43] synthesized L-proline+glycerol DESs and used the DESs to extract quercetin, kaempferol and isorhamnetin glycosides from Flos sophorae with ultrasound-assistance. A sample power of 50 mg was extracted by UAE for 45 min using 1.00 mL of an aqueous solution containing 90% L-proline+glycerol DES with a mass ratio of 2 : 5, which was found to be a greener and more efficient than common extraction methods such as methanol-based UAE. Recovery of the extracted flavonoids from the DES was 75% with the use of water as an anti-solvent, and could reach as high as 92% with the simple application of C18 solid phase extraction (SPE). Redovniković *et al.* [44] synthesized ChCl+malic acid DES and found that the DES could efficiently extract wine lees anthocyanins with the ultrasound-assistance method.

In 2015, Cui *et al.* [45] extracted three major active compounds, genistin, genistein and apigenin, from pigeon pea roots using DESs and MAE. The yields of genistin, genistein and apigenin reached 0.449, 0.617 and 0.221 $mg·g^{-1}$, respectively. The above DES and MAE method show higher extraction efficiency than other extraction methods. The results showed that DES could be a kind of green solvent for fast and efficient extraction of the active ingredients from plant materials.

Bakirtzi *et al.* [46] synthesized lactic acid-based NADESs and used them to extract antioxidant polyphenols from common native Greek medicinal plants. Selected native Greek medicinal plants included dittany, fennel, marjoram, mint, and sage. The NADESs included lactic acid+ChCl, lactic acid+sodium acetate, lactic acid+ammonium acetate and lactic acid+glycine+water, with corresponding molar ratios of 3 : 1, 3 : 1, 3 : 1 and 3 : 1 : 3, respectively. The last NADES exhibited higher efficiency than others.

In 2017, Sun *et al.* [47] designed several hydrophobic DESs based on methyl trioctyl ammonium chloride as HBA to extract artemisinin from artemisia annua leaves with ultrasound assistance. A hydrophobic DES by methyl trioctyl ammonium chloride+1-butanol, named N81Cl-NBA, with a molar ratio of 1 : 4 showed the highest extraction yield. At optimal conditions of solvent/solid ratio 17.5 : 1, ultrasonic power 180 W, temperature 45 °C, particle size 80 mesh, and extraction time 70 min, an extraction yield of 8 $mg·g^{-1}$ was obtained, which is much higher than that obtained using the conventional organic solvent petroleum ether.

Peng *et al.* [48] extracted five target phenolic acids, namely chlorogenic acid, caffeic acid, 3,5-dicaffeoylquinic acid, 3,4-dicaffeoylquinic acid, and 4,5-dicaffeoylquinic acid from Lonicerae japonicae Flos using DES-MAE method. The DESs, based on the ChCl and diols, urea, glucose, sorbitols, sucrose, lactic acid, showed remarkable effects on the extraction efficiency of phenolic acids. The recovery rates of active compounds of chlorogenic acid, caffeic acid, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid, and 4,5-dicaffeoylquinic acid were 79.3%, 80.0%, 86.0%, 86.0% and 85.5%, respectively, from DESs.

Fu *et al.* [49] synthesized 14 DESs composed of ChCl and maltose and used them to extract phenolics in Cajanus cajan leaves using MAE. The optimal conditions were an extraction solvent of 20% water in ChCl/maltose (1 : 2), an extraction temperature of 60 °C, a liquid/solid ratio of 30 : 1 $mL·g^{-1}$ and an irradiation time of 12 min.

Moreover, Khezeli *et al.* [50] extracted tert-butylhydroquinone (TBHQ) from edible oils with ultrasonic assistance using DESs based on ChCl and different HBDs, like urea, EG, lactic acid, glycerol, and water. The method was successfully applied to determine TBHQ in 13 edible oil samples, which was close to the conventional L-L extraction with ethanol as solvent.

