NJC



View Article Online PAPER



Cite this: New J. Chem., 2017, 41, 290

Received (in Montpellier, France) 7th October 2016, Accepted 28th November 2016

DOI: 10.1039/c6nj03140d

www.rsc.org/njc

Screening of deep eutectic solvents (DESs) as green CO2 sorbents: from solubility to viscosity†

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Deep eutectic solvents (DESs) as ionic liquid (IL) analogues show great potential for CO2 capture. They exhibit favorable solvent properties and are considered to be economical alternatives to conventional ILs. In this study, we prepare 35 DESs and screen them in terms of their CO₂ solubility and viscosity, both crucial factors to be considered when designing efficient CO2 sorbents. The influence of salt and HBD type and structure, as well their molar ratio on the CO2 solubility and viscosity of the DESs is investigated. The viscosity and CO2 solubility of the DESs are compared with those of other DESs and conventional ILs. 15 DESs, which exhibit comparable CO2 absorption capacity to choline chloride-urea DESs, glycerol DESs and fluorinated ILs, are chosen as the promising ones. The viscosities of the selected DESs are below 200 mPa s and are lower than those of choline chloride-based DESs. Since the viscosity of the DESs is relatively high, on a par with those of conventional ILs, the effect of water as a co-solvent is investigated in order to decrease the viscosity. The addition of water to the glycerol-based DESs improves the kinetics of absorption by decreasing the viscosity, thus increasing the CO2 absorption capacity. Dry or aqueous DESs that demonstrate a high sorption capacity and low viscosity are chosen for additional analysis and characterization, and further functionalization will be carried out in the future to improve their sorption capacity.

1. Introduction

The anthropogenic emission of CO₂ results in global warming and remains a matter of great concern in our time. Carbon capture and storage (CCS) is one feasible solution to reduce CO₂ emissions from fossil fuel combustion, which is the largest human source of CO₂. Developing new technologies to inexpensively and efficiently capture CO2 is of great importance. 1-4 Current technologies for CO₂ capture from power plants are mainly based on aqueous amine solutions. Generally, the amine-based technologies result in high energy penalties in the regeneration of sorbent. Due to the volatile and corrosive nature of amine sorbents, they are considered as potential threats to the environment and humans.5-7

Using ionic liquids (ILs) for reversible CO2 capture is proposed as one of the most promising methods, due to the inherent advantages of ILs over traditional aqueous amine

solutions. ILs are well known as physical CO₂ sorbents with high CO₂ solubility, and their CO₂-philicity can be tuned by choosing an appropriate anion or cation. Taking the advantages of the tunability of ILs into consideration, task specified ILs can be designed to chemically react with CO2.8,9 For example, taskspecific ILs that contain amine groups are capable of reversibly bonding CO₂ molecules via the formation of carbamate salts. However, employing ILs for CO₂ capture in large scale industrial applications is hindered due to several drawbacks such as high viscosity and complicated and high-cost synthesis and purification processes. Furthermore, there are growing concerns in regard to the toxicity of several ILs. 10,11

Deep eutectic solvents (DESs) are a new class of ILs containing asymmetric and large ions with low lattice energy and hence low melting points.¹² DESs are typically formed by mixing a hydrogen bond acceptor (HBA) (quaternary ammonium or phosphonium salts) and a hydrogen bond donor (HBD) such as a carboxylic acid, amide, amine, alcohol or metal halide. An appropriate molar ratio is required to form a eutectic mixture with a lower melting point. HBAs and HBDs are able to interact with each other via hydrogen bonds. 13,14 The hydrogen bonding results in charge delocalization between the HBA and HBD and consequently, the freezing point of the eutectic mixture is much lower compared to the individual compounds.¹⁵ Meanwhile, their physicochemical properties depend on the nature of HBA and HBD, as well as the molar ratio of HBA: HBD. These compounds have acquired remarkable

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^{10.1039/}c6nj03140d

attention due to their inherent advantages, such as high thermal and chemical stability, negligible vapour pressure, non-flammability and broad adjustability, making them promising alternatives for common organic solvents in industrial applications. These new solvents have been employed in different areas of chemistry like metal extraction, 12 nanotechnology, 16 separation processes, 17 stabilization of DNA, 18 material chemistry, 19 organic synthesis 20 and so on. DESs can be easily prepared at a low cost and in high purity without further purification. Many inexpensive quaternary salts are available, in addition to a wide choice of cheap, biodegradable and non-toxic HBDs. Therefore, it is possible to form many novel and inexpensive DES systems. 15,21 Indeed, DESs are considered to be a green and environmentally benign CO2 capture medium, and they have been extensively explored during the last few decades due to their similarities with ILs.

The first DES was introduced by Abbott et al. 22 It was made up of choline chloride (ChCl) and urea in a molar ratio of 1:2. Both of these components are non-toxic, readily available and biodegradable.²² Recently, the possibility of applying DESs as CO2 separation media has been extensively surveyed. For the first time, Li et al. reported on the solubility of CO2 in eutectic mixtures of ChCl and urea in molar ratios of 1:1.5, 1:2 and 1:2.5, as a function of pressure (up to 13 MPa) and temperature (313.15, 323.15 and 333.15 K).²³ Their studies revealed that the CO₂ solubility in the DESs depends on the molar ratio of salt-to-HBD, pressure and temperature. The CO₂ solubility increased with increasing pressure and decreasing temperature. Among the investigated DESs, ChCl-urea (1:2) exhibited the highest solubility. The CO₂ solubilities in the studied DESs were in the same order as those of ammonium-based ILs, but were lower than those of imidazolium-based ILs under similar conditions. The nature of HBDs has a significant influence on the CO2 solubility in DESs. For example, by choosing lactic acid as the HBD, the CO₂ absorption capacity is lower than that of ureabased DESs with an identical molar ratio (1:2).24 On the contrary, using glycerol or ethylene glycol as the HBD results in the promotion of the CO₂ absorption capacity up to the level of that of imidazolium-based ILs. 25,26 All these DESs are capable of physically absorbing CO₂. Sze and coworkers reported the first task-specific DES system composed of ChCl, glycerol, and a superbase.²⁷ The superbase was responsible for the deprotonation of the OH groups in glycerol and ChCl, resulting in the formation of active alkoxide anions. This species facilitated the reversible capture of CO₂ under ambient conditions. However, compared to conventional ILs, research on DESs as CO2 sorbents is still limited, and the CO₂ absorption capacities of the available DESs are still relatively low.

The main goal of our study is to develop novel DESs with high CO₂ sorption capacity and low viscosity for CO₂ separation. To achieve this, 35 DESs are synthesized as the first step, in order to understand how the HBD, HBA and other factors affect the properties of DESs. The synthesized DESs are screened based on their viscosity and CO₂ absorption capacity to find appropriate DESs for CO₂ separation. Following this study, the performance of the promising DESs will be improved by functionalization or the addition of appropriate co-solvents.

