Russian Chemical Reviews **81** (5) 435 – 457 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n05ABEH004288

Capturing CO_2: conventional versus ionic-liquid based technologies

E I Privalova, P Mäki-Arvela, D Yu Murzin, J-P Mikkola

Contents

I.	Introduction	435
II.	Types of CO_2 capturing technology	436
III.	New processes for removing CO_2 using ionic liquid absorbents	441
IV.	Comparison of classical and novel solutions in terms of CO_2 capture	454
V.	Conclusions	454

Abstract. Since CO_2 facilitates pipeline corrosion and contributes to a decrease of the calorific value of gaseous fuels, its removal has become an issue of significant economic importance. The present review discusses various types of traditional CO_2 capture technologies in terms of their efficiency, complexity in system design, costs and environmental impact. The focus is hereby not only on conventional approaches but also on emerging 'green' solvents such as ionic liquids. The suitability of different ionic liquids as gas separation solvents is discussed in the present review and a description on their synthesis and properties in terms of CO_2 capture is provided. The bibliography includes 136 references.

I. Introduction

The today society's dependence on the energy is more obvious than ever before. Worldwide, thousands of machines and appliances have been invented that use energy in manufacturing as well as to improve standards of living and quality of life in general. Moreover, significant amount of energy is consumed by heating and the ever increasing transportation in our globalized world. At the same time, global energy consumption and the level of CO_2 emissions are continuously increasing.

E I Privalova, P Mäki-Arvela, D Yu Murzin Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Turku/Åbo, Finland. Fax (358-2) 215 44 79, tel. (358-2) 215 44 31, e-mail: Elena.Privalova@abo.fi (E I Privalova), tel. (358-2) 215 44 24, e-mail: pmakiarv@abo.fi (P Mäki-Arvela), tel. (358-2) 215 49 85, e-mail: dmurzin@abo.fi (D Yu Murzin)
J-P Mikkola Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Turku/Åbo, Finland. Fax (358-2) 215 44 79,
Technical Chemistry, Chemical-Biological Centre, Umeå University, SE-901 87 Umeå, Sweden, tel. (46-90) 786 50 00,
tel. (358-2) 215 45 74, e-mail: Jyri-Pekka.Mikkola@chem.umu.se

Received 11 November 2011
Uspekhi Khimii **81** (5) 435 – 457 (2012)

CO_2 is considered as a greenhouse gas. The development of efficient methods to capture CO_2 from industrial gas mixtures has become an important issue in the recent years. Various technologies for CO_2 capture can be used, including absorption, adsorption, membranes, and hybrid applications combining these techniques. Currently, capture with aqueous amines seems to be dominant in industrial processes. Although these aqueous amine solutions are effective, there are some serious drawbacks inherently connected to the use of them. For example, the concurrent loss of some volatile amines and the uptake of water into the gas stream lead to intensive energy consumption, cost increases, and corrosion problems. Therefore, it is desirable to search for new chemical agents for CO_2 capture exhibiting favourable characteristics, such as a negligible vapour pressure and high stability.

Recently, the interest towards the development of new CO_2 capturing media had risen significantly.[1] Among the most promising solvents for CO_2 removal, a number of solvent mixtures can be listed. Examples such as ionic liquids and their mixtures with amine solutions, polyionic liquids, 'switchable' ionic liquids, and so forth demonstrate viable alternatives.

Ionic liquids (ILs) and their derivatives are gaining increasing interest due to their unique properties such as extremely low vapour pressure, wide liquid temperature range, high thermal and chemical stability, and their ability to dissolve a variety of chemical compounds. For instance, application of supercritical CO_2/IL biphasic systems has a promising future in separation and chemical reactions, since this technique can be used to separate various species without any cross-contamination, provided that the conditions are chosen appropriately.[2]

Carbon capture and storage (CCS) technologies are targeting a reduction in CO_2 emissions. The appropriate method should be selected taking into account not only capital and operating costs, but also the possible environmental adverse effects. A promising alternative for CO_2 storage could be CO_2 utilization. Sustainable technologies will emerge after matching together CO_2 removal and CO_2 utilization processes.[3]

This paper provides a helicopter view on the conventional and novel solvents for CO_2 removal. The CO_2 capturing technologies can be developed either by means of an improvement in the technical design of the system or by replacing the current solvent systems with new, more efficient media. Therefore, the information is presented in terms of engineering methodologies and chemistry of a new innovative class of solvents.

II. Types of CO_2 capturing technology

The fixation of carbon dioxide is currently one of the most urgent challenges in chemistry, since the enhanced magnitude of CO_2 emissions is quite often assigned to be responsible for global warming. Moreover, together with water CO_2 can cause corrosion in metal pipes. Consequently, CO_2 has to be removed for efficient transportation of gaseous fuel in pipelines and to improve the fuel quality (*i.e.* heating value).

There is a range of emerging technologies for removal of CO_2 that have traditionally been used for upgrading of flue gases and for purification processes in ammonia and hydrogen generation industry. Obviously, flue gases usually consist mostly of nitrogen (typically more than two-thirds), carbon dioxide, water vapour and oxygen.[4] Moreover, flue gases contain a small percentage of pollutants such as particulate matter, carbon monoxide, nitrogen oxides and sulfur oxides.[4]

It is evident that CO_2 is a major constituent not only in flue gases, but also in biogas which is considered to be a carbon dioxide neutral biofuel. However, carbon dioxide should often be removed from biogas to improve the heating value, decrease the transportation costs and avoid the corrosion of pipelines. Consequently, for upgrading purposes, one could eventually use similar techniques as used in ammonia industry. However, it is necessary to consider existing gas separation technologies in view of evaluating their capability for CO_2 capture.

The following CO_2 removal technologies have been implemented in the gas industry:

— chemical solvent scrubbing,
— physical solvent scrubbing,
— chemical mineral trapping,
— adsorption,
— membranes,
— cryogenics.

These methods are described below in more detail.

1. Basic concepts: gas purification processes

Any gas purification process is typically designed for continuous operations. They mostly use solvents which can be regenerated and reused. Hence, the flow sheets usually contain two characteristic sections: absorption and regeneration.

The simplest one is the so called 'one stage' process. Here Fig. 1 only displays the lean absorption and stripper sections.[5] The gas stream flows through a vessel where acid gases (CO_2, H_2S) are removed. The rich solution is fed to the regeneration system where the acid gases are stripped off and thereafter the solvent is recycled to the absorption section. There are many different modifications of these 'prototype' flow sheets for gas treating processes, depending on the initial CO_2 content of the stream to be treated as well as the application area.

