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CO_2 Capture by Ionic Liquids – An Answer to Anthropogenic CO_2 Emissions?

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Abstract: Ionic liquids (ILs) are efficient solvents for the selective removal of CO_2 from flue gas. Conventional, off-the-shelf ILs are limited in use to physisorption, which restricts their absorption capacity. After adding a chemical functionality like amines or alcohols, absorption of CO_2 occurs mainly by chemisorption. This greatly enhances CO_2 absorption and makes ILs suitable for potential industrial applications. By carefully choosing the anion and the cation of the IL, equimolar absorption of CO_2 is possible. This paper reviews the current state of the art of CO_2 capture by ILs and presents the current research in this field performed at the ChemTech Institute of the Ecole d'Ingénieurs et d'Architectes de Fribourg.

Keywords: Carbon dioxide · Capture · Chemisorption · Ionic liquids · Physisorption

Introduction

The level of CO_2 in the atmosphere is rising dramatically, reaching for the first time in May 2013 the level of 400 ppm in Mauna Loa (Hawaii) (Fig. 1).[1] Thus a great effort is made to find solutions to reduce greenhouse gas (GHG) emissions and especially its major contributor, CO_2. Industries and transport are the major segments responsible for GHG emissions in Switzerland (Fig. 2) with 11.2 million tonnes CO_2 equivalents in 2007.[2]

Three basic possibilities exist to mitigate anthropogenic CO_2 emissions: reducing them at the source, sequestering CO_2 or utilizing CO_2. Carbon capture and sequestration (CCS) technologies can be used to stock the captured CO_2, for example in geological systems.[3] Instead of treating CO_2 as a waste, it can also be considered as a chemical raw material. For example it can be recycled in the food industry or used as chemical feedstock in the synthesis of chemicals (urea, salicylic acid, cyclic carbonates).[4] This approach is known as carbon capture and utilization (CCU) and it is the most promising and energetically 'useful' approach.

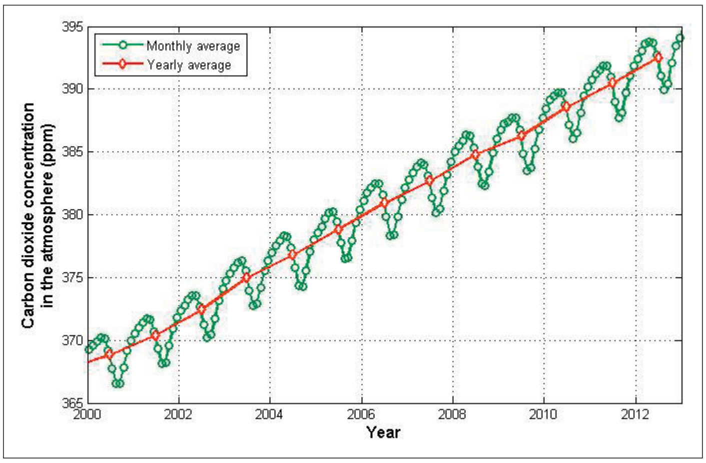

Fig. 1. Evolution of the global CO_2 concentration in the atmosphere.[1]

Current technologies available on the market to remove CO_2 from flue gas are based on amines solutions such as monoethanolamine (MEA), diethylamine (DEA) or methyldiethanolamine (MDEA), whereby primary amines react with CO_2 forming a carbamate by a 2:1 stoichiometry (Scheme 1). Table 1 presents an overview of commercial solutions. For example the FLUOR process is used to capture 330 tonnes per day at the Bellingham Energy center (USA) and the captured CO_2 is recycled in the food industry.

The drawbacks of aqueous amine technologies are their corrosivity, degradation, and energy cost for regeneration due to the water present in the system.[13] Furthermore, they can degrade to nitrosamines, which are known to be carcinogenic.[14]

ILs are organic salts with melting points typically below 100 °C. ILs have

Table 1. Non-exhaustive review of commercial amine solutions for CO_2 removal.[5]

Company	Product	Molecule
Fluor[6]	Econamine	Aqueous MEA
Mitsubish Heavy Industries[7]	KS-1 Solvent	Sterically hindered amine
Cansolv Technologies[8]	CANSOLV CO_2 capture	Aqueous diamine
Aker Clean Carbon[9]	–	Amine
Alstom[10]	CAP	Chilled ammonia
Powerspan[11]	ECO_2	Mixture of aqueous amines
Siemens[12]	PostCap	Amino acid solution