2. Experimental section

2.1. Chemicals

 CO_2 (mole fraction $\geq 99.9\%$) was received from AGA AB (Linde group). N-Benzyl-2-hydroxy-N,N-dimethyl ethanaminium choride (BHDE) and octanoic acid (OCT) were delivered by Sigma-Aldrich. Acetic acid (AC), ethanolamine (EA) and urea were purchased from Shanghai Shenbo Chemical Company, VWR, and Merck, respectively. Lactic acid (LA) and 1,2-propanediol (1,2-PDO) were obtained from Shanghai Lingfeng chemical reagent company. Choline chloride (ChCl), benzyltimethylammonium chloride (BTMA) and glycerol (Gly) were purchased from the Simopharm chemical reagent company. Benzyltriethylammonium chloride (BTEA), guanidinium hydrochloride (Gua), methyltriphenyl phosphonium bromide (MTPP), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetraethylammonium chloride (TEAC), triethylmethylammonim chloride (TEMA), tetramethylammonium chloride (TMAC), tetrapropylammonium chloride (TPAC), ethylene glycol (EG) and levulinic acid (LV) were purchased from the Aladdin company. All chemicals were analytical grade reagents and were used as received.

2.2. Preparation of DESs

In the present work, we synthesized 35 novel DESs composed of ammonium or phosphonium salts and different HBDs. The eutectic mixtures were prepared by mixing the appropriate molar ratio of salt and HBD under vigorous stirring at 333-353 K. The resulting clear homogeneous and colourless solution was stirred for an additional 2 hours and then left to cool down to room temperature. At this stage, the DESs were ready to use and no purification step was needed. The reason for this is that during preparation of the DESs, no solvents were employed and the obtained mixture was pure. The melting points of all synthesized DESs are lower than room temperature, i.e. all DESs are in the liquid phase at room temperature. Table 1 shows the abbreviations for the synthesized DESs and lists their compositions.

2.3. CO₂ solubility measurements

CO₂ solubility measurements were performed on a vapor-liquid equilibrium set-up. The employed set-up used in this work is described in previous works.^{28,29} The apparatus contains a gas reservoir, an equilibrium cell, a magnetic stirrer and two pressure transducers with a precision of 0.075%. During measurements, the equilibrium cell and gas reservoir were placed in a water bath where the temperature was kept constant using a thermostat with an accuracy of ± 0.1 K. An adequate amount of the DES sample was loaded into the equilibrium cell. After that, an appropriate amount of gas was introduced into the equilibrium cell and dissolved in the solvent. The pressure of the equilibrium cell was then recorded. When the pressure became constant, this point was indicated as the equilibrium state and the corresponding pressure was measured. Using the pressure changes in the gas reservoir, the equilibrium pressure and the volume of the equilibrium cell, the number of moles of dissolved gas in the liquid phase was determined by assuming that only CO₂ existed in the vapour phase. This is a reasonable

Table 1 DESs synthesized in this work

DES	Salt	HBD	Molar ratio (salt: HBD	
BHDE-AC	N-Benzyl-2-hydroxy-N,N-dimethyl ethanaminium chloride	Acetic acid	1:2	
BHDE-LA	N-Benzyl-2-hydroxy-N,N-dimethyl ethanaminium chloride	Lactic acid	1:2	
BDDE-GLY-H ₂ O	N-Benzyl-2-hydroxy-N,N-dimethyl ethanaminium chloride	Glycerol-H ₂ O	1:3:0.11	
BTEA-AC	Benzyltriethylammonium chloride	Acetic acid	1:2	
BTMA-AC	Benzyltrimethylammonium chloride	Acetic acid	1:2	
BTMA-GLY	Benzyltrimethylammonium chloride	Glycerol	1:2	
BTMA-GLY-H ₂ O	Benzyltrimethylammonium chloride	Glycerol-H ₂ O	1:2:0.05	
BTMA-GLY-H ₂ O	Benzyltrimethylammonium chloride	Glycerol-H ₂ O	1:2:0.11	
ChCl-EA	Choline chloride	Ethanolamine	1:7	
ChCl-GLY-AC	Choline chloride	Glycerol-acetic acid	1:1:1	
Gua-EA	Guanidinium hydrochloride	Ethanolamine	1:2	
MTPP-1,2-PDO	Methyltriphenyl phosphonium bromide	1,2-Propanediol	1:4	
MTPP-AC	Methyltriphenyl phosphonium bromide	Acetic acid	1:4	
MTPP-EG	Methyltriphenyl phosphonium bromide	Ethylene glycol	1:3	
MTPP-GLY	Methyltriphenyl phosphonium bromide	Glycerol	1:4	
MTPP-LV	Methyltriphenyl phosphonium bromide	Levulinic acid	1:3	
MTPP-LV-AC	Methyltriphenyl phosphonium bromide	Levulinic acid-acetic acid	1:3:0.03	
TBAB-AC	Tetrabutylammonium bromide	Acetic acid	1:2	
TBAB-EA	Tetrabutylammonium bromide	Ethanolamine	1:6	
TBAB-EA	Tetrabutylammonium bromide	Ethanolamine	1:7	
TBAC-AC	Tetrabutylammonium chloride	Acetic acid	1:2	
TEAC-AC	Tetraethylammonium chloride	Acetic acid	1:2	
TEAC-AC	Tetraethylammonium chloride	Acetic acid	1:3	
TEAC-OCT	Tetraethylammonium chloride	Octanoic acid	1:3	
TEMA-AC	Triethylmethylammonium chloride	Acetic acid	1:2	
TEMA-EG	Triethylmethylammonium chloride	Ethylene glycol	1:2	
TEMA-GLY	Triethylmethylammonium chloride	Glycerol	1:2	
TEMA-GLY-H ₂ O	Triethylmethylammonium chloride	Glycerol-H ₂ O	1:2:0.05	
TEMA-GLY-H ₂ O	Triethylmethylammonium chloride	Glycerol-H ₂ O	1:2:0.11	
TEMA-LA	Triethylmethylammonium chloride	Lactic acid	1:2	
TEMA-LV	Triethylmethylammonium chloride	Levulinic acid	1:2	
TMAC-AC	Tetramethylammonium chloride	Acetic acid	1:4	
TPAC-AC	Tetrapropylammonium chloride	Acetic acid	1:6	
TPAC-EA	Tetrapropylammonium chloride	Ethanolamine	1:4	
TPAC-EA	Tetrapropylammonium chloride	Ethanolamine	1:7	

assumption, as the vapour pressures of DESs are negligible. In this work, the CO₂ solubility was measured at pressures of up to 2 MPa at 298.15 K. The overall uncertainty of the CO₂ solubility measurement, which includes system errors in the pressure (0.075%), temperature (0.1 K) and volumes of the gas reservoir and the equilibrium cell ($\pm 0.5~\text{mL}$), was estimated to be within $\pm 0.01.$

2.4. Viscosity measurements

The viscosity of the DESs was measured using a Bohlin CVO 100 rheometer. The lower plate had a diameter of 60 mm. A cone-onplate geometry was used with a 1° cone angle and a 20 mm cone diameter. The viscosity measurements were carried out in the temperature range of 293.15-333.15 K.