The above results indicate that NADESs are non-toxic, renewable and exceptionally efficient solvents and used as green and safe extraction solvents for extraction of bioactive compounds from natural feeds.

4.3 Extraction of metal ions and metal oxides

As we know, metal oxides are insoluble in most molecular solvents and are generally soluble in aqueous acid or alkali. The dissolution of metal oxides is important to their processes such as catalyst preparation, metal winning, and corrosion remediation.

Abbott *et al.* [51] found that ChCl+urea DESs could dissolve several metal oxides, such as ZnO, PbO_2 and CuO, and the dissolved metals were reclaimed from a mixed metal oxide matrix using electrodeposition. The reduction potentials of the metals in DESs are different, which is different with the standard aqueous reduction potentials due to the coordinated by some combination of oxide/hydroxide, chloride, and urea ligands. The measured solubilities of PbO_2, Cu_2O, ZnO, MnO_2, CuO, NiO and Fe_2O_3 were 9157, 8725, 8466, 493, 470, 325, 49 $μg·g^{-1}$ in the DES of urea+ChCl DES with a mole ratio of 1 : 2 at 60 °C.

In 2016, Kroon *et al.* [52] synthesized hydrophobic DESs from capric acid and lidocaine and used the hydrophobic DESs to remove metal ions from non-buffered water. The extraction occurs via an ion exchange mechanism in which all transition metal ions could be extracted with high distribution coefficients, even for high Co^{2+} concentrations and low DES/water mass ratios. Maximum extraction efficiency could be reached within 5 s and regeneration was possible.

4.4 Extraction of sulfur compounds and nitrogen compounds from fuel oils

4.4.1 Extraction of sulfur-contained compounds

Organic sulfides in fuels have become one of the main sources of serious pollution. Therefore, many stringent environment legislations have been issued to limit the sulfur content of fuels. The desulfurization of fuels has become a frontier scientific topic demanding prompt solution. How to efficiently remove sulfur compounds in fuel oils is important. Because of their cheap and easily obtained raw materials, higher extraction desulfurization efficiencies, and simple and environmentally friendly synthesis process, DESs have drawn much attention in the removal of organic sulfides in fuels.

Li *et al.* [53] designed and synthesized several DESs, using ChCl, tetramethylammonium chloride (TMAC), and tetrabutylammonium chloride (TBAC) as HBA, and MA, Gly, tetraethylene glycerol (TEG), EG, polyethylene glycol (PEG), and propionate (Pr) as HBD. In optimal conditions, the extraction efficiency of TBAC+PEG DES can reach as high as 82.8%, which is much higher than the traditional and functionalized ILs. After five cycles, the extraction efficiency can reach up to 99.5%. In addition, sulfur content in fuels can be reduced to less than 8.5 $μg·g^{-1}$ and deep desulfurization is realized.

In 2016, Li *et al.* [54] also designed and synthesized a series of

three-component ‘metal ions’ based deep eutectic solvents (MDESs), and investigated the extraction desulfurization performance of these MDESs. An MDES of TBAC+PEG+$FeCl_3$ with a mole ratio of 4 : 1 : 0.05 achieved the highest desulfurization efficiency, which could reach up to 89.5% for one cycle. Compared to existing traditional DESs, the extraction efficiency of these MDESs was higher. Apart from the hydrogen bonding interactions, metal ions in MDESs also act as coordination compounds, resulting in higher desulfurization efficiencies. This work may provide a way to design high efficient DESs for desulfurization of fuels.

Gano *et al.* [55] reported extractive desulfurization of simulated fuel containing dibenzothiophene (DBT) and thiophene as sulfur compounds using $FeCl_3$-based DES. The results showed that extraction efficiencies as high as 64% and 44% (for DBT and thiophene) could be achieved with the solvent in a single stage extraction, thus showing that the solvent has higher DBT removal than thiophene.