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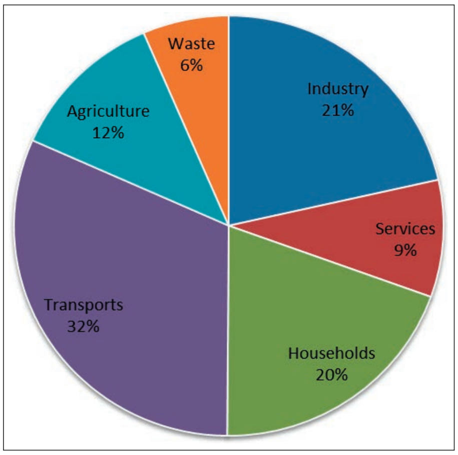
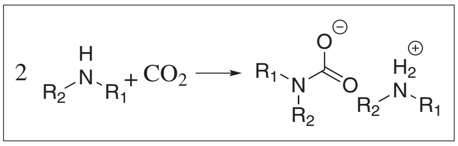


Fig. 2. Graphic showing the repartition of the sources of CO_2 emissions in Switzerland in 2007.[2]



Scheme 1. Reaction of absorption of CO_2 by aqueous amines.

recently proven to be efficient media for the capture of acidic gases such as carbon dioxide or hydrogen sulfide.[15–18] Their negligible vapor pressure and their stability offer a strong advantage compared to the amine solutions currently used in the flue gas treatment industry.

The use of ILs ensures no contamination of the treated gas as well as no loss of the ILs by evaporation. Moreover, by tuning their anion and cation, one is able to design their physical and chemical properties such as corrosivity, viscosity and, above all, their CO_2 absorption capacity, which makes ILs ideal sorbents for any industrial applications.

This review focuses on the capture of CO_2 by ILs. The steric and electronic effects and the influence of the anion and cation on the absorption capacity will be discussed.

Absorption of CO_2 by Ionic Liquids

Literature Review
Physisorption

Many research groups are active in the field of CO_2 capture by ionic liquids. Commercial, off-the-shelf ILs (Fig. 3) usually show rather poor absorption capacities. There is no task-specific CO_2 binding, resulting in processes where only physisorption occurs, meaning 'simple' dissolving CO_2 in the IL. The solubility of CO_2 in those ILs is comparable to conventional solvents (Table 2) with Henry's constants (H) around 30–70 bar, which correspond

Table 2. Henry's constants (H) for the solubility of CO_2 in ionic liquids and solvents.

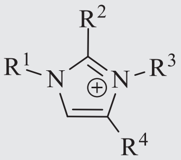
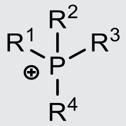
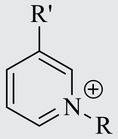
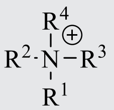
Imidazolium						
R¹	**R²**	**R³**	**R⁴**	**Anion**	**T [°C]**	**H [bar]**
3,3,4,4,5,5,6,6,7,7,8,8,8 -tridecafluorooctyl	H	Me	H	Tf_2N	25	4.5[19] 27.3[20]
Et	H	Me	H	OAc	30	12.62[21]
hexyl	H	Me	H	bFAP	25	20.2[20]
pentyl	H	Me	H	bFAP	25	20.2[22]
hexyl	H	Me	H	pFAP	25	21.6[20]
hexyl	H	Me	H	eFAP	25	25.2[20]
hexyl	H	Me	H	Tf_2N	25	28.2[23] 31.6[20] 34[24] 35[19]
3,3,4,4,5,5,6,6,6-nonafluorohexyl	H	Me	H	Tf_2N	25	28.4[20]
octyl	H	Me	H	Tf_2N	25	30[19]
perfluorohexyl	H	Me	H	Tf_2N	25	31[25]
					30	32[25]
Et	H	Me	H	Tf_2N	25	31.3[23] 35.6[26] 37[24]
					30	39[27]
Et	H	Me	H	BETI	25	33[23]
Bu	H	Me	H	Tf_2N	25	33[20,24,28] 34.3[25] 37[19]
					30	42[25]
triethylamineboronium	H	Me	H	Tf_2N	25	33.1[20]
benzyl	H	Me	H	Tf_2N	22	36[24]
Pr	H	Me	H	Tf_2N	25	37[19]
Pr	Me	Me	H	Tf_2N	25	38.5[25]
					30	40.4[25]
Et	Me	Me	H	Tf_2N	25	39.6[26]
octyl	H	Me	H	BF_4	25	43[23]
Et	H	Me	H	TfA	25	43[23]
Et	H	Me	H	TfO	25	50[23]
					30	73[27]
Pr	H	Me	H	PF_6	25	52[19]
Bu	H	Me	H	PF_6	25	53.4[20,26,28]
					30	59[27]
Bu	H	Me	H	BF_4	25	56[25] 56.5[26] 57[24] 59[22,28]
					30	63[25]
hexyl	H	Me	H	BF_4	25	57[23]
Bu	Me	Me	H	BF_4	25	61[26]
Bu	Me	Me	H	PF_6	25	61.8[26]
Bu	H	Ph	Bu	Tf_2N	25	63[19]