3. Results and discussion

3.1. CO₂ solubility

3.1.1. Validation of the experimental method. Before measuring the CO₂ solubility in the synthesized DESs, to validate our experimental method, we measured the CO₂ solubility in ethylene glycol (at 303.15 K), in ChCl-1,2-propanediol DES (1:2, at 308.15 K), and in water (at 308.15 K). The measured CO₂ solubilities in these three samples were compared with the

experimental data reported in the literature. The comparison is presented in Fig. 1. As can be seen, the results obtained in this work agree well with those reported in the literature, confirming the validity of our experimental method as well as the reliability of our reported data. 30-32

3.1.2. CO₂ solubility in the synthesized DESs. The CO₂ solubility in the synthesized DESs was further measured at 298.15 K and pressures of up to 2 MPa. The measured experimental data for all studied systems are reported in Table 2. Based on the measured experimental results for the different DESs, the influence of salt and HBD type, their structure, molar ratio and pressure on CO2 solubility was further analyzed and discussed. The influence of these different factors on the CO₂ solubility of the DESs is described below:

Pressure. For all the studied systems, the solubility increased with increasing pressure, as is typically expected for gas solubility in liquids. Generally, the CO2 solubility in the DESs follows Henry's law, *i.e.*, the CO₂ solubility is proportional to its partial pressure.³³

Nature of the HBD. The type of HBD used affected the CO₂ solubility of the DESs. As an example, the CO₂ solubility in the DESs composed of tetraethylammonium chloride as the HBA, as well as acetic acid, lactic acid or levulinic acid as the HBD, is depicted in Fig. 2. As can be seen, the studied systems follow

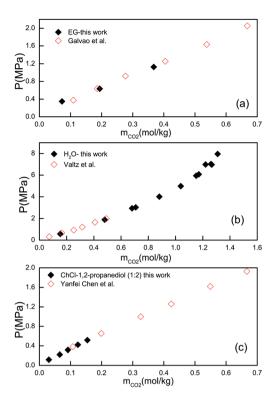


Fig. 1 Solubility of CO₂ in (a) ethylene glycol, (b) H₂O and (c) ChCl-1,2propanediol (1:2).

the trend: TEMA-LA < TEMA-LV < TEMA-AC. These differences are attributed to the interactions between the groups in the HBDs and CO2.

Based on the molecular structure of the HBDs in lactic acid, due to the vicinity of the hydroxyl group to the carboxylic group, the intermolecular hydrogen bonds are stronger compared to those of levulinic acid or acetic acid, and thus it is difficult to break intermolecular hydrogen bonds to interact with CO2 molecules. Consequently, the CO2 solubility in the lactic acidbased DES is the lowest. In the case of acetic acid, the intermolecular hydrogen bonds are the weakest.

Consequently, acetic acid molecules can interact with CO₂ easily, and thus the CO2 solubility in the acetic acid-based DES is higher than that of the other DESs.

Alkyl chain length in the HBA or HBD. The comparison of CO₂ solubility in the acetic acid-based DESs indicates that the CO₂ solubility increases with increasing alkyl chain length of the HBA. For example, the CO₂ solubility increased from 1.177 to 1.411 mol kg⁻¹ when the alkyl chain length increased from ethyl to butyl (i.e. from tetraethylammonium to tetrabutylammonium).

Similarly, the increase in the number of carbon atoms in the alkyl chain of HBD also leads to an increase of CO2 solubility. For example, by increasing the alkyl chain length from acetic acid to octanoic acid in TEAC-AC and TEAC-OCT, the CO2 solubility increased from 1.230 to 1.390 mol kg^{-1} . It is plausible that the length of the alkyl chain had a significant effect on the free volume within the DESs. 34,35 By increasing the alkyl chain length, the molar volume and the free volume consequently

Table 2 CO₂ solubility (m_{CO_2}) as a function of pressure in the synthesized DESs at T = 298.15 K

P/MPa	$m_{{ m CO}_2}$	P/MPa	m_{CO_2}			
BHDE-AC (1:2	2)	BHDE-LA (1	BHDE-LA (1:2)			
0.210	0.064	0.283	0.016			
0.533	0.199	0.516	0.043			
0.857	0.313	0.866	0.122			
1.167	0.463	1.134	0.179			
1.440	0.621	1.458	0.279			
1.771	0.775	1.722	0.391			
2.026	0.843	2.086	0.498			
BTMA-AC (1:2	2)	BTMA-GLY (1:2)			
0.219	0.078	0.394	0.037			
0.530	0.271	0.672	0.056			
0.886	0.713	0.999	0.096			
.141	0.937	1.345	0.177			
.563	1.108	1.711	0.227			
1.874	1.308	2.026	0.259			
.037	1.454					
ChCl-EA (1:7)		ChCl-GLY-A	C (1:1:1)			
0.182	0.784	0.262	0.052			
.346	1.902	0.542	0.112			
.651	2.700	0.833	0.177			
.010	2.829	1.134	0.289			
.365	3.183	1.426	0.342			
.741	3.511	1.746	0.385			
.035	3.584	2.011	0.433			
MTPP-AC (1:4	n)	MTPP-EG (1	• 3)			
0.173	*	,	,			
	0.073	0.192	0.045			
0.380	0.213	0.437	0.090			
.652	0.390	0.710	0.137			
.938	0.710	1.134	0.192			
.134	1.008	1.528	0.244			
.524	1.760	2.018	0.352			
.843	2.257					
.014	3.022					
MTPP-LV-AC	(1:3:0.03)	TBAB-AC (1:	2)			
.287	0.175	0.388	0.137			
.516	0.327	0.715	0.380			
.850	0.505	1.302	0.665			
.312	0.777	1.730	0.885			
.633	1.070	2.011	1.130			
.061	1.316					
BAC-AC (1:2)	TEAC-AC (1:	2)			
.348	0.184	0.281	0.144			
.631	0.393	0.530	0.284			
.943	0.606	0.822	0.482			
.319	0.869	1.304	0.683			
.673	1.188	1.699	0.929			
.002	1.411	2.018	1.177			
EMA AC (1)))	TEMA EC (4	. 2)			
EMA-AC (1:2		TEMA-EG (1	,			
.198	0.081	0.138	0.062			
.413	0.192	0.314	0.199			
.806	0.419	0.543	0.381			
.155	0.612	0.802	0.474			
	0.810	1.041	0.575			
	0.985	1.345	0.626			
.624	1.176					
.624						
624 837 CEMA-GLY (1	,		, ,			
410 624 837 FEMA-GLY (1	(2) 0.017	TEMA-GLY-I 0.226	H ₂ O (1:2:0.05) 0.009			
.624 .837 EMA-GLY (1	,		,			
.624 .837 CEMA-GLY (1 .150	0.017	0.226	0.009			
.624 .837 EMA-GLY (1 .150 .420	0.017 0.059	$0.226 \\ 0.544$	0.009 0.032			
.624 .837 EMA-GLY (1: .150 .420 .833	0.017 0.059 0.126	0.226 0.544 0.854	0.032 0.098			