DESs provide a new route for the deep extraction desulfurization of fuels, because of their cheap and easily obtained raw materials, high desulfurization efficiencies and environmentally friendly properties, and insolubility in fuels. The hydrogen bonds formed between DESs and sulfur-contained compounds account for the high desulfurization efficiency.

4.4.2 Extraction of nitrogen compounds from fuel oils

Because of the necessity to reduce nitrogen oxide emission and improve sulfur elimination, the removal of nitrogen compounds (N-compounds) from fuels has attracted considerable attention. In 2015, Ren *et al.* [56] first reported a denitrogenation method of fuels using DESs as extractants, like ChCl+urea, ChCl+malonic acid, ChCl+phenylacetic acid DESs. ChCl+phenylacetic acid DES with a mole ratio of 1 : 2 presented the best denitrogenation performance, showing simultaneous efficient removal of both basic and non-basic N-compounds. Without chemical reactions, the extraction efficiencies of pyridine and carbazole at 35 °C with a 1 : 1 DES : oil mass ratio were 99.2% and 98.2%, respectively. This was better than the performance of compared conventional solvents. The extraction efficiency was not sensitive to the DES:oil mass ratio and temperature, and remained unchanged after four regeneration cycles.

Hizaddin *et al.* [57] screened the performance of 94 DESs based on different combinations of salt cation, anion, HBD and salt : HBD molar ratio with COSMO-RS for potential use in the extractive denitrogenation of diesel. Based on their previous results, Hizaddin *et al.* [58] synthesized TBAB+EG and tetrabutylphosphonium bromide (TBPB)+EG DESs at a molar ratio 1 : 2, and used them to remove pyrrole, pyridine, indoline and quinoline from a model diesel compound, *n*-hexadecane. Ternary (liquid+liquid) equilibrium data were measured at room temperature with nitrogen concentrations in the feed ranging from 5% to 50% (*w*), and correlated with the nonrandom two-liquid (NRTL) model.

In addition to the “green solvents” character of DESs, these results collectively demonstrate the considerable potential of DESs as promising materials for efficient denitrogenation of fuels.

4.5 Separation of phenolic compounds in oils

Phenolic compounds are basic materials for the organic chemical industry and are mainly derived from coal liquefaction, coal tar, petroleum, and biomass *via* pyrolysis. The traditional method to separate phenolic compounds from oils is alkali washing, which uses large amounts of both strong alkalis and acids and the production of excessive amounts of wastewater containing phenols. Therefore, it is necessary to develop alternative methods to separate phenols from oils.

In 2012, our research group [59, 60] found that when solid QASs was added to oil with phenolic compounds at room temperature, phenolic compounds could interact with ChCl to form DES. The DES was not soluble in oil and then phenolic compounds could be separated from oils. The effects of the structure of QAS on separation efficiency and the interaction were investigated. The separation efficiencies of phenol by NH_4Cl, TMAC, tetraethylammonium chloride (TEAC), tetrapropylammonium chloride (TPAC), and TBAC at 30.0 °C were 0, 95.5%, 99.8%, 99.3%, and 0, which means that QAS cation has a significant influence on the separation efficiency. Hydrogen bonding between QAS and phenols accounts for DES formation. DESs can be regenerated by an anti-solvent method. The water content in oil also influences on the separation because water can interact with QASs more than phenols [61].

In 2015, Li *et al.* [62, 63] found that imidazole-based compounds and amide compounds could extract phenols from coal tar *via* forming DESs with the removal efficiencies more than 90%.

Recently, our research group designed imidazolium-based dicationic ionic liquids (DILs) [11] and trimethylamine-based DILs [10] which are solid at room temperature. But the DILs could be used to separate phenolic compounds from oil mixtures *via* forming DESs with high efficiencies. Importantly, the amount of DILs is much lower than that of normal ILs, and the solubility of DILs in oil is reduced greatly. For instance, the concentration of [Bmim]Br in toluene (1.45×10^{-3} mol·dm^{-3}) was 25.3 times more than that of 1,4-bis[*N*-(*N*'-methylimidazolium)]butane dibromide (5.71×10^{-5} mol·dm^{-3}).