Table 2. continued

R¹	**R²**	**R³**	**R⁴**	**Anion**	**T [°C]**	**H [bar]**
Et	H	Me	H	DCA	30	78[27]
Et	H	Me	H	BF_4	25	81[24]
Bu	H	Ph	H	Tf_2N	25	180[19]
Phosphonium						
R¹	**R²**	**R³**	**R⁴**	**Anion**	**T [°C]**	**H [bar]**
hexyl	hexyl	hexyl	tetradecyl	DCA	30	29.3[29]
hexyl	hexyl	hexyl	tetradecyl	Cl	30	30[27] 35[29]
Bu	Bu	Bu	tetradecyl	DBS	30	30[29]
hexyl	hexyl	hexyl	tetradecyl	Tf_2N	30	33[29]
Et	Bu	Bu	Bu	DEP	30	69[29]
Pyridinium						
R	**R'**			**Anion**	**T [°C]**	**H [bar]**
hexyl	Me			Tf_2N	25	32.8[20]
Bu	Me			Tf_2N	25	33[25] 38.6[28]
					30	35[25]
Bu	Me			BF_4	25	60[23]
Ammonium						
R¹	**R²**	**R³**	**R⁴**	**Anion**	**T [°C]**	**H [bar]**
Me	Bu	Bu	Bu	Tf_2N	25	43.5[28]
Solvent					**T [°C]**	**H [bar]**
MEA 30% in water					-	~ 3.16[17]
THF					25	45.2[24]
acetone					25	46.9[24]
methyl acetate					25	47.6[24]
acetonitrile					25	61.2[24]
propylene carbonate					25	67.8[24]
DMF					25	71.5[24]
methyl chloride					25	78.8[24]
n-hexane					25	82.7[24]
DMSO					25	110[24]
methanol					25	156[24]
water					25	1662[24]

to a solubility of 0.01–0.03 mol CO_2 per mol solvent.

Henry's law is represented in Eqn. (1) where p is the partial pressure of the gas above the solution and x the molar fraction of the gas in the solution.

$$H = \frac{p}{x} \tag{1}$$

A low Henry's constant means a high solubility and vice versa. High pressure of CO_2 or low temperature is therefore needed to achieve significant absorption with those ILs.

Absorption by conventional imidazolium-based ILs is well described in the literature. Studies show that the solubility tends to rise with the increase of the alkyl chain on the imidazolium[19] because of the gain of free volume within the molecule.

It has been found that carbon dioxide solubility in the ionic liquids depends more on the nature of the anion than on the cation,[16,28] mainly because of the intrinsic basic nature of the anion.[30] The affinity of CO_2 for the anion follows the order:[21] $[BF_4] < [TfO] < [B(CN)_4] \approx [Tf_2N] < [pFAP]$ with a factor of roughly 3 between $[BF_4]$ and [pFAP]. This illustrates that fluorination of the anion increases the CO_2 solubility. However, the fluorinated groups raise environmental concerns because of their toxicity.[17] Fluorinated anions can also decompose into HF in the presence of water, making them unsuitable for large industrial applications, as well as being pricey.

ILs limited to absorption of CO_2 solely by physisorption are unable to compete with aqueous amines (Henry constant of H = 3.16 bar for MEA). Thus, adding functional groups to the IL that can 'react' with CO_2 increases absorption because it leads to chemisorption instead of physisorption.

Chemisorption

Various strategies have been developed to enhance the CO_2 absorption capacity by functionalization of ILs. The advantage of task-specific ionic liquids (ionic liquids functionalized for specific applications) is that by attaching an additional functionality capable of linking to CO_2, one moves from physisorption to chemisorption. A literature summary of absorption capacities of various task-specific ILs is presented in Table 3.

To compete with aqueous amines, ILs should not only have a higher absorption capacity but also a low molecular weight, limiting the amount of IL needed for an industrial process of CO_2 removal. In the next paragraphs we will discuss three different strategies to chemically absorb CO_2.