Table 2 (continued)

Tuble 2 (continue	-u j				
P/MPa	m_{CO_2}	P/MPa	m_{CO_2}		
TPAC-AC (1:6)		TPAC-EA (1:4)			
0.350	0.251	0.481	0.338		
0.554	0.481	0.784	0.636		
	0.722				
0.826		1.057	0.935		
1.220	1.010	1.317	1.148		
1.652	1.373	1.700	1.294		
2.030	1.721	2.009	1.427		
DIFF. 0111 11 0	(4 2 2 44)	PPT 4 C (4 a)			
BHDE-GLY-H ₂ O	` ,	BTEA-AC (1:2)			
0.233	0.037	0.325	0.127		
0.542	0.048	0.551	0.265		
0.854	0.083	0.957	0.417		
1.214	0.119	1.377	0.595		
1.636	0.144	1.664	0.785		
2.016	0.206	2.054	0.974		
BTMA-GLY-H ₂ O	(1:2:0.05)	BTMA-GLY-H ₂ O (1:2:0.011)		
0.208	0.044	0.255	0.016		
0.530	0.089	0.616	0.062		
0.831	0.139	1.041	0.087		
1.121	0.177	1.442	0.140		
1.547		1.746	0.255		
	0.225				
1.767	0.260	2.031	0.325		
2.018	0.285				
Gua-EA (1:2)		MTPP-1,2-PDO (1:	. 4)		
0.226	0.206	,	· · · · · ·		
	0.306	0.220	0.022		
0.563	0.827	0.528	0.095		
0.836	1.183	0.861	0.228		
1.129	1.357	1.120	0.296		
1.480	1.433	1.547	0.383		
1.787	1.531	1.834	0.487		
2.025	1.663	2.026	0.549		
MTPP-GLY (1:4)		MTPP-LV (1:3)			
0.161	0.009	0.301	0.024		
0.443	0.033	0.698	0.072		
0.875	0.111	0.994	0.161		
1.225	0.203	1.209	0.272		
1.696	0.258	1.526	0.400		
2.026	0.289	1.759	0.572		
		2.068	0.688		
		2.000	0.000		
TBAB-EA (1:6)		TBAB-EA (1:7)			
0.351	0.439	0.381	0.533		
0.654	1.036	0.637	1.208		
0.918	2.104	0.940	2.142		
1.172	2.445	1.251	2.650		
1.645	2.665	1.627	2.888		
2.021	2.779	2.040	3.009		
2.021	2.773	2.040	3.003		
TEAC-AC (1:3)		TEAC-OCT (1:3)			
0.397	0.126	0.353	0.157		
0.654	0.315	0.624	0.342		
0.957	0.506	0.940	0.600		
1.230	0.731	1.277	0.850		
1.634	0.982	1.619	1.102		
2.016	1.230	2.018	1.390		
TEMA-LA (1:2)		TEMA-LV (1:2)			
, ,	0.047		0.057		
0.143	0.047	0.136	0.057		
0.418	0.109	0.409	0.163		
0.938	0.265	0.735	0.310		
1.265	0.369	1.043	0.439		
1.500	0.453	1.617	0.613		
1.863	0.532				
TTT (
TEMA-GLY-H ₂ O (TMAC-AC (1:4)	0.4		
0.135	0.025	0.294	0.120		
0.427	0.202	0.519	0.296		

Table 2 (continued)

P/MPa	m_{CO_2}	P/MPa	m_{CO_2}
0.731	0.322	0.882	0.518
1.015	0.383	1.297	0.810
1.312	0.458	1.718	1.218
1.741	0.663	2.096	1.560
TPAC-EA (1:	7)		
0.357	1.714		
0.645	2.051		
0.952	2.683		
1.232	3.157		
1.673	3.441		
2.019	3.525		

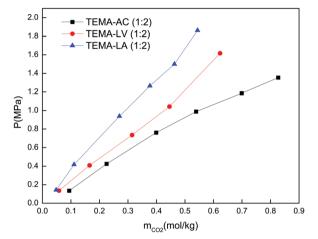


Fig. 2 CO₂ solubility in TEMA-based DES at 298.15 K.

increase, and the increased free volume results in higher CO2 solubility. 36,37 Therefore, we can conclude that the underlying reason for the observed trend is related to the free volume mechanism, as the DESs with a longer alkyl chain exhibit a lower density and a larger free volume.35

Nature of the salt. The CO₂ solubilities in the DESs that were made up of three different salts and ethanolamine as the HBD in a molar ratio of 1:7 were compared. The CO2 solubilities in TPAC-EA, TBAB-EA and ChCl-EA under identical conditions were 3.525, 3.009 and 3.584 mol kg⁻¹, respectively, and they followed the trend: TBAB-EA < TPAC-EA < ChCl-EA.

The symmetry of the salt. The CO₂ solubility in the DES composed of tetraethylammonium chloride-acetic acid (1:2) at 298.15 K and 2 MPa was 1.235 mol kg⁻¹. By introducing one benzyl group instead of one ethyl group, the CO2 solubility was changed to 0.974 mol kg⁻¹ in benzyltriethylammonium chlorideacetic acid (1:2) due to the change in salt symmetry.

Using water as a co-solvent. The DESs consisting of glycerol as the HBD exhibited high viscosity. Meanwhile, their viscosities increased considerably with an increase in the amount of dissolved CO2. To cope with this problem, we chose H2O as a co-solvent to decrease the viscosity of these DESs in order to improve the kinetics of CO2 absorption. In the studied systems,

the addition of 0.11 mol of H₂O to the DES of BTMA-GLY (1:2) resulted in a considerably reduced viscosity from 716.55 to 20.36 mPa s at 298.15 K, and an increased CO2 solubility from $0.259 \text{ to } 0.325 \text{ mol kg}^{-1}$. The contribution of H_2O to the uptake of CO2 was very limited. By further increasing the amount of H₂O, the gas solubility decreased at a constant temperature and pressure due to the low solubility of CO2 in H2O. Similar behaviour was reported for (2-hydroxyethyl)-trimethyl-ammonium (S)-2-pyrrolidine-carboxylic acid salt [Cholin][Pro]-polyethylene glycol 200 (PEG200) by Li et al.38 The addition of PEG200 also resulted in a decrease in viscosity of the IL and thus improved the CO2 absorption rate. However, PEG200 exhibited a limited contribution to the CO₂ absorption capacity, and the CO₂ solubility decreased with increasing the amount of PEG200 due to the low solubility of CO₂ in PEG200.³⁸

Based on the results presented in Table 2, 15 DESs which exhibited CO₂ solubilities above 1 mol kg⁻¹ were considered as promising candidates to carry out the comparative study detailed in Section 3.3. These promising DESs were: BTEA-AC, BTMA-AC, ChCl-EA, Gua-EA, MTPP-AC, MTPP-LV-AC, TBAB-AC, TBAB-EA, TBAC-AC, TEAC-AC, TEAC-OCT, TEMA-AC, TMAC-AC, TPAC-AC and TPAC-EA.