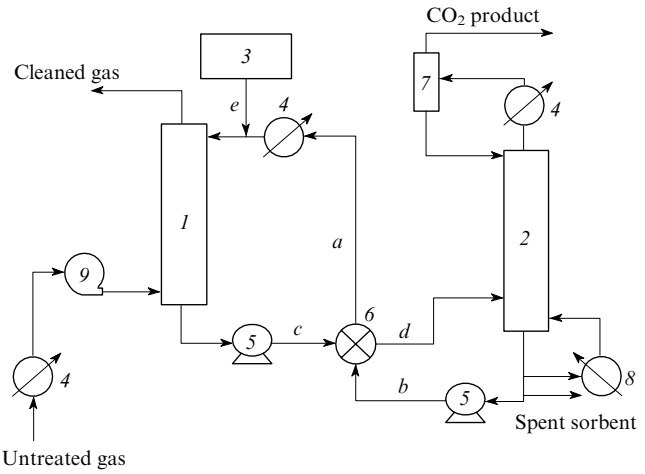


Figure 1. Process layout for a CO_2 capture process for flue gases using monoethanolamine (MEA) as a solvent.[5]
(*1*) Absorber, (*2*) regenerator, (*3*) MEA storage, (*4*) cooler, (*5*) pumps, (*6*) heat exchanger, (*7*) condenser, (*8*) reboiler, (*9*) blower; (*a*) cold and (*b*) hot lean absorbent, (*c*) rich cold and (*d*) rich hot spent (saturated with CO_2) absorbent, (*e*) MEA make up.

2. Chemical solvent scrubbing

Chemical solvent scrubbing is currently the most favoured method to capture CO_2 from process gases.[6] It involves the reaction between CO_2 and the absorbent. The chemical absorbents used are often aqueous solutions of mono-, di- or triethanolamines (Fig. 2), diisopropanolamine, sodium carbonate, sodium hydroxide, and potassium carbonate.[7] During a long time the most common solvent used for CO_2 removal from exhaust gases was monoethanolamine (MEA) (see Fig. 1).

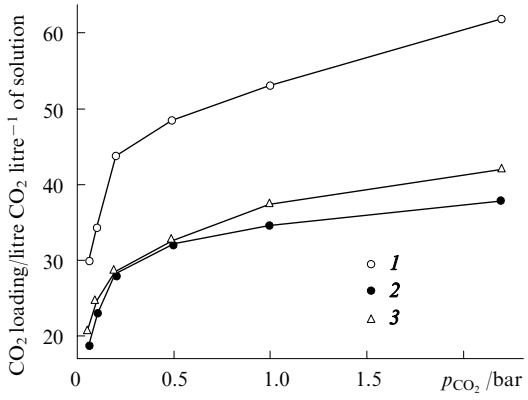


Figure 2. CO_2 loading isotherms of aqueous amine solutions (15 wt %) measured at a CO_2 flow of 52 ml min^{-1} in a loop reactor, volume is 50 ml at 293.5 K (authors' data).
(*1*) MEA, (*2*) *N*-methyldiethanolamine (MDEA), (*3*) diethanolamine (DEA).

Amine scrubbing technology, established over 60 years ago in the chemical and oil industries for removal of hydrogen sulfide and CO_2 from gas streams, still remains the most commonly used technology for gas applications.[5,8–11] Unfortunately, amine treatment being an effective CO_2 capturing process possesses several drawbacks[12]

such as high energy inputs on the regeneration step, corrosivity of amines, limited CO_2 loading capacity and degradation of amines. It is noteworthy that amine selection should be carefully considered to match the desired requirements and solvent properties for effective scrubbing applications.[12]

Nowadays, the most widely applied gas scrubbing technologies are BASF's activated MDEA process and UOP's Benfield processes.[13] The Benfield process uses a chemical absorbing solution based on 30 % hot potassium carbonate (K_2CO_3) in water and an activator. The activator in low concentration has to be added into the carbonate solution to improve the absorption rate of CO_2.[14–18]

Modern, energy-efficient activated *N*-methyldiethanolamine (aMDEA) process by BASF was released for licensing as the aMDEA technology in 1982.[19] Later on, a revamp strategy was introduced to the original two-stage scrubbing systems now comprising both lean and semi-lean solution sections in a single absorption column (Fig. 3).[18] The tertiary amine has a high acid-gas loading capacity and possesses a low regeneration energy requirement. Since CO_2 binds chemically to MDEA much less stronger than to MEA, therefore, the partial regeneration of the solvent can be carried out by simple flashing (physical characteristics). The character of this solution is more like a hybrid of being a strong chemical and a purely physical solvent.[18]

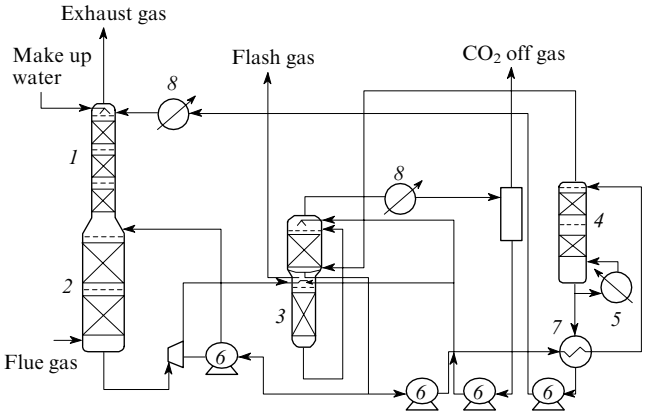


Figure 3. Process layout for BASF activated MDEA (aMDEA) process.[18]
(*1*) Lean absorber, (*2*) bulk absorber, (*3*) low pressure flash column, (*4*) regenerator (stripper), (*5*) reboiler, (*6*) pumps, (*7*) heat exchanger, (*8*) cooler.

MDEA/water solution contains a certain amount of an activator.[20, 21] Different chemical species, namely 2-amino-2-methyl-1-propanol (AMP), piperazine, *N*-methylpiperazine, morpholine *etc*. have been explored as viable activator compounds, out of which piperazine became the most common choice. The plausible explanation to this is that piperazine contains two reactive amine groups, which can attach to CO_2. Further, piperazine bonds very strongly with CO_2 and does not readily release it to MDEA. This means that the equilibrium partial pressure of CO_2 over the solution is lower than with MDEA alone. Recently, a new activator 2-(1-piperazinyl)ethylamine was proposed.[20]

The character of solvent may be deflected to chemical or physical side depending on the presence of an activator and its concentration (Fig. 4). This makes it possible to retrofit and adapt the process for different situations.