Switchable Liquids

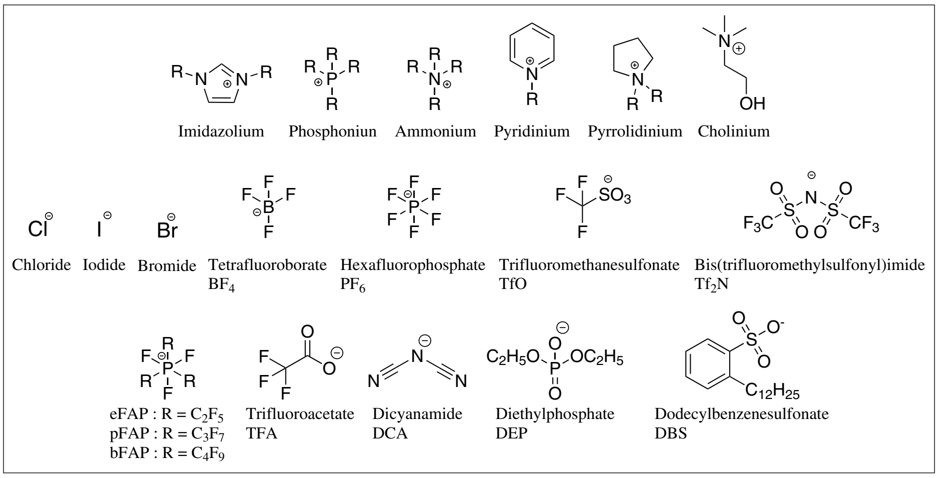
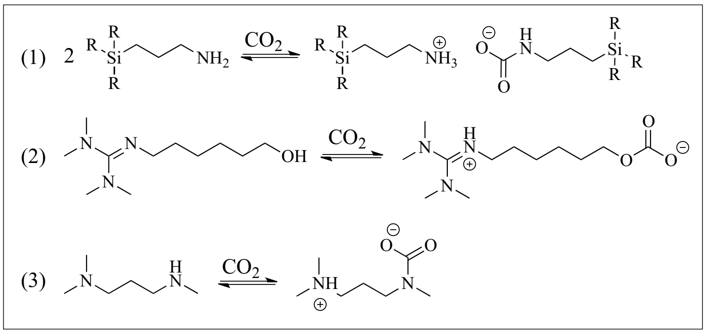
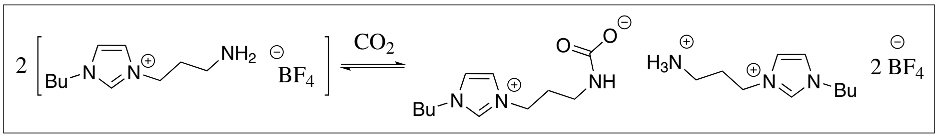


Fig. 3. Common cations and anions of ionic liquids.



Scheme 2. Reversible ILs formed by bubbling CO_2 through molecular liquids: (1) trialkylsilamines, (2) alkanol guanidines and (3) diamines.



Scheme 3. Reaction of CO_2 capture by an amine functionalized imidazolium.[33]

A special type of liquid chemically binds to CO_2 forming salts or molten salts. This phenomenon is reversible upon heating to desorb the CO_2. Trialkylsilamines have this property to form reversible ILs in contact with CO_2.[45] Two molecules of this compound are required to catch one molecule of CO_2. On the other hand, alkanol guanidines, alkanol amidines and diamines react with CO_2 to form zwitterions.[46] The zwitterionic form has the advantage to follow a 1:1 mechanism (Scheme 2) – thus an equimolar absorption of CO_2.

Functionalization of Cation

Bates *et al.*[33] were the first to propose to functionalize ILs with an amine to increase the capacity. They added a primary amine moiety to an imidazolium cation. They reached an absorption of 0.5 mol CO_2/mol IL for their aminopropylbutylimidazolium tetrafluoroborate, which is the stoichiometric maximum because two amines are necessary to catch one CO_2 molecule (Scheme 3). But they reported a high viscosity for their ionic liquid. Other researchers added an ether moiety to the imidazolium cation with common anions and obtained absorption up to 1 mol CO_2/mol IL.[31] In this case, the lone pair of the oxygen atom on the imidazolium attacks the carbon of the CO_2 to form a carboxylic acid.

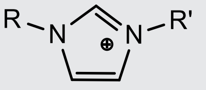
Xue *et al.*[32] also functionalized an imidazolium cation with an amine but they used taurine as an anion. They obtained absorption of up to 0.9 mole of CO_2 for one mole of IL – but they also reported high viscosity of the IL-CO_2 compounds. Zhang *et al.*[39] functionalized both the cation and the anion by amines. They synthesized a series of 20 ionic liquids with amino acid anions and an amino-functionalized phosphonium cation. To overcome the issue of high viscosity, they supported the ILs on SiO_2. Using this approach, absorptions close to equimolar were reached.

Functionalization of Anion

By adding the functional group to the anion, a 1:1 mechanism is theoretically possible.[47] Wang *et al.*[41] developed ionic liquids with a phosphonium cation and phenols as anions (Scheme 4) – with this IL, absorption of 0.9 mol CO_2/mol IL at 30°C was reached. The position of the substituent on the phenolic ring significantly influences the viscosity of the IL. The electronic nature, the position and the number of the substituents affect strongly the CO_2 absorption capacity. The researchers also observed a linear relationship between the pKa of the phenolic anion (PhO) and the absorption capacity of the IL.

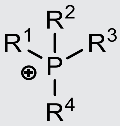
Table 3. Review of CO_2 absorption in various functionalized ILs at atmospheric pressure.