3.2. Viscosity

Viscosity describes the resistance of a fluid to flow and in fact, it is a measure of the internal friction of a moving fluid.³⁹ DESs, similar to conventional ILs, have a relatively higher viscosity in comparison to other organic solvents, causing problems in handling, filtering and stirring. Investigating the viscosity of DESs for industrial applications, such as CO₂ capture processes, is very important.

For some DESs during the CO₂ capture process, the viscosity increases with increasing amount of CO₂. ^{7,27,40,41} The increase in viscosity results in a reduction in the heat and mass transfer, which in turn results in a decreased CO2 absorption rate and higher energy utilization in the CO₂ separation cycle. In order to capture CO2 with a high efficiency, it is essential to obtain a balance between the viscosity and the CO₂ absorption capacity. In this work, the viscosities of the synthesized DESs were measured in the temperature range of 293.15-333.15 K. The measured results are listed in Table 3. The viscosity of the DESs is sensitive to temperature, the type of salt and HBD, the salt symmetry, the water content of the DESs and the molar ratio of salt: HBD.

- 3.2.1. Temperature. Increasing the temperature had a converse effect on viscosity. The reason is that high temperatures promote molecular movement and kinetic energy, thus weakening the attractive forces between molecules and contributing to decreasing viscosity. For all the studied DESs, the viscosity decreased with increasing temperature.
- **3.2.2. HBD type.** The effect of the nature of the HBD on the viscosity is undeniable. The presence of carboxylic or hydroxyl groups leads to the establishment of hydrogen bonds, thus resulting in increased viscosity. As an example, glycerol contains three hydroxyl groups, which are capable of forming a strong hydrogen bond network. The strong hydrogen bond

network results in low mobility of free species within the DES. Therefore, the DESs based on glycerol exhibit high viscosity, and this is illustrated by our experimental results listed in Table 3.

The comparison of the viscosity of the DESs composed of TEMA-GLY and TEMA-EG reveals that the presence of one extra hydroxyl group in glycerol compared to ethylene glycol gives rise to higher viscosity (from 41.69 to 236.59 mPa s at 298.15 K). The increased viscosity is attributed to the establishment of an extensive hydrogen bond network. On the basis of hole theory, the DESs containing bigger HBD molecules give rise to an increased ionic radius due to the formation of a hydrogen bond network between anions and HBDs, resulting in a very small free volume. The extensive hydrogen bond network lowers the mobility of free species within the DESs, and thus results in higher viscosity. 42,43

- 3.2.3. Alkyl chain length of HBD. The alkyl chain length of the HBD and that of the salt affected the viscosity of the DESs. As demonstrated, for the DESs based on triethylmethylammonium chloride (TEAC), an increase in the alkyl chain length of HBD from acetic acid to octanoic acid led to an increase in the viscosity from 21.50 to 65.86 mPa s at 298.15 K.
- 3.2.4. Molar ratio of (salt: HBD). By increasing the molar ratio of salt: HBD, the viscosity of the synthesized DESs decreased. For example, the viscosity of TPAC-EA at 298.15 K decreased from 55.13 to 38.72 mPa s by increasing the molar ratio from 1:4 to 1:7. By increasing the amount of acetic acid in TEAC-AC from 1:2 to 1:3, the viscosity decreased from 27.52 to 21.50 mPa s. Similar behaviour was observed for the choline acetate-glycerol system, as well as the tertrabutylammonium bromide-based DESs.44,45
- **3.2.5.** Using co-HBD. The viscosity of the DESs can be tuned by selecting an appropriate HBD or using a co-HBD based on the measured viscosity results. When choosing acetic acid (0.035 mol) as a co-HBD in the DES composed of MTPP-LV (1:3), the viscosity was significantly reduced from 957.09 to 33.95 mPa s at 298.15 K. Similarly, by adding glycerol as the second HBD to the DES composed of ChCl-sugar-based polyols, a solution with lower viscosity was obtained. For example, by adding glycerol at 323.15 K, the viscosity of ChCl: glucose (1:1) decreased from 34 400 to 930 mPa s in ChCl:glucose:glycerol $(1:0.5:0.5)^{46}$

3.3. Comparison with other DESs

3.3.1. CO₂ solubility. Until now, various different DESs have been studied as CO2 sorbents, and most of them have been based on choline chloride (ChCl) and different types of HBDs. Table S1 (ESI†) summarizes the CO2 solubilities of the DESs reported by others until today.

Leron et al. reported the solubility of CO2 in a variety of ChCl-based DESs at moderate pressures in the temperature range of 303.15-343.15 K. The studied DESs were composed of ChCl and urea, ethylene glycol and glycerol with a molar ratio of 1:2. These DESs exhibited high CO₂ solubility (3.1265-3.6929 mol kg⁻¹). ^{25,26,47} Li and co-workers measured CO₂ solubility in ChCl-urea DESs with different molar ratios (1:1.5, 1:2 and 1:2.5) in the temperature range of 313.15-333.15 K and

Table 3 Viscosity (mPa s) of the synthesized DESs at different temperatures

293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
BHDE-AC (1: 334.28	2) 238.16	166.52	122.72	94.54	75.82	59.99	57.86	41.67
BHDE-GLY (1 1434.36	962.20	619.78	414.50	297.01	213.60	160.74	148.30	93.36
BHDE-GLY-H 32.76	I ₂ O (1:3:0.11) 29.98	27.29	24.35	21.41	19.79	18.28	17.52	17.11
BHDE-LA (1: 1434.23	2) 900.26	570.50	385.16	266.06	214.46	142.45	112.76	84.09
BTEA-AC (1:2 341.10	2) 244.04	173.29	133.86	112.70	96.15	84.90	80.89	74.12
BTMA-AC (1: 151.30	2) 113.01	85.38	68.62	55.25	49.83	39.11	35.04	22.39
BTMA-GLY (1 1017.67	716.55	453.89	319.51	229.15	172.40	133.51	103.43	83.20
BTMA-GLY-H 70.76	H ₂ O (1:2:0.055) 55.32	47.94	40.98	37.22	32.10	29.73	28.48	26.81
BTMA-GLY-H 22.19	H ₂ O (1:2:0.11) 20.36	18.98	17.68	16.68	15.96	15.56	14.72	14.41
ChCl-EA (1:7 50.49	7) 39.58	32.47	28.14	23.39	20.18	18.34	18.43	17.62
ChCl-GLY-AC	C (1:1:1) 101.44	78.19	62.66	51.54	43.77	38.00	33.92	28.81
Gua-EA (1:2) 104.34	78.32	58.59	45.65	36.91	30.62	25.69	23.63	19.29
MTPP-1,2-PD	O (1:4) 119.53	86.33	67.43	52.49	43.48	36.44	30.66	21.59
MTPP-AC (1: 142.95	4) 118.49	97.73	80.56	67.73	55.87	49.01	45.23	43.24
MTPP-EG (1: 149.85	3) 110.52	82.47	66.19	53.79	41.94	36.12	30.75	27.12
MTPP-LV (1: 1658.36	3) 957.09	574.67	365.74	243.95	170.58	124.79	91.20	71.33
MTPP-LV-AC 40.12	(1:3:0.035) 33.95	28.75	25.18	21.58	19.50	18.03	17.01	16.16
MTPP-GLY (1 2753.21	:4) 1748.19	1036.18	632.81	436.33	280.14	210.18	178.36	113.94
TBAB-EA (1:6	55.66	43.58	36.01	30.16	26.54	24.36	21.76	18.76
TBAB-EA (1:7	7) 51.76	42.66	33.28	28.63	24.99	22.67	21.27	19.26
TBAB-AC (1:2	2) 256.81	177.91	134.48	112.46	92.16	79.55	72.67	64.07
TBAC-AC (1:2 22.64	2) 20.85	19.19	17.67	16.28	15.02	13.91	12.93	12.08
TEAC-AC (1:3	2) 27.52	23.70	21.18	19.35	16.59	14.64	14.05	13.86
TEAC-AC (1:3	3) 21.50	19.45	16.99	15.51	14.56	13.71	12.39	11.45