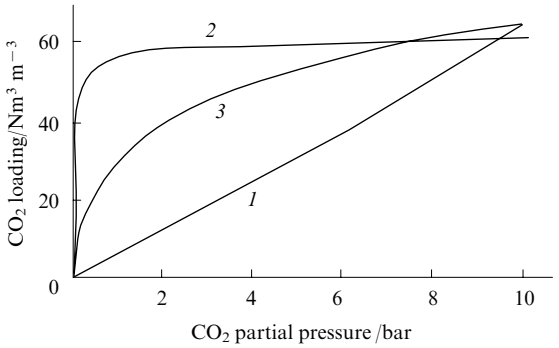


Figure 4. CO_2 loading characteristics of various solutions depending on CO_2 pressure.[18]
(*1*) 'physical' solvent; (*2*, *3*) 'chemical' solvents MEA and aMDEA, respectively.

When comparing these two technologies (Benfield *vs*. BASF), it is evident that the BASF activated MDEA process has more preferable energy consumption characteristics than the Benfield process.[22]

Thus, aMDEA technology remains the most widely used modern gas scrubbing technology[23] due to the following advantages: superior loading capacity and absorption kinetics, high energy efficiency, non-corrosivity, absence or low level of solvent degradation, low solvent losses, high reliability, rather low-toxic and reasonably biodegradable absorption solution and low foaming tendency.

3. Physical solvent scrubbing

Besides chemical absorbents, physical absorbents can be a good rival for effective CO_2 removal (Fig. 5).[24]

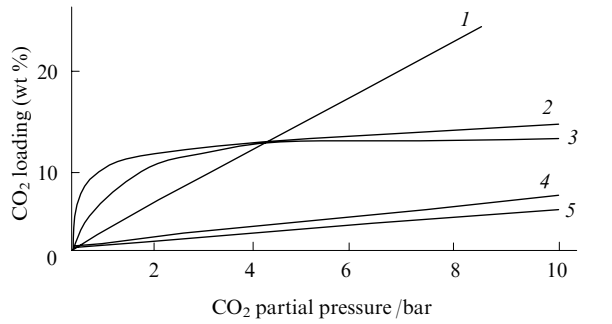


Figure 5. CO_2 bulk removal capacity of 'physical' solvents compared to the 'chemical' ones.[24]
(*1*) Rectisol process, 253 K; (*2*) aMDEA process (50 wt. %), 343 K; (*3*) MEA (25 wt. %), 333 K; (*4*) Purisol process, 313 K; (*5*) Selexol process, 313 K.

Physical absorbents usually show their advantages for gas mixtures containing very high partial pressures of CO_2. They tend to be chosen over chemical solvents while operating under high pressures.

The technologies developed for CO_2 removal using physical solvents are, in principle, similar to those using chemical solvents. The CO_2-bearing gas is typically con-

tacted counter-currently with the absorbent in a packed or tray tower. The advantage of this technology is that the regeneration is performed by pressure reduction resulting in much lower energy consumption and the absorbed CO_2 is flashed into the vapour phase.[5] The solvents are relatively non-corrosive and, therefore, carbon steel can be used.[25] They could be a perfect choice but possess, however, several disadvantages[12] such as low CO_2 absorption capacity, solvent losses, absorption of hydrocarbons and high circulation rates resulting in higher capital and operating costs.

The main physical solvents used for CO_2 capture are typically cold methanol (Rectisol process), *N*-methyl-2-pyrrolidone (Purisol process), dimethyl ether of polyethylene glycol (Selexol process) and propylene carbonate (Fluor Solvent process).

The Selexol process has been one of the most often applied acid-gas removal systems based on physical solvents. Solvents containing DEPG [a mixture of dimethyl ethers of polyethylene glycol $CH_3O(C_2H_4O)_nCH_3$, n is between 2 and 9] are licensed and/or manufactured by several companies including Coastal Chemical Company (as Coastal AGR), Dow (Selexol) and UOP (Selexol).[25]

The Rectisol process[26,27] seems to be the dominating physical acid-gas scrubbing processes. This process, which uses methanol as a solvent, was developed by Lurgi in collaboration with Linde. The Rectisol process is very adjustable and can be tailored by product specification or process objectives.

4. Chemical mineral trapping

Trapping and long-term storage of CO_2 may be achieved by mineral carbonation as an alternative to geological storage in underground aquifers.[28–30]

Naturally occurring silicate minerals that contain high concentrations of magnesium oxide (MgO) and calcium oxide (CaO) are serpentine and olivine.[31] In this case various carbonates can be formed such as calcite, magnesite, dolomite, and siderite. This process may occur *via* simplified reactions shown below.[32]

$$CO_2\,(gas) \rightleftharpoons CO_2\,(aq.)$$

$$CO_2\,(aq.) + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3\,(calcite)$$

$$Ca^{2+} + Mg^{2+} + 2\,CO_3^{2-} \rightleftharpoons CaMg(CO_3)_2\,(dolomite)$$

$$Fe^{2+} + CO_3^{2-} \rightleftharpoons FeCO_3\,(siderite)$$

$$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3\,(magnesite)$$

Binding carbon dioxide in carbonates can be carried out through different processes, ranging from the most basic accelerated weathering of limestone, where carbonates are transformed to bicarbonate, to advanced multistep processes. All existing variations have inherently two main processes namely direct and indirect carbonation.

Direct carbonation is a single process step, when both the extraction of metals from the feedstock and the subsequent reaction with the dissolved carbon dioxide take place in the same reactor. Indirect carbonation process is divided into several steps. At first, the reactive component (usually Mg or Ca) is extracted from the feedstock as oxide or hydroxide. After that, it is made to react with carbon dioxide to form the desired carbonates.[28] In general, mineral trapping is controlled by pH and to a lesser extent by CO_2 pressure and temperature. Basic conditions promote carbonate precipitation, while acidic conditions favour carbonate dissolution.[33] It has been claimed that these carbonate formations can be stored in saline aquifers for millions of years.[33–36] It is environmentally benign, permanent storage of CO_2 by using abundant mineral resources. This provides a leakage-free long-term binding of CO_2 in contrast to undeground storage.

Conversion of CO_2 to stable carbonate in nature is, however, slow; *e.g.* hundreds of years are needed in retrospect.[35] Thus, mineral trapping contributes to CO_2 sequestration, but only in the long term.[32] Another problem is the destiny of the CO_2-containing end product. Thus, this method has several disadvantages and is too expensive compared to other CO_2 capture methods.