Interestingly, our research group [64] also found that environmentally benign quaternary ammonium-based zwitterions, betaine and L-carnitine, could be used as new extractants for the separation of phenol from model oils by forming DESs. The DESs were insoluble in model oils. Phenol in model oils could be extracted with extraction efficiencies up to 94.6% at an L-carnitine : phenol mole ratio of 0.4 and 25.0 °C. Phenol in DES could be recovered using an anti-solvent, and betaine and L-carnitine could be regenerated

and reused. Betaine and L-carnitine formed DESs with phenol through hydrogen bonding.

4.6 Separation of aromatics and aliphatics mixtures

Aromatic compounds, widely used in the chemical industry, are produced mainly from petroleum and coal processes and they are always mixed with aliphatics. The separation of aromatics from alkanes is a challenging process since these compounds have boiling points in a close range, and several combinations form azeotropes. Commercial separation methods used for this specific task are liquid-liquid extraction using organic compounds, such as sulfolane, dimethyl sulfoxide, *N*-methylpyrrolidone, and *N*-formylmorpholine. However, these organic solvents are toxic and flammable, and they can dissolve in the raffinate phase (aliphatics rich phase) when aromatics are extracted from aromatics/aliphatics mixtures. Therefore, it is necessary to develop new extraction solvents to overcome the above disadvantages. Due to their tunable properties, DESs have attracted considerable attention in the field of separating aromatics from aromatics/aliphatics mixtures.

In 2012, Kareem *et al.* [65] first used DESs to extract aromatic hydrocarbons from aromatic/aliphatic mixtures. They found that TBPB+EG DES could efficiently separate various mixtures of benzene and hexane, where HBD EG plays the main role, and HBA TBPB a second role. But it is difficult to realize both high extraction rate and selectivity. The same group [66] measured liquid-liquid equilibrium data for ternary systems of toluene and heptane with TBPB+EG and TBPB+sulfolane DESs at 40, 50 and 60 °C. The work illustrates the possibility of applying these DESs as solvents for the separation of aromatics and aliphatics mixtures.

In 2014, Mulyono *et al.* [67] studied the separation of BTEX aromatics from *n*-octane using a TBAB+sulfolane DES, and reported phase equilibrium data of the ternary system at 25 °C. There was no sulfolane in the oil phase, indicating that the interaction between TBAB and sulfolane is very strong.

Kroon *et al.* [68] synthesized DESs of tetrahexylammonium bromide (THAB)+EG, and THAB+Gly with a mole ratio 1 : 2, and used the DESs to separate aliphatic and aromatic compounds. They measured liquid-liquid-equilibrium (LLE) data of the ternary systems of hexane+benzene+DES at 25.0 °C and 35.0 °C. The results show that the DESs are promising extraction solvents for separating low aromatic concentration naphtha streams. Recently, the same group [69] synthesized several DESs using QASs (TMAC, TEAC, TBAC and THAC) as HBA and polyols (EG and Gly) as HBD. They measured LLE data of hexane+benzene+DES system at room temperature and correlated the Data with conductor-like screening model for real solvents (COSMO-RS) model.

Our research group [70] found that DES formed by levulinic acid and TBPB could efficiently separate aromatic hydrocarbons from aromatic/aliphatic mixtures. Levulinic acid/TBPB mole ratio, DES/toluene mole ratio, toluene mole fraction, and extraction temperature had an influence on the selectivity and extraction rate of toluene. The extraction could be performed at optimal conditions of 6 : 1 mol ratio of levulinic acid to TBPB and 6.4 : 1 mol ratio of DES to toluene at room temperature. The DES could be reused by distillation of toluene at 100 °C under reduced pressure.