Table 3 (continued)

Paper

293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
TEAC-OCT (2	1:3) 65.86	53.37	46.41	40.65	34.89	32.47	31.31	31.07
TEMA-AC (1 32.69	: 2) 25.97	22.09	18.93	17.35	15.49	13.94	12.61	11.38
TEMA-EG (1 46.78	: 2) 41.69	32.89	27.05	22.59	20.04	19.31	16.25	15.40
TEMA-GLY (333.02	1:2) 236.59	172.68	128.73	97.59	76.53	59.78	52.53	42.57
TEMA-GLY-1 90.98	H ₂ O (1:2:0.055) 72.75	56.15	45.40	39.17	30.79	28.07	26.76	23.56
TEMA-GLY-1 48.63	H ₂ O (1:2:0.11) 37.24	33.62	28.08	26.98	23.94	23.31	20.55	19.31
TEMA-LA (1 170.21	: 2) 117.46	87.65	69.03	54.36	43.77	37.18	32.66	30.66
TEMA-LV (1 129.47	:2) 96.45	71.49	56.09	45.15	37.32	32.23	28.65	24.38
TPAC-AC (1: 32.97	6) 32.66	32.39	32.12	31.95	31.60	31.37	31.07	30.89
TPAC-EA (1: 71.63	4) 55.13	42.58	34.85	27.21	26.96	22.05	24.85	16.99
TPAC-EA (1: 49.32	7) 38.72	30.91	25.41	22.87	19.82	18.12	16.79	15.71

up to 13 MPa. In this study, ChCl-urea (1:2) at 313.15 K and 12.5 MPa exhibited a CO₂ solubility of 5.1646 mol kg⁻¹, which is the highest among all studied DESs up to now.³⁸ In another study, a task-specific DES also exhibited a high CO2 absorption capacity (2.4 mol kg⁻¹) under ambient conditions.²⁷ Other ChCl-based DESs such as ChCl-phenol, 48 ChCl-lactic acid, ChCl-levulinic acid, 49 ChCl-furfuryl alcohol 49 and ChCl-diols, 31 have also been studied, but their CO2 absorption capacities are low (below 1 mol kg⁻¹).

Similar to ILs, DESs are capable of either physical or chemical absorption of CO₂. According to the available studies performed by others and us, the reported DESs generally absorb CO2 physically, and thus they exhibit a relatively low absorption capacity. In the open literature, just one single taskspecific DES system composed of ChCh-Gly-superbase has been designed to chemically capture CO2 under ambient conditions.²⁷ Similarly, switchable ILs composed of an amidine coupled with an alcohol or amino alcohol were considered as efficient CO2 sorbents at atmospheric pressure. 50 Privalova et al. reported that these switchable ILs were capable of both physical and chemical sorption of CO_2 .⁵⁰

Fig. 3 compares the CO₂ solubility of the promising DESs synthesized in this work with those reported in the literature. The CO₂ solubility in the DESs synthesized in this work is comparable with that of other choline chloride-based DESs, such as ChCl-glycerol, ChCl-urea or ChCl-glycerol-superbase. 25-27,51 Based on this comparison we can conclude that our selected

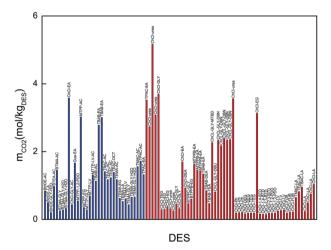


Fig. 3 Comparison of CO₂ solubility in the synthesized DESs in this work with those reported in the literature (the blue columns represent our synthesized DESs and the red ones represent those reported in the literature)

DESs along with the ChCl-based DESs (with urea, glycerol, ethanolamine and task-specific DESs) and MTPP-EA can be considered as promising DESs.

3.3.2. Viscosity. Viscosity has been extensively measured for all the available DESs due to the importance of this property in industrial applications. 45,46,52-55 All studies have been carried out at atmospheric pressure and in different temperature ranges.

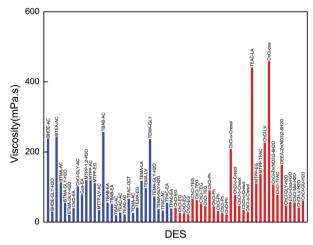


Fig. 4 Comparison of the viscosities of the synthesized DESs in this work with those reported in the literature (the blue columns represent our synthesized DESs and the red ones represent those reported in the literature).

The viscosities of DESs reported in the literature are summarized in Table S2 (ESI†).

The comparison of the viscosity of our synthesized DESs with those reported in the literature is illustrated in Fig. 4. In order to show a clear and better comparison, only the DESs with a viscosity below 400 mPa s are shown. Our synthesized DESs exhibit lower viscosities (below 200 mPa s at 298.15 K) in comparison to the ChCl-based or other DESs, with the exception of BHDE-LA, BHDE-GLY, BTMA-GLY, MTPP-LV and MTPP-GLY. The viscosities of all the selected promising DESs are below 200 mPa s.

3.4. Screening and comparison with conventional ILs

3.4.1. CO_2 solubility. We compared the CO_2 solubilities for the selected promising DESs with those of conventional ILs, in terms of molality. The CO2 solubilities in some conventional ILs are summarized in Table S3 (ESI†). The comparison is illustrated in Fig. 5. As can be seen, the CO₂ solubilities in our synthesized DESs are in the same range as the CO2 solubilities in [C₆MIM][Tf₂N], [C₈MIM][Tf₂N], [C₄MIM][DCA], [C₄MIM][TfO], [C₂MIM][TFA] and [C₆MIM][eFAP], but are lower than those for $[C_2MIM][AC]$, $[C_4MIM][AC]$ or $[C_4MIM][LEV]$. $^{34,56-58}$

It is worth noting that phosphonium-based DESs present the same problems as traditional ILs, such as toxicity and high cost. As shown in Fig. 5, the DESs exhibit comparable CO₂ absorption capacity with that of fluorinated ILs. Therefore, these DESs can be considered as benign promising alternatives to expensive and toxic ILs for CO₂ separation.