5. Adsorption

Adsorption takes place due to the significant intermolecular forces between gases and the surfaces of certain solid materials. Some solid materials with high surface areas, such as activated carbon and molecular sieves (zeolites)[37] and new metal organic frameworks (MOFs) can be used to separate CO_2 from gas mixtures by adsorption. These adsorbents are normally arranged as packed beds of spherical particles.[38]

The process operates with the basic adsorption and regeneration steps on a repeated cycle. Gas is fed into a solid bed in the adsorption step adsorbing CO_2 and allowing other gases to pass through the bed. When the bed becomes completely saturated by CO_2, the feed gas is switched to another adsorption bed and the completely saturated bed is regenerated by removing the bound CO_2. Adsorption of a single gas or multiple layers of gases can be carried out, depending on the temperature, partial pressures, surface forces and adsorbent pore sizes.[7]

In the pressure swing adsorption (PSA) unit, the gas mixture flows through the beds at elevated pressures and at low temperatures until the adsorption of the desired compound approaches equilibrium conditions at the bed exit and the adsorbent is regenerated by pressure reduction. Once regenerated, the beds are ready for another adsorption cycle. In the temperature swing adsorption (TSA) process, hot inert gas or external heat is used to regenerate adsorbents by raising their temperature. In the electric swing adsorption (ESA) process, regeneration takes place by passing a low-voltage electric current through the adsorbent. PSA and TSA are used commercially for gas separation and also to some extent in hydrogen production and in the removal of CO_2 from natural gas. It has been found that PSA is superior to TSA in all cases due to the high-energy requirements and low speed of regeneration in TSA. ESA is not yet commercially available but it is anticipated to offer the prospect of lower energy consumption than the other two processes. Adsorption is not yet a highly attractive approach for the large-scale industrial separation of CO_2 since the available adsorbents have low capacity and selectivity for CO_2 adsorption. The adsorption method may, however, be successful when coupled to another capturing technology.[35]

a. Adsorption by means of membranes

The differences in physical or chemical interactions between gases and membrane material cause one component to pass through the membrane faster than another component. Multiple stages and/or recycle of one of the streams are necessary to achieve high degrees of separation with the membrane process. This leads to increased complexity, energy consumption and costs. This technology is likely to be more expensive compared to other capture techniques in large scale installations. Several membranes with different characteristics may be required to separate high-purity CO_2. Various types of membranes are currently available, including porous inorganic palladium, polymeric and zeolitic membranes.

Gas separation and gas absorption membranes are the two types of membrane processes of choice. In the former case, the porous structure of the solid membrane permits the preferential permeation of the mixture constituents. The gas mixture containing CO_2 is introduced into the membrane separator at elevated pressure and CO_2 passes preferentially through the membranes and is recovered on the shell side of the separator, at reduced pressure. Gas permeability and membrane selectivity are the main parameters considered for designing and operating a separation process. Membranes for CO_2 separation from, for instance, flue gases have not been widely explored because of the low pressure of the flue gases. The atmospheric flue gas needs to be pressurized to achieve the desired separation and the costs are almost twofold higher than in the case of a conventional amine capturing process because of the compression energy.[37]

On the other hand, gas absorption membranes are microporous solids that are used as contacting appliances between a gas and a liquid. The CO_2 diffuses through the membrane and is removed selectively by an absorption liquid such as an amine. This type of membrane is more compact than the conventional membrane separators. In contrast to the gas separation membranes, it is the absorption liquid, not the membrane that gives the process its selectivity.[39]

b. Adsorption by means of metal organic frameworks

Porous metal organic frameworks (MOFs) are constituent constructions consisting of organic and inorganic building blocks.[40–41] They are build of metal ions, their clusters or metal oxides surrounded by polymeric clusters bridged by organic ligands (Fig. 6).[38,42]

Recently, a potential interest was aroused by this type of adsorbents considered as versatile CO_2 capturing agents,[38,43] due to their unique properties such as high surface area, high porosity, low crystal density combined with high thermal and chemical stability.[38] Comprehensive knowledge on MOFs and their applications for CO_2 capture are thoroughly collected in the reviews.[38,41,43,44] The CO_2 adsorption isotherms of different MOFs adsorbents have a Langmuir-like behavior and show relatively high efficiency (Fig. 7).[45]

Different metals can expedite different CO_2 capturing capacity. For example, among the series based on Zn,[35] Li, Ni, Cu, Co, Mg,[38,41] the MOFs with Mg showed the highest CO_2 capture.[38] The adsorption isotherms of different gas mixtures were presented and separation mechanisms suggested by Remy *et al.*[46]

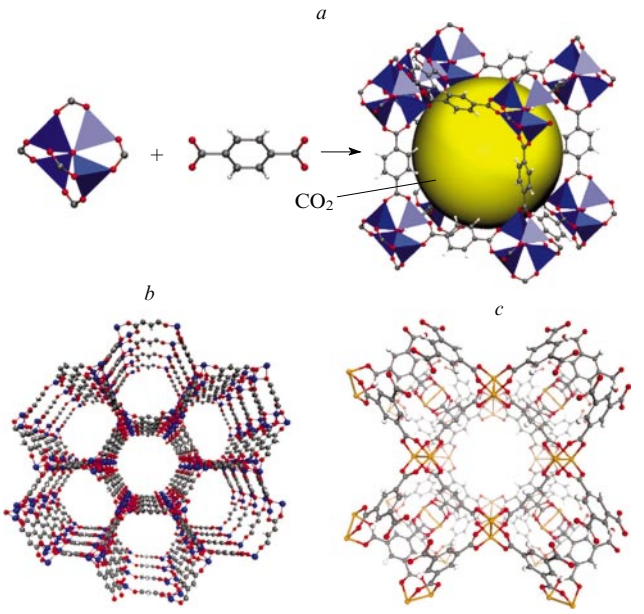


Figure 6. Examples of MOFs: (IRMOF-1) obtained by the modular synthesis of metal oxide corners Zn_4O and organic benzenedicarboxylic acid linkers (*a*), Mg-MOF-74 [Mg_2(DHBDC), DHBDC is 2,5-dihydroxybenzene-1,4-dicarboxylate] (*b*), HKUST-1 [$Cu_3(BTC)_2$, BTC is 1,3,5-benzenetricarboxylate] (*c*).[38]