Imidazolium



R	R'	Anion	T [°C]	Absorption [mol CO_2/mol IL]
methoxymethyl	Me	Tf_2N	30	0.9775[31]
methoxymethyl	Me	TfO	30	0.967[31]
methoxymethyl	Me	PF_6	30	0.955[31]
methoxymethyl	Me	DCA	30	0.92[31]
methoxymethyl	Me	BF_4	30	0.91[31]
aminoethyl	Me	taurine	30	0.9 [32]
aminopropyl	Me	BF_4	22	0.5[33]
Bu	Me	PF_6	25 30	0. 167[34] 0.0173[35] 0.017[36] 0.0146[37]
Bu	Me	BF_4	25 30	0. 158[34] 0.0167[35]
aminopropyl	Me	BF_4	30	0.1447[35]
aminopropyl	Me	Tf_2N	30	0.1013[35]
aminopropyl	Me	DCA	30	0.0601[35]

Table 3. continued

R	R'	Anion	T [°C]	Absorption [mol CO_2/mol IL]
Et	Me	Tf_2N	30	0.0297[35] 0.027[36] 0.0232[37]
2-diethylaminoethyl	Me	BF_4	30	0.0294[35]
octyl	Me	BF_4	30	0.0219[35]
Bu	Me	BETI[a]	30	0.0206[37]
Bu	Me	DCA	30	0.0153[35]
Et	Me	TfO	30	0.015[37] 0.014[36]
Bu	Me	MeSO4	30	0.0149[35]
2-hydroxyethyl	Me	Tf_2N	30	0.0146[35]
Et	Me	DCA	30	0.013[36]
Bu	Me	SCN	30	0.0102[35]
Phosphonium				

R¹	R²	R³	R⁴	Anion	T [°C]	Absorption [mol CO_2/ mol IL]
hexyl	hexyl	hexyl	tetradecyl	Lys	22	1.37[38]
butyl	butyl	butyl	aminopropyl	Gly	-	~ 1.2[b][39]
butyl	butyl	butyl	aminopropyl	Ala	-	~ 1.15[b][39]
butyl	butyl	butyl	aminopropyl	Val	-	~ 1.1[b][39]
butyl	butyl	butyl	aminopropyl	Lau	-	~ 1.08[b][39]
hexyl	hexyl	hexyl	tetradecyl	pyrazoline (Pyr)	23	1.02[40]
hexyl	hexyl	hexyl	tetradecyl	imidazolide	23	1[40]
hexyl	hexyl	hexyl	tetradecyl	indazolide	23	0.98[40]
hexyl	hexyl	hexyl	tetradecyl	Pro	22	0.96[38]
hexyl	hexyl	hexyl	tetradecyl	triazolide	23	0.95[40]
hexyl	hexyl	hexyl	tetradecyl	m-dimethylamino-PhO	30	0.94[41]
hexyl	hexyl	hexyl	tetradecyl	p-methoxy-PhO	30	0.92[41]
hexyl	hexyl	hexyl	tetradecyl	3-(trifluoromethyl)-Pyr	22	0.92[42]
hexyl	hexyl	hexyl	tetradecyl	p-methyl-PhO	30	0.91[41]
hexyl	hexyl	hexyl	tetradecyl	oxooxazolidinide	23	0.91[40]
hexyl	hexyl	hexyl	tetradecyl	1-naphtholate	30	0.89[41]
hexyl	hexyl	hexyl	tetradecyl	2-cyano-Pyr	22	0.89[42]
hexyl	hexyl	hexyl	tetradecyl	2-naphtolate	30	0.86[41]
hexyl	hexyl	hexyl	tetradecyl	PhO	30 23	0.85[41] 0.49[40]
hexyl	hexyl	hexyl	tetradecyl	p-Cl-PhO	30	0.82[41]
hexyl	hexyl	hexyl	tetradecyl	taurine	22	0.8[38]
hexyl	hexyl	hexyl	tetradecyl	m-Cl-PhO	30	0.72[41]
hexyl	hexyl	hexyl	tetradecyl	o-Cl-PhO	30	0.67[41]
butyl	buty	butyl	butyl	Ala	-	0.65[b][43]
hexyl	hexyl	hexyl	tetradecyl	p-trifluoromethyl-PhO	30	0.61[41]

The same research group[40] studied the influence of the basicity of the anion on the absorption of CO_2 (Fig. 4). This strategy takes advantage of the acidity of the CO_2 and the inherent basicity of the anion. They discovered a linear relationship between the pKa of the anion and the enthalpy of absorption. The anion with the lowest pKa (tetrazolide, 8.2 in DMSO) and the highest pKa (pyrazolide, 19.8 in DMSO) showed, respectively, an absorption enthalpy of 19.1 kJ/mol and 89.9 kJ/mol and absorption capacities of 0.08 mol CO_2/mol IL and 1.02 mol CO_2/mol IL. A high enthalpy of absorption means more difficult desorption. They identified triazolide as an ideal anion, which showed good absorption of 0.95 mol CO_2/mol IL and a relatively low absorption enthalpy of 56 kJ/mol. Moreover triazolides are aprotic, inhibiting the formation of hydrogen bonds that are responsible for an increase in viscosity during CO_2 absorption.