3.4.2. Viscosity. The viscosities of the selected DESs were also compared with those of conventional ILs. The viscosities of conventional ILs are summarized in Table S4 (ESI†). Fig. 6 represents the comparison of the viscosities for the selected promising DESs with those of conventional ILs. As can be seen, the viscosity of the selected DESs is lower than those of conventional ILs, except for ChCl-based DESs.

When comparing the results for the CO₂ solubility and viscosity, we can conclude that the glycerol or urea-based DESs exhibit higher CO₂ affinity, but their viscosity is high and results in high pumping

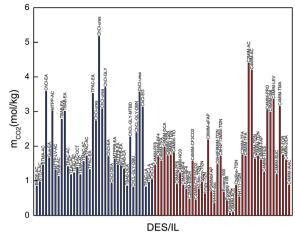


Fig. 5 Comparison of CO₂ solubilities in promising DESs with those in conventional ILs (the blue columns represent selected DESs and the red ones represent conventional ILs)

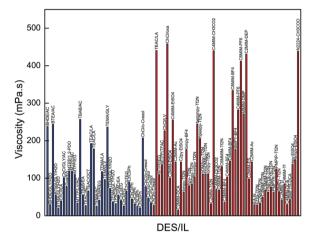


Fig. 6 Comparison of the viscosities of promising DESs in this work with those of conventional ILs (the blue columns represent our selected DESs and the red ones represent conventional ILs).

costs as well as poor mass and heat transfer. To overcome their high viscosity, one efficient way is to use an appropriate co-solvent. In this work, water was proposed as a promising co-solvent. However, to find the optimum amount of water to decrease the viscosity of the DESs without obtaining a remarkable reduction in their CO₂-philicity, a more detailed investigation is required.

4. Conclusion

In the present study, a series of deep eutectic solvents based on ammonium or phosphonium salts and different hydrogen bond donors were synthesized. Their CO2 solubilities were measured at 298.15 K and at pressures of up to 2 MPa.

Their viscosities were also measured in the range of 293.15-333.15 K. The influence of the nature of the hydrogen bond donor and salt, pressure and alkyl chain length of the hydrogen bond donor and salt, were also investigated. Among the synthesized deep eutectic solvents, 15 samples exhibit higher CO2 solubilities and

1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide

tetrafluoroborate

hexafluorophosphate

dicyanamide

1-Methoxymethyl-3-methylimidazolium

1-Methoxymethyl-3-methylimidazolium

1-Methoxymethyl-3-methylimidazolium

1-Methoxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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 $[C_2MMIM][Tf_2N]$

 $[C_2OMIM][BF_4]$

 $[C_2OMIM][DCA]$

 $[C_2OMIM][PF_6]$

 $[C_2OMIM][Tf_2N]$

their viscosities are lower than those of conventional ionic liquids. These prototype deep eutectic solvents were then chosen for a more thorough investigation, and in a future study, their structures will be altered in order to improve their CO₂ absorption performance. In the future, we plan to functionalize these deep eutectic solvents to reach even higher CO2 sorption capacities, surpassing the performance of the so far reported task specific ILs.

Abbreviations

7 (DDI CVIGATION	3	$[C_2OMIM][TFO]$	1-Methoxymethyl-3-methylimidazolium
[aP4443][Ala]	(3-Ainopropyl)tributylphosphonium		trifluoromethanesulfonate
	L-α-aminopropionic acid	[C ₂ py][EtSO4]	1-Ethylpyridinium ethylsulfate
[aP4443][Gly]	(3-Aminopropyl)tri-butylphosphonium	$[C_4MIM][Ac]$	1-Butyl-3-methylimidazolium acetate
22 72	aminoethanoic acid	[C ₄ MIM][BETI]	1-Butyl-3-methylimidazolium
[aP4443][Ile]	(3-Aminopropyl)tri-butylphosphonium	2 - 32 3	bis(perfluoroethylsulfonyl)imide
	L-α-amino-3-methylvaleric acid salt	$[C_4MIM][BF_4]$	1-Butyl-3-methylimidazolium
[aP4443][Leu]	(3-Aminopropyl)tributylphosphonium	L - 3L -3	tetrafluoroborate
	L-α-amino-4-methylvaleric acid salt	$[C_4MIM][C_7F_{15}CO_2]$	1-Butyl-3-methylimidazolium
[aP4443][Lys]	(3-Aminopropyl)tri-butylphosphonium	2 - 323	pentadecafluorooctanoate
	L-α-Diaminocapronic acid	$[C_4MIM][CF_3CO_2]$	1-Butyl-3-methylimidazolium
[aP4443][Met]	(3-Aminopropyl)tri-butylphosphonium	[1][0 2]	trifluoroacetate
	L-α-amino-(methylthio)butyric acid salt	$[C_4MIM][DCA]$	1-Butyl-3-methylimidazolium
[aP4443][Phe]	(3-Aminopropyl)tri-butylphosphonium		dicyanamide
	L-α-aminohydrocinnamic acid salt	$[C_4MIM][FSI]$	1-Butyl-3-methylimidazolium
[aP4443][Pro]	(3-Aminopropyl)tri-butylphosphonium		bis(fluorosulfonyl)imide
	2-pyrrolidinecarboxylic acid salt	$[C_4MIM][IAAC]$	1-Butyl-3-methylimidazolium iminoacetic
[aP4443][Ser]	(3-Aminopropyl)tri-butylphosphonium	2 - 32 3	acid acetate
	L-α-amino-3-hydroxypropionic acid salt	$[C_4MIM][ISB]$	1-Butyl-3-methylimidazolium isobutyrate
[aP ₄₄₄₃][Thr]	(3-Aminopropyl)tributylphosphonium	[C ₄ MIM][LEV]	1-Butyl-3-methylimidazolium levulinate
[1110][]	L-α-amino-3-hydroxybutyric acid salt	$[C_4MIM][NO_3]$	1-Butyl-3-methylimidazoliumnitrate
[aP4443][Val]	(3-Aminopropyl)tributylphosphonium	$[C_4MIM][PF_6]$	1-Butyl-3-methylimidazolium
	L-α-aminoisovaleric acid salt	[hexafluorophosphate
[b ₂ -Nic][Tf ₂ N]	1-Butyl-nicotinic acid butyl ester	$[C_4MIM][PRO]$	1-Butyl-3-methylimidazolium propionate
	bis(trifluoromethylsulfonyl)imide	[C ₄ MIM][SUC]	1-Butyl-3-methylimidazolium
[bmpy][BF ₄]	1-Butyl-3-methylpyridinium	2 2 32 3	succinamate
£ 173£ 43	tetrafluoroborate	$[C_4MIM][Tf]$	1-Butyl-3-methylimidazolium triflate
[bmpy][Tf ₂ N]	1-Butyl-3-methylpyridinium	$[C_4MIM][Tf_2N]$	1-Butyl-3-methylimidazolium
t 173t 2 3	bis(trifluoromethylsulfonyl)imide		bis(trifluoromethylsulfonyl)imide
[BMPYR][Ac]	1-Butyl-3-methyl pyridinium acetate	$[C_4MIM][TFA]$	1-Butyl-3-methylimidazolium
[BMPYR][DCA]	1-Butyl-1-methylpyrrolidinium	2 - 32 3	trifluoroacetate
2 32 3	dicyanamide	$[C_4MIM][TFES]$	1-Butyl-3-methylimidazolium
$[BMPYR][Tf_2N]$	1-Butyl-1-methylpyrrolidinium	2 - 32 3	1,1,2,2-tetrafluoroethanesulfonate
2 32 - 3	bis(trifluoromethylsulfonyl)imide	$[C_4MIM][TMA]$	1-Butyl-3-methylimidazolium
$[C_2MIM][Ac]$	1-Ethyl-3-methylimidazolium acetate	2 32 3	trimethylacetate
$[C_2MIM][DMP]$	1-Ethyl-3-methylimidazolium diethyl	$[C_4MIM]_2[IDA]$	bis(1-Butyl-3-methylimidazolium)-
2 22 3	phosphate		iminodiacetate
$[C_2MIM][ES]$	1-Ethyl-3-methylimidazolium ethyl sulfate	$[C_6H_4F_9MIM][Tf_2N]$	1-Methyl-3-(3,3,4,4,5,5,6,6,6-
[C ₂ MIM][EtSO ₄]	1-Ethyl-3-methylimidazolium ethylsulfate		nonafluorohexyl)imidazoliumbis-
[C ₂ MIM][FAP]	1-Ethyl-3-methylimidazolium		(trifluoromethylsulfonyl)imide
2 22 2	tris(pentafluoroethyl)trifluorophosphate	$[C_6MIM][ACE]$	1-Hexyl-3-methylimidazolium
$[C_2MIM][HS]$	1-Ethyl-3-methylimidazoliumhydrogen		acesulfamate
- 25 2	sulfate	[C ₆ MIM][eFAP]	1-Hexyl-3-methylimidazolium
$[C_2MIM][Tf]$	1-Ethyl-3-methylimidazolium triflate	-	tris(pentafluoroethyl)trifluorophosphate
$[C_2MIM][TFA]$	1-Ethyl-3-methylimidazolium	[C ₆ MIM][pFAP]	1-Hexyl-3-methylimidazolium
_ 	trifluoroacetate		tris(heptafluoropropyl)trifluorophosphate