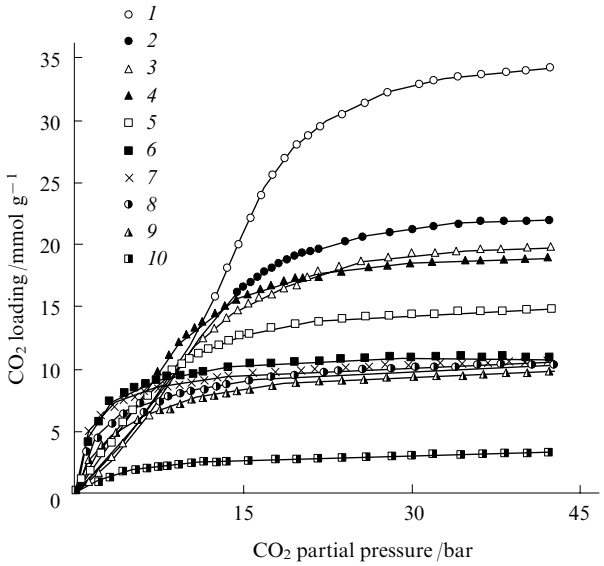
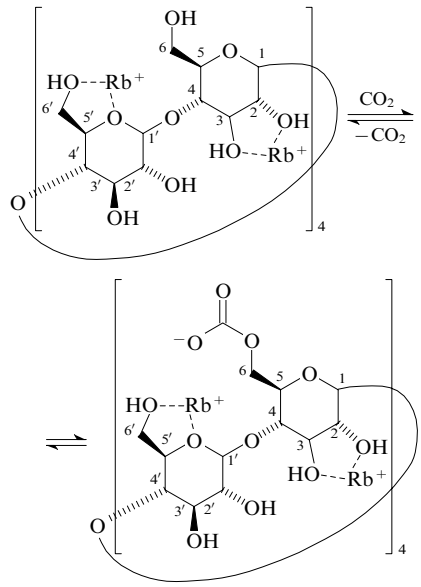


Figure 7. Adsorption isoterms of CO_2 for several MOFs at 298 K: MOF-177 (*1*), IRMOF-1 (*2*), IRMOF-6 (*3*), IRMOF-3 (*4*), IRMOF-11 (*5*), Cu_3 $(BTC)_2$ (*6*), MOF-74 (*7*), MOF-505 (*8*), MOF-2 (*10*); for comparison data of the activated carbon Norit RB2 (*9*).[45]
IRMOF-n is $ZnOQ_3$: $n = 1$, Q is BDC, (benzene-1,4-dicarboxylate ligand); $n = 3$, Q is 2-aminobenzene-1,4-dicarboxylate; $n = 6$, Q is 2,3-cyclobutabenzene-1,4-dicarboxylate; $n = 11$, Q is HPDC (4,5,9,10-tetrahydropyran-2,7-dicarboxylate); MOF-2 is $Zn_2(BDC)_2$, MOF-177 is $Zn_4O(BTB)_3$ (BTB, benzene-1,3,5-tribenzoate); MOF-505 is Cu_2(BPTC) (BPTC, biphenyl-3,3′,5,5′-tetracarboxylate).

CO_2 is meant to be trapped through the covalent forces.[40] The development of CO_2 removal processes based on MOFs can be optimized through such key factors as pore-size control, open metal sites, immobilized functional groups and introduction of different cations.[38]

These adsorbents are reversible. Thus, the following mechanism of chemisorption of CO_2 by CD-MOF-2, consisting of the renewable cyclic oligosacchatide γ-cyclodextrin and RbOH was proposed:[40]



Depending on their specific composition, MOFs can be regenerated at temperatures above 373 K [38] or some even at room temperature.[40] In order to obtain data on diffusivity of guest molecules and heats of adsorption, a number of molecular simulation approaches were applied.[41, 47]

Apart from efficiency of adsorbents their selectivity comes as one of the important features. After comparing selectivity for such gas mixtures as CO_2-CH_4 (Fig. 8), CO_2-N_2 and CO_2-O_2, it appeared that besides pore size the selectivity is often related to the presence of highly polar functional groups.[40] For example, the NO_2, CN and OH groups have high dipole moments and facilitate better CO_2 capture and selectivity than other functional groups.[38, 48] Moreover, the selectivity for different MOFs can be predicted by combining experimental data with the ideal adsorbed solution theory model.[49]

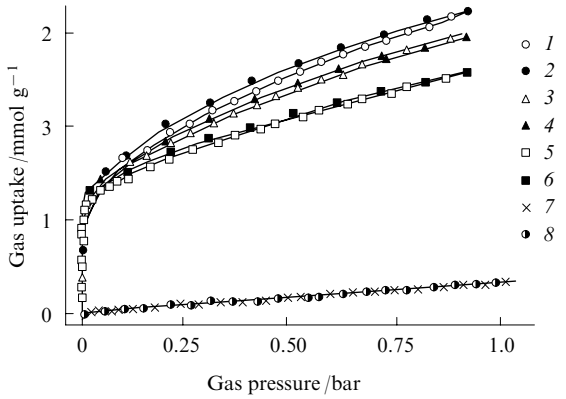


Figure 8. Comparative study of selectivity of CO_2 and CH_4 sorption for CD-MOF-2.[40]
(*1*, *3*, *5*) CO_2 capture at 273, 283 and 293 K, respectively; (*2*, *4*, *6*) CO_2 desorption at the same temperatures, respectively; (*7*, *8*) sorption and desorption of CH_4 at 298 K.

c. Zeolites and carbonaceous adsorbents: comparison in terms of CO_2 capture

The adsorbents for carbon dioxide may be molecular sieve materials (zeolites),[50] activated carbons,[51] activated charcoals [52] or any other suitable absorbents. The gas purification usually includes at least two absorbent materials, activated carbon, molecular sieves, and/or silica gel, which may be mixed together and/or be present as discrete layers.[53] As a rule, carbon dioxide is removed from the dry air stream and, thus, the gas stream needs to be passed through the silica gel bed (or any other process step to remove the water in air) in which water is desorbed.