Wang *et al.*[44] also developed ILs with superbase cations that provide the thermodynamic driving force for the protic anion to react with CO_2. They obtained equimolar absorption for [MTBDH][trifluoroethanol] and [MTBDH][imidazole] and up to 2 mol CO_2/mol IL for [MTBDH][hexafluoropentanediol].

A strong effort has been made to develop ILs from 'green' sustainable sources. Zhang *et al.*[43] synthesized a series of amino acid-based ILs (AAILs) with tetrabutylphosphonium as cation. Because of their high viscosity, they supported the AAILs on silica gel or added small amounts of water. The absorption capacities of the supported AAILs were between 0.6 and 0.7 mol CO_2/mol IL and close to 1 mol CO_2/mol IL for the AAILs with water. They suggested that for supported AAILs, the proportion of captured CO_2 higher than 0.5 mol CO_2/mol IL is due to physisorption. They observed a white precipitate when water was present. They proposed a mechanism based on analytical investigations showing that the white precipitate is the zwitterionic form of the amino acid. Gurkan *et al.*[48] contested the 1:2 mechanism and favored the 1:1 mechanism based on molecular simulations (Scheme 5).

Goodrich *et al.*[38] obtained experimental values of absorption for different AAILs slightly lower than 1 mol CO_2/mol IL. To explain this behavior they assumed a competition between a 1:2 mechanism and a 1:1 mechanism, the 1:2 being less favorable.

Moreover, by capturing CO_2, the viscosity increases further[49] due to the hydrogen bonding network being formed, which slows the dynamics of absorption.[50] Gurkan *et al.*[42] addressed the problem of high viscosity by designing aprotic heterocyclic anions that suppress the formation of the hydrogen bond network when capturing CO_2. Anions such as 2-cyanopyrrolide or 3-(trifluoromethyl)pyrazolide (Fig. 5) have been proposed and showed capacities of absorption of 0.89 mol CO_2/mol IL and 0.92 mol CO_2/mol IL, respectively, with a trihexyltetradecylphosphonium cation.

Ma *et al.*[51] prepared ditetraalkylammonium amino acids ILs and dissolved them in water for CO_2 absorption measurement. The 20% solution showed the highest solubility of 0.66 mole CO_2 per mole anion (glycine).

Other polymerized ionic liquids were functionalized with methacrylate or vinylbenzyl. By this method Henry's constant was lowered from 59 bar for [bmim][BF_4][22] to 37.7 bar for polymeric [MABI][BF_4] and 26.0 bar for polymeric [VBBI][BF_4].[52]

Using carboxylic anions is another possibility that decreases the Henry's constant to 13 bar for [emim][OAc] at 30°C.[21]

Research at the EIA-FR

The ChemTech Institute is active in the development of a green industrial process to remove CO_2 from flue gas or air. The goal is to absorb CO_2 in an ionic liquid and then use it to synthesize chemicals.

We adapted a stoichiometric method[53] to characterize the absorption of CO_2 in our synthesized ILs. A tightly closed vial with a precise volume placed in a thermostated bath is filled with CO_2 at atmospheric pressure. A known amount of IL is then injected in the vial and the pressure is monitored. The absorption capacity is calculated from the pressure difference by the ideal gas law (Eqn (2)).

$$n_{CO_2} = \frac{pV}{RT} \qquad (2)$$

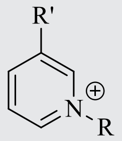
First we screened different anions with trihexyltetradecylphosphonium (P66614) and propylmethylimidazolium (PrMIM) cations (Table 4).

The 2-cyano-Pyr anion is the most promising because of its low viscosity and good absorption properties (0.9 mol CO_2/mol IL). However, its price is prohibitive for large scale applications. Amino acid anions showed very good absorption capacities but high viscosities. Nevertheless, their renewability and easy availability made us pursue our efforts in this direction. To obtain 'green' ILs, we switched to the cation cholinium (Cho). Cho is available on large scale as an additive in chicken feed and it is relatively cheap. Choline combined to amino acids give 'green' ILs with good absorption properties. But their