To reveal the effect of structures of HBA and HBD on the extraction ability of DES, our research group [71] synthesized a series of DESs and evaluated their selective extraction of toluene from toluene/*n*-heptane mixtures. The results showed that the selectivity of toluene was distinctly enhanced by short side chain, small central atom of cation and large anion of HBA, together with adequate position for alkyl chain and appropriate functional group of HBD. An increase of extraction temperature could enhance the selectivity of toluene. The work provided information for designing more effective DESs for aromatics extraction.

Recently, DESs have proven to be excellent extracting agents in the separation of aromatic components from their mixtures with aliphatic compounds. These may provide an environmentally friendly method to separate aromatic/aliphatic mixtures, which avoids using a large number of toxic organic solvents.

4.7 Separation of alcohols and water mixtures

Some mixtures of alcohols and water can form azeotropes, which make them not easily separated by distillation. Nerea *et al.* [72] found that the ethanol-water azeotrope could be broken by MA + ChCl DES with a mole ratio of 1 : 1, glycolic acid+ChCl DESs with mole ratios of 1 : 1 and 3 : 1, and it can be moved to the pure ethanol side with lactic acid+ChCl with a mole ratio of 2 : 1.

Gjineci *et al.* [73] synthesized two DESs, ChCl+urea with a mole ratio of 1 : 2 and ChCl+triethylene glycol with a mole ratio of 1 : 3, and evaluated as entrainers for the separation of the ethanol/water azeotropic mixture. In all cases, an increase of the relative volatility and, consequently, a displacement of the azeotropic point was observed. Depending on the entrainer, concentrations of about 5.5%–9% (*w*) were adequate for the complete elimination of the azeotrope.

4.8 Separation of glycerol for purifying biodiesel

Biodiesel is a remarkable alternative to the decreasing resources for fossil fuels, and it can be produced from triglyceride oil. Triglyceride oil extracted from plants is transesterified into alkyl esters using a catalyst to yield 3 mol of ester and 1 mol of glycerol per mol of triglyceride used. The glycerol is an unwanted byproduct and must be removed before the biodiesel can be used as a fuel. One of the critical steps in producing biodiesel is its purification from the byproduct glycerol. Recently, DESs were used in the synthesis of biodiesel and removal of glycerol.

In 2007, Abbott *et al.* [4] found that glycerol in biodiesel could form DESs with ChCl and 3-methyl-1-ethylammonium chloride, which was used to separate glycerol from biodiesel

formed from the reaction of triglycerides with ethanol. The DES with a mole ratio of 1 : 1 shows the best performance. The ChCl in DES can be regenerated by an anti-solvent method using1-butanol. The work provides a new method to separate glycerol from biodiesel mixtures.

In 2010, Hayyan *et al.* [74] also used ChCl to separate glycerol from reaction products of palm oil-based biodiesel *via* forming DES. The results also indicate that the DESs with a mole ratio of 1 : 1 show the best performance. The lab-scale purification experiments proved the viability of the separation technique. The purified biodiesel fulfilled the EN 14214 and ASTM D 6751 standard specifications for biodiesel fuel regarding glycerine content.

A year after, Shahbaz *et al.* [75] used methyltriphenylphosphonium bromide (MTPPB) to replace ChCl as HBA to separate glycerol from reaction mixtures of palm oil-based biodiesel. Three different HBDs, namely Gly, EG and triethylene glycol, were selected to synthesize three DESs. The results revealed that the EG-based and triethylene glycol-based DESs were successful in removing all free glycerol from the palm-oil-based biodiesel.

As shown above, the previous complicated and costly purification processes involved in the production biodiesel may be simplified by using DESs.