Silica gel typically has micropores in the range of 2–4 nm, which facilitates removal of small molecular weight hydrocarbons and siloxanes [for example, compounds with the molecular mass (MM) $\leqslant$ 300 g mol^{-1} for hydrocarbons and MM $\leqslant$ 225 g mol^{-1} for siloxanes).[21] The value of CO_2 adsorbed for monosilane-functional Davison grade 62 silica gel was around 0.36 mmol g^{-1} (296 K, 1 bar) and decreased with a temperature increase. Pressure elevation up to 12 bar provided a two-fold capacity increase.[44]

Among other solid adsorbents zeolites are attracting a wide attention due to their numerious properties.[44] A possible mechanism [54] of CO_2 adsorption on CaY-zeolite is illustrated in Fig. 9. Among unmodified zeolites, zeolite 13 X was reported to have the highest CO_2 adsorption capacity (3.5 mmol g^{-1} at 298 K and pressure 1 bar).[44, 55] On the contrary H-ZSM-5 with a different Si : Al ratio at similar conditions provided a capacity of no more than 2 mmol g^{-1}.[56] The CO_2 loading capacity of zeolites decreases with temperature rise. In case of the zeolite 13X,

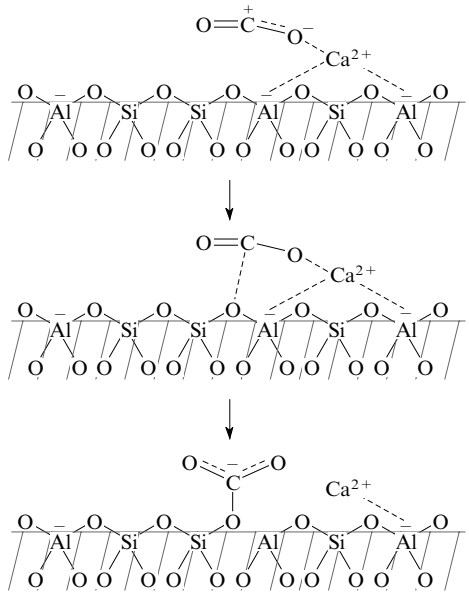


Figure 9. Suggested mechanism of CO_2 adsorption on CaY zeolite.[54]

a decline in CO_2 loading (from 4 mmol g^{-1} to 2 mmol g^{-1}) was observed when the temperature was increased from 273 K to 353 K.[55]

Activated carbon (AC) is a highly microporous material with a large surface area. It is used as an absorbent in a wide range of applications. Many activated carbons possess internal surface areas in the region of 1200 m^2 g^{-1}. This material is manufactured by partial burn-off (pyrolysis) of carbon-rich materials such as coal, wood and nut shells and is then either steam or chemically activated to develop the internal pore structure.[57] In fact, any carbon-containing material can be used as a precursor of such a product. Activated carbon materials typically have large size micropores, about 2 to 10 nm and, therefore, the materials can be used for the removal of the high-molecular-mass hydrocarbons (for example, compounds, which have the MM $\geqslant$ 300 g mol^{-1}) and high-molecular-mass siloxanes (with MM $\geqslant$ 225 g mol^{-1}).[53] In terms of CO_2 adsorption, activated carbon is less efficient than zeolite 13X at low pressures (Fig. 10).[5, 51] However, since its efficiency

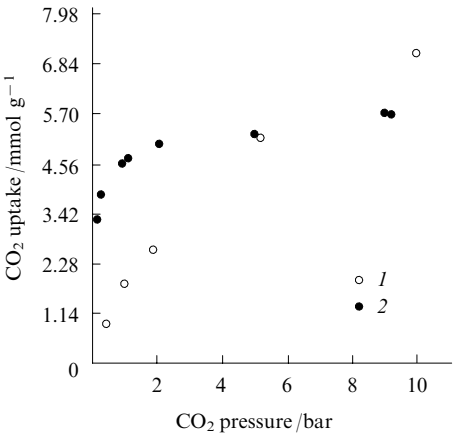


Figure 10. Adsorption isotherms of CO_2 on activated carbon (*1*) and zeolite 13X (*2*) at 298 K.[51]

increases with increasing pressure, in the pressure range exceeding 5 bar, the CO_2 capture of AC exceeds by far that of ZEO 13X due to more extended surface area and specific pore volume (see Fig. 10). Similar results were shown by Siriwardane *et al.*[58] There is a number of papers devoted to amines immobilized on zeolites in order to improve CO_2 capturing efficiency.[44] A remarkably high CO_2 uptake of 110 mg g^{-1} (298 K and 1 bar) for N-enriched activated carbon was reported by Thote *et al.*[59] However, the results of Bezerra *et al.* demonstrated a decrease in efficiency after MEA impregnation (Table 1).[51] In case of zeolite 13X, the decrease was on average 1.5 times at 298 K and at 348 K. Similar behaviour was obtained for activated carbon at 298 K. However, at higher temperatures (348 K) the system was less sensitive and the CO_2 loading for amino-impregnated activated carbons increased on average twice in the pressure range from 0.1 bar to 10 bar. This behaviour was explained by extensive chemisorption on the surface of impregnated samples to form carbonates.[55] Activated carbon materials are utilized in several gas separation applications, but the drawback of using them is the low selectivity

Table 1. Comparison of CO_2 adsorption efficiency (mg CO_2 per 1 g of adsorbent) for solid adsorbents before and after amine impregnation.[51]

Adsorbent	Adsorbed amount of CO_2					
	298 K			348 K		
	0.1 bar	1 bar	10 bar	0.1 bar	1 bar	10 bar
AC	10	83	340	3	31	156
AC/MEA	8	45	214	7	75	260
Zeolite 13X	83	206	255	54	142	197
Zeolite 13X/MEA	74	136	162	26	94	180

of carbon dioxide over methane, which may limit their use in CO_2 removal.

To summarize, one can conclude that at low pressures (1 bar), the efficiency of adsorbents in terms of CO_2 capture varies in the following order: modified silica gel < activated carbon < MOFs < 13X zeolite. At higher pressures (10 bar), some alterations can be observed in this order due to abovementioned material characteristics: modified silica gel < 13X zeolite < activate carbon < MOFs.