Table 3. continued

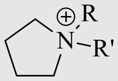
R¹	R²	R³	R⁴	Anion	T [°C]	Absorption [mol CO_2/ mol IL]
butyl	buty	butyl	butyl	Gly	-	0.6[b][43]
hexyl	hexyl	hexyl	tetradecyl	2,4-Cl-PhO	30	0.48[41]
hexyl	hexyl	hexyl	tetradecyl	p-nitro-PhO	30	0.3[41]
hexyl	hexyl	hexyl	tetradecyl	benzotriazolide	23	0.17[40]
hexyl	hexyl	hexyl	tetradecyl	tetrazolide	23	0.08[40]
hexyl	hexyl	hexyl	tetradecyl	2,4,6-Cl-PhO	30	0.07[41]
hexyl	hexyl	hexyl	tetradecyl	Cl	30	0.035[37] 0.034[36]

Pyridinium



R	R'	Anion	T [°C]	Absorption [mol CO_2/mol IL]
Me	Bu	BF_4	30	0.0177[35]
Me	Bu	DCA	30	0.0177[35]
Me	Bu	SCN	30	0.0105[35]

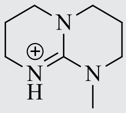
Pyrrolidinium



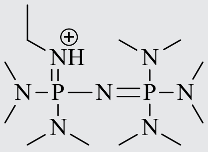
R	R'	Anion	T [°C]	Absorption [mol CO_2/mol IL]
aminoethly	Me	BF_4	30	0.1273[35]
Me	Bu	TFA	30	0.02[35]
Me	Bu	DCA	30	0.0153[35]
Me	Bu	SCN	30	0.0106[35]

Miscellaneous

MTBDH:



(P2-Et)H:



Cation	Anion	T [°C]	Absorption [mol CO_2/mol IL]
MTBDH	2,2,3,3,4,4-hexafluoropentane-1,5-diol	23	2.04[44]
MTBDH	trifluoroethanol	23	1.13[44]
(P2-Et)H	trifluoroethanol	23	1.04[44]
MTBDH	imidazolide	23	1.03[44]
(P2-Et)H	imidazolide	23	0.96[44]
MTBDH	2,2,2-trifluoro-1-phenylethanol	23	0.93[44]
MTBDH	Pyr	23	0.92[44]
(P2-Et)H	Pyr	23	0.86[44]
MTBDH	PhO	23	0.49[44]
(P2-Et)H	PhO	23	0.45[44]
MtBDH	Tf_2N	23	0.02[44]

[a]BETI: bis(perfluoroethyl)sulfonyl)imide; [b]supported on SiO_2

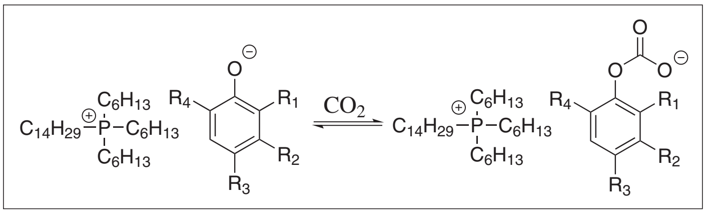
Table 4. CO_2 absorption on ILs synthesized at the EIA-FR; measurements made at 30°C and atmospheric pressure.

Cation	Anion	Absorption [mol CO_2/ mol IL]
P66614	Lys	1.0
P66614	2-cyano-Pyr	0.9
P66614	*p*-methoxy-PhO	0.9
PrMIM	Lys	1.0
PrMIM	*p*-Cl-PhO	0.6
PrMIM	*p*-methoxy-PhO	0.7
PrMIM	Ala	0.7
PrMIM	Gly	0.9
Cho	Gly	0.8
Cho	Ala	0.8
Cho	Pro	0.7
Cho	Sar	0.6
Cho	Lys	1.3
Cho	Met	1.3
Cho	*p*-methyl-PhO	0.9
Cho	p-methoxy-Pho	0.9
Cho	Pyr	0.8

high viscosity is a major drawback and it increases further when absorbing CO_2. As described by Zhang *et al.*[43] we observed also a white precipitate during absorption with AAILs when water was present in the system.

Para-methoxy-phenol (*p*-methoxy-PhO) seems to be a more suitable anion: the increase in viscosity during absorption is less pronounced. Furthermore phenolates do not give rise to the problem of precipitation in the presence of water – amino acids form zwitterions when water is present during absorption (Scheme 5). The recyclability of [Cho][*p*-methoxy-PhO] was tested in the presence of PEG 400 to reduce the viscosity (Fig. 6). After the second cycle, the absorption capacity stabilized itself slightly higher than 0.7 mol CO_2/mol IL and did not change for the seven following cycles. A good recyclability of the IL upon absorption–desorption is crucial for a CCU process. CO_2 should be quantitatively recovered to be used as a chemical starting material and to retain the activity of the IL.

Furthermore, the relatively low molecular mass of Cho (compared to phosphonium or imidazolium) provides low molar weight ILs, thus high mass absorption capacities.