4.9 Other applications in separation

4.9.1 Separation of mixtures of alcohols and esters

Due to their designable properties, DESs were also used in also the separation of mixtures of alcohols and esters. Maugeri *et al.* [76] found that DES could efficiently dissolve molecules containing hydrogen-bond-donors (alcohols), whereas esters remained as the second phase. A DES of Gly+ChCl with a mole ratio of 2 : 1 was used as extractant to separate mixtures of alcohols (like benzyl alcohol, n-butanol) and esters (like benzyl acetate, benzyl butyrate, and butyl acetate). Alcohols can dissolve in DES and esters do not dissolve, which results in the separation of alcohols from esters. By using this concept, tedious separation chromatographic steps may be easily overcome with bio-based nonhazardous solvents.

4.9.2 Separation of radioactive nuclear contaminants

Efficient removal and storage of radioactive nuclear contaminants are important for the application of nuclear power. In 2016, Mu *et al.* [77] proposed a method to remove and storage iodine (I_2, a model compound of radioactive nuclear contaminants) using DESs. The DESs were obtained by simply mixing two simple, cheap and biodegradable components as HBDs and HBAs. Some DESs had higher efficiencies for I_2 removal than the previously reported materials. Among them, choline iodide(ChI)-methylurea DES shows the best I_2 uptake efficiency of approximately 100% within 5 h. The high efficiency for I_2 capture by DESs mainly comes from the formation of halogen bonding between DESs and I_2. The work extended the application of DESs.

4.9.3 Separation of isomer mixtures of BCAs

Due to their similar properties and very low volatility, isomer mixtures of BCAs are very difficult to separate. In our previous work [78], we found that isomer mixtures of BCAs could be separated efficiently by ChCl, TMAC and TEAC *via* forming DESs. TEAC shows the best performance and can completely separate BPCA isomers in methyl ethyl ketone solutions. The hydrogen bond forming between QAS and BPCA results in the selective separation of BPCA isomers. QAS in DES was regenerated effectively by an anti-solvent method.

As shown above, DES methods were used in the separation of mixtures in two ways. One is that DES is formed by HBD and HBA with a mole ratio and then the DES is used to separate a compound or compounds from a mixture. For instance, DESs are used in the absorption of acidic gases, extraction of bioactive compounds, extraction of sulfur compounds and nitrogen compounds from fuel oils, separation of aromatics and alkanes mixtures. The other is that HBA is used directly to interact with HBD in a mixture and then form a DES, a new phase that does not dissolve in the previous mixture, for instance, separation of phenolic compounds in oils, separation of alcohols and water mixtures, and removal of glycerol from biodiesel. The second method needs a very low amount of extractant. For instance, not more than one mole of ChCl is needed to separate one mole phenol from oil mixtures *via* forming DES.

5 Conclusions

This review summarizes the properties of DESs and their applications in the past decade. The similarity in physical properties between DESs and ILs suggests that they belong in the same class of liquid which is distinct from molecular liquids. While DESs are found to be biodegradable and easily prepared, ILs exhibited lower biodegradation capacity and more complicated than DESs. The disparity in chemical properties between DESs and ILs means that DESs have different application fields than those of ILs. The properties of DESs make them suitable for efficient separation. In the past decade, DESs have been applied in absorption of acidic gases, extraction of bioactive compounds, extraction of sulfur compounds and nitrogen compounds from fuel oils, separation of phenolic compounds in oils, separation of aromatics and aliphatics mixtures, separation of alcohols and water mixtures, removal of glycerol from biodiesel and other separations, which show a bright future in applications.

Although various DESs have been broadly developed for separations, many studies are still needed for the further development of DESs. First, the properties of DES in physical chemistry are seldom reported in the literature, such as the property of DES with extract or absorbed acidic gases, specific heat capacity, extraction or absorption heat. Second, the compositional flexibility can allow the preparation of new DESs, and more promising properties of DESs can be developed for novel applications, especially functional DESs.

Third, extracts, such as bioactive compounds, are always polar and have low volatility, while DESs also have very low volatility. Hence, it is necessary to develop efficient methods to regenerate DESs for reuse. Fourth, due to the high viscosity of some DESs, it is better to be combined with other techniques, such as ultrasound assistance and ultrasound assistance, to intensify extraction processes.

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