6. Cryogenics

Cryogenics is a low-temperature separation technique. Cryogenic separation of a gas mixture involves compressing and cooling down the CO_2 bearing gas mixture in several stages in order to induce phase changes in CO_2 and, invariably, other mixture components in the case of, for example, flue gases. A major disadvantage of cryogenic separation of CO_2 is its inherent energy intensiveness to provide the refrigeration necessary for the process, particularly for dilute gas streams. Another disadvantage is the possible plugging of solid CO_2 clusters and ice formation from the water vapour freezing in the CO_2 feed mixture. Cryogenic separation has, however, the advantage of enabling direct production of liquid CO_2. This liquid CO_2 could be easily transported and shipped to the storage. Cryogenic separation is widely used in commercial operations for purification of CO_2 from streams which contain high CO_2 concentrations (typically >90%). It is not normally used for more dilute CO_2 streams, although it has recently been claimed[60] that CO_2 can be captured (by freezing it as a solid) from flue gases being under atmospheric pressure. The most promising applications for cryogenics are expected to be for separation of CO_2 from high-pressure gases, which occur in pre-combustion capture processes, or in oxyfuel combustion in which the input gas contains a high concentration of CO_2.[60]

III. New processes for removing CO_2 using ionic liquid absorbents

1. Comparison of ionic liquid absorption with chemical and physical absorptions

Since both chemical and physical solvents are operating under different conditions and have certain limitations, it would be desirable to have a CO_2 removal process that would merge their versatile advantages and depreciate intrinsic drawbacks. Thus, an ideal CO_2 capturing sorbent should be able to provide such properties as fast adsorption and desorption kinetics, stability and regenerability. In

addition, a large sorption capacity and a wide tunable range of operational conditions in order to adjust to the process requirements should be realized.[44]

Ionic liquids have been identified as a novel alternative, not only as solvents but also as candidates for other applications such as gas purifications. The typical characteristics of ionic liquids are tackled briefly in Section III.2.a. Thus, ionic liquids represent a new, clean and potentially green technology offering the promise of minimized waste streams, atom efficient operations and, therefore, environmental and cost benefits.

The concept of absorption of CO_2 in ionic liquids based on their unique properties providing some advantages over the traditional processes such as a high level of CO_2 absorption, while hydrocarbon co-absorption and corrosion problems are advantageously minimized. Moreover, the magnitude of solvent losses and regeneration energy are remarkably low compared to abovementioned processes.

Recently, ionic liquids were explored to be used in gas separation processes. Ionic liquids containing a carboxylate moiety have considerable preferences for CO_2 removal.[12]

Pure CO_2 loading curves for several solvents as a function of CO_2 partial pressure, at room temperature, are introduced in Fig. 11.[12] Under the studied conditions, the favoured chemical solvents are aqueous amines (curves *1–3*, Fig. 11), all of which possess the highest volumetric CO_2 loadings over the entire pressure range. The physical solvents listed here (curves *6–10*, Fig. 11), all display lower volumetric CO_2 loadings than chemical solvents. It is essential that their loading curves are linear over the entire pressure range, whilst CO_2 is physically dissolved without chemical forces.

The behaviour of ionic liquids containing different anions differs and is characteristic of either chemical (curve *4*, Fig. 11) or physical solvents (curve *5*, Fig. 11). For instance, 1-butyl-3-methylimidazolium acetate [bmim]OAc acts mostly as a chemical solvent, while 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] tends to be a physical solvent. Thus, a search for proper ionic liquids for gas separation will provide a new class of solvents superior to classical chemical absorption processes.[12]

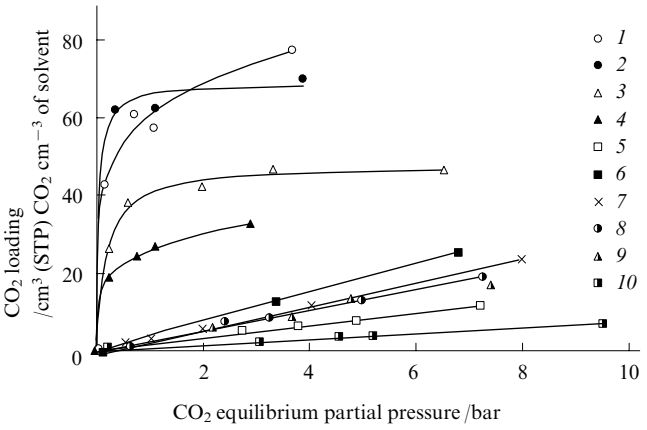


Figure 11. Absorption isoterms of CO_2 by different solvents at 297 K.[12] (*1*) Aqueous MDEA (50 wt %), (*2*) aqueous MEA (30 wt %), (*3*) aqueous MEA (15 wt %), (*4*) aqueous [bmim]OAc (14 wt % H_2O), (*5*) aqueous [bmim][BF_4] (0.2 wt % H_2O), (*6*) Selexol, (*7*) *N*-acetylmorpholine (NAM), (*8*) aqueous *N*-formylmorpholine (NFM) (0.2 wt % H_2O), (*9*) aqueous solution (1 : 1) NAM – NFM (3.0 wt % H_2O), (*10*) water; bmim is 1-butyl-3-methylimidazolium.

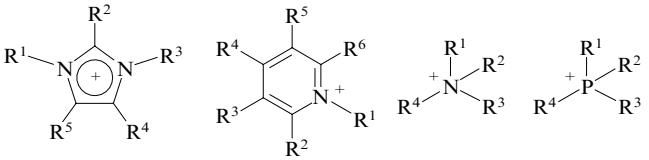
2. Properties and synthesis of ionic liquids

a. Characteristic properties of ionic liquids

Ionic liquids are a category of compounds which are made up of ionic species. Moreover, they should remain liquids at or below process temperatures. The simplest ionic liquids consist of a single cation and a single anion.

The properties of ionic liquids can be tailored by varying the cation and anion pairing (Fig. 12).[61] One should mention the general progression of the changes in IL properties with anion type: the combination containing $[AlCl_4]^-$ is sensitive to moisture and air, being reactive to water. The combinations containing other anions (see Fig. 12) are both air- and water-stable. For the second type of compounds, decreasing coordinating ability and increasing hydrophobicity emerge as characteristic features.

Cations:



R^i = H, Alk, substituted Alk

Anions: $[AlCl_4]^-$, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, $CF_3CO_2^-$, $CF_3SO_3^-$ (TfO^-), $[BF_4]^-$, $[PF_6]^-$, $[(CF_3SO_2)_2N]^-$ (Tf_2N^-)

Figure 12. Examples of common cation and anion pairs used in the formation of ionic liquids.[61]

Favoured ILs are non-volatile and often thermally stable up to over 623 K, which can minimize solvent losses due to evaporation and environmental release. Low volatility also adds a safety benefit by ensuring that the flash point for combustion is high. Chemicals can be recovered from non-volatile ILs by distillation/sublimation and pervaporation. On the other hand, non-volatility also means that typical ILs cannot be purified by distillation.[61]

ILs can be distinguished from higher temperature molten salts in several ways, *i.e.* ILs exhibit several types of coordination possibilities, *e.g.* through hydrogen-bond donor and acceptor functions, dipole interactions, CH-aromatic packing and adjustable co-solvent miscibility ranging from miscible to immiscible with polar solvents (*i.e.*, water) as well as with non-polar liquids.[61]