Scheme 4. Capture of CO_2 by substituted phenolic ionic liquids.

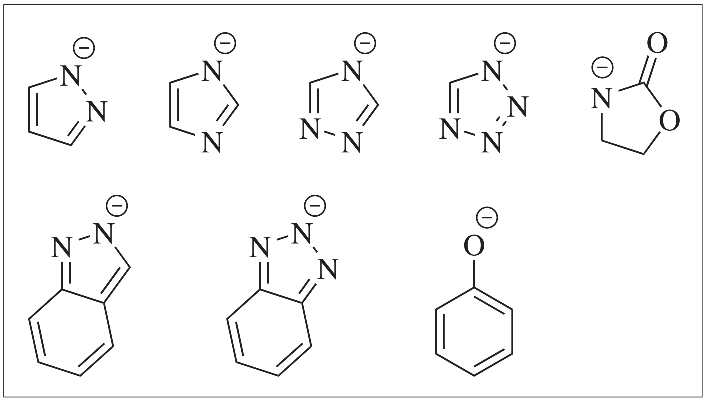
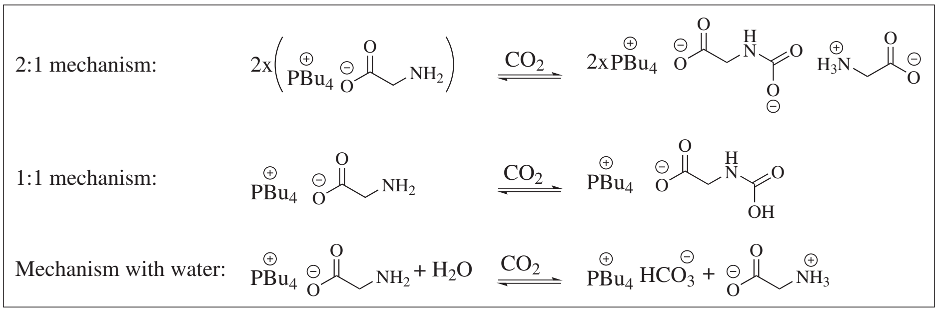


Fig. 4. Basic anions studied. From left to right and top to bottom: pyrazolide, imidazolide, triazolide, tetrazolide, 2-oxooxazolidinide, indazolide, benzotriazolide and phenolate.



Scheme 5. Reaction of absorption of CO_2 by $[PBu_4]$[Gly] following a 2:1 mechanism, a 1:1 mechanism and the mechanism when the IL contains water.

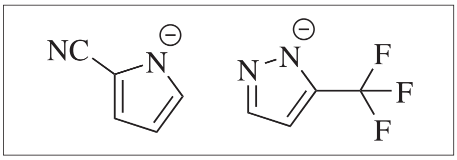


Fig. 5. Structures of 2-cyanopyrrolide and 3-(trifluoromethyl)pyrazolide.

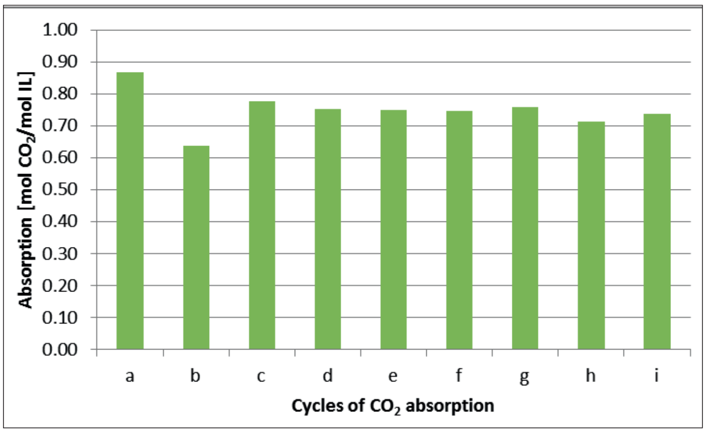


Fig. 6. Cycles of absorption of CO_2 in [Cho][4-MeO-PhOH] 33% in PEG.

Conclusion

Task-specific ionic liquids are efficient media for CO_2 capture – especially anion-functionalized ionic liquids. However, their viscosity can be an issue, particularly because it further increases upon binding with CO_2. Thus, efforts have to be continued in order to design low viscosity ionic liquids. Selectivity of ionic liquids to CO_2 should not be ignored – H_2S will compete with CO_2 if present.[54] Toxicity of the IL should also be taken into account.[55] However by carefully designing the anion and the cation, it is feasible to optimize the ILs in terms of toxicity, efficacy of CO_2 capture and viscosity which makes them promising solvents for industrial applications of CO_2 removal.

We developed green, cheap ionic liquids that absorb up to 1 mol CO_2 per mol IL. Moreover our ILs show a good recyclability upon absorption–desorption.

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