$[C_6MIM][SAC]$	1-Hexyl-3-methylimidazolium
	saccharinate
$[C_6MIM][Tf_2N]$	1-Hexyl-3-methylimidazolium
[c , ex el[mnox]	bis(trifluoromethyl sulfonyl)imide
$[C_6MIM][TFSI]$	1-Hexyl-3-methylimidazolium
[O II E MIM][mf N]	bis(trifluoromethylsulfonyl)imide
$[C_8H_4F_{13}MIM][Tf_2N]$	1-(3,3,4,4,5,5,6,6,7,7,8,8,8-
	Tridecafluorooctyl)-3-methylimidazolium bis[trifluoromethylsulfonyl]amide
$[C_8MIM][BF_4]$	1-Octyl-3-methylimidazolium
	tetrafluoroborate
[C ₈ MIM][PF ₆]	1-Octyl-3-methylimidazolium
[08111111][116]	hexafluorophosphate
$[C_8MIM][Tf_2N]$	1-Octyl-3-methylimidazolium
[-8][2]	bis(trifluoromethyl sulfonyl)imide
[Choline][Tf ₂ N]	(2-Hydroxyethyl)-trimethyl-ammonium
. 1. 2 1	bis(trifluoromethylsulfonyl)imide
[EA][N]	Ethylammonium nitrate
Ecoeng 41M	1-Butyl-3-methylimidazolium
_	2-(2-methoxyethoxy)ethylsulfate
Ecoeng 500	PEG-5 cocomonium methylsulfate
[empy][EtSO ₄]	1-Ethyl-3-methylpyridinium
[epy][EtSO ₄]	1-Ethylpyridinium
[Et ₂ Nic][EtSO ₄]	1-Ethyl-nicotinic acid ethyl ester
$[Et_3S][Tf_2N]$	Triethylsulfonium
	bis(trifluoromethylsulfonyl)imide
[H ₃ D ₃ PHO][Cl]	Trihexyltetradecylphosphonium
	chloride
[hDMApy][Tf ₂ N]	1-Hexyl-4-(dimethylamino)pyridinium
F1 3F-41	bis(trifluoromethylsulfonyl)imide
[hemmpy][Tf ₂ N]	1-Hexyl-2-ethyl-3,5-dimethylpyridinium
[lData][mf.ar]	bis(trifluoromethylsulfonyl)imide
[hmDMApy][Tf ₂ N]	1-Hexyl-3-methyl-4-(dimethylamino)- pyridinium
	bis(trifluoromethylsulfonyl)imide
[hmmpy][Tf ₂ N]	1-Hexyl-3,5-dimethylpyridinium
	bis(trifluoromethylsulfonyl)imide
[hmpy][Tf ₂ N]	1-Hexyl-3-methylpyridinium
[bis(trifluoromethylsulfonyl)imide
[hpeepy][Tf ₂ N]	1-Hexyl-2-propyl-3,5-diethylpyridinium
	bis(trifluoromethylsulfonyl)imide
[hpy][Tf ₂ N]	1-Hexylpyridinium
2 1032 - 3	bis(trifluoromethylsulfonyl)imide
[MMIM][DMP]	1,3-Dimethylimidazolium dimethyl
	phosphate
$[N_{4111}][Tf_2N]$	Tributylmethylammonium
	bis(trifluoromethanesulfonyl)-
	imide
$[N_{4444}][doc]$	Tetrabutylammonium docusate
[N-bupy][BF ₄]	<i>N</i> -Butylpyridinium tetrafluoroborate
$[O_3MN][Tf_2N]$	Methyltrioctylammonium
	bis(trifluoromethylsulfonyl)imide
$[OMPY][Tf_2N]$	1-Octyl-3-methylpyridinium
[ps cpvp35=4 2	bis(trifluoromethylsulfonyl)imide
$[PMPIP][Tf_2N]$	1-Methyl-1-propylpiperidinium
	his(trifluoromethylsulfonyl)imide

 $[PMPYR][Tf_2N]$ 1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide [TBP][FOR] Tetrabutylphosphonium formate

Acknowledgements

Kempe Foundations is gratefully acknowledged for funding this research. The Swedish Energy Agency, Bio4Energy program and Wallenberg Wood Science Center under the auspices of Knut and Alice Wallenberg foundation are acknowledged. This work is also a part of the activities of the Johan Gadolin Process Chemistry Centre at Åbo Akademi University.

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