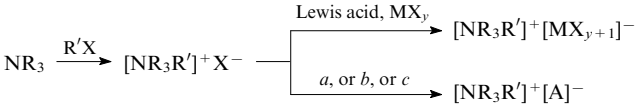
b. Synthesis of ionic liquids

The synthesis of ionic liquids consists of several steps. Combining a nitrogen-containing heterocyclic ring, preferably a heteroaromatic ring, with an alkylating agent (for example, an alkyl halide) provides formation a quaternary ammonium salt, followed by an ion exchange reaction with various Lewis acids (most notably $AlCl_3$) to form ionic liquids. There is a number of heteroaromatic rings suitable for this purpose such as pyridines, imidazoles, pyrroles and their substituted derivatives. These rings can be alkylated

with virtually any C_{1-20} groups. Essentially, groups larger than C_{20} tend to produce low melting solids rather than ionic liquids.[12]

Plenty of counter-ions can be involved in the synthesis of ionic liquids and, consequently, in affecting their properties. Among the anions, the most often used ones contain tetrachloroaluminate, tetrabromoaluminate, tetrachlorogallate, tetrafluoroborate, hexafluorophosphate, nitrate, trifluoromethanesulfonate, methanesulfonate, *p*-toluenesulfonate, hexafluoroantimonate, hexafluoroarsenate, perchlorate hydroxide, dichlorocuprate, trichloroferrate or trichlorozincate anion, as well as various lanthanum, nickel, cobalt, manganese and other metal ions.[12]

The synthesis of ionic liquids can generally be split into two sections: the formation of the desired cation, followed by an anion exchange, thus leading to the final, desired product. The synthesis of ILs for ammonium salts is demonstrated below.[62]



(*a*) metal salt MA (−MX), (*b*) Brønsted acid HA (−HX), (*c*) ion exchange resin

In some cases only the first synthesis step of an IL is required. This is the case, for instance, in the synthesis of ethylammonium nitrate. In many cases, the desired cation is commercially available at reasonable cost, most commonly as a halide salt. Thus, only an anion exchange (anion metathesis) is required for the formation of the final ionic liquid. However, this methodology has two drawbacks: first of all, large amounts of waste halide salts are formed and, secondly, the resulting ionic liquid almost inevitably contains residual halide contamination. Examples of these are the symmetrical tetraalkylammonium salts and trialkylsulfonium iodide.

The formation of the cations may be carried out either *via* protonation with a free acid or by quaternization of an amine or a phosphine, most commonly with a haloalkane. The protonation reaction, important in the formation of salts such as ethylammonium nitrate, involves the addition of 3 M nitric acid to a cool, aqueous solution of ethylamine.[63] The alkylation process possesses the advantages that (i) a wide range of cheap haloalkanes are available, and (ii) the substitution reactions generally occur smoothly at reasonable temperatures. Furthermore, the halide salts formed can easily be converted into salts with other anions. The quaternization reactions are extremely simple: the amine (or phosphine) is mixed with the desired haloalkane, and the mixture is then stirred and heated. The reaction may be carried out with chloroalkanes, bromoalkanes, and iodoalkanes. The most important requirement to perform quaternization reaction is to keep reaction mixture free of moisture, since the products are often extremely hygroscopic. Quaternization reactions between 1-alkylimidazoles and methyl triflate,[64] trialkylamines and methyl tosylates,[62] and triphenylphosphine and octyl tosylate [65] have also been used for the direct preparation of ionic liquids. In principle, any alkyl compound containing a facile leaving group may be used in this manner.

The anion-exchange reactions of ionic liquids can be divided into two distinct categories: direct treatment of halide salts with Lewis acids and the formation of ionic liquids by anion metathesis. These two approaches are dealt with separately, as quite different experimental methods are required for each.[62]

The most common method for the synthesis of ionic liquids by anion-exchange reaction is simple mixing of the Lewis acid and the halide salt. Some ionic liquids have been prepared by treatment of halide salts with metal halides which are not usually considered as Lewis acids. Examples of these include salts of the type $[emim]_2[MCl_4]$ (M = Co, Ni) [66] and $[emim]_2$ $[VOCl_4]$ ([emim] is 1-ethyl-3-methylimidazolium).[67] These are formed by treatment of two equivalents of [emim]Cl with one equivalent of MCl_2 and $VOCl_2$, respectively.

Metathesis reaction is applied for the preparation of relatively air- and water-stable ionic liquids. Iodide [emim]I reacts with a range of silver salts ($AgNO_3$, $AgNO_2$, $AgBF_4$, AgOAc, and Ag_2SO_4) in methanol or aqueous methanol solution. This method [62] is most efficient for the synthesis of water-miscible ionic liquids, but is obviously limited by the relatively high cost of silver salts, and also the large quantities of solid by-products are produced. Moreover, as already stated, residual halide contamination is expected.

The main goal in all anion exchange reactions is the formation of the desired ionic liquid uncontaminated with unwanted cations or anions, a task which is easier for water-immiscible ionic liquids. The most common approach for the preparation of water-immiscible ionic liquids is firstly to prepare an aqueous solution of a halide salt of the desired cation. The cation exchange is then carried out either with the free acid of the appropriate anion, or with a metal or ammonium salt.

c. Gas solubilities in ionic liquids and gas separation

A wide variety of physical properties are important in the evaluation of ionic liquids for potential use in industrial processes. Knowledge of the phase behaviour of ionic liquids with gases, liquids, and solids is necessary to assess the feasibility of their use for reactions, separations, and processing materials. High solubility or selective solubility of the desired gases might make ILs quite attractive.

The solubilities of many gases in normal liquids are quite low and can be adequately described at ambient pressure or below it by Henry's law. The Henry's law constant (H) is defined as

$$H(T,p) \equiv \lim_{x \to 0} \frac{f^{L}}{x}, \tag{1}$$

where x is the mole fraction of gas in the liquid and f^{L} is the fugacity of the gas in the liquid phase. If the gas phase behaves ideally (*i.e.*, the fugacity coefficient is close to 1), then the fugacity is equal to the pressure of gas above the IL sample, *i.e.* there is essentially no IL in the vapour phase, due to its non-volatility. Experimentally, the Henry's law constant can be determined from the limiting slope of the solubility as a function of pressure. A large Henry's law constant indicates low gas solubility, and a small Henry's law constant indicates high gas solubility.

Temperature is an important factor influencing the gas solubility. The differential molar enthalpy (Δh) and entropy (Δs) changes can be determined as follows:

$$\Delta h = \overline{h} - h^{ig} = R\left(\frac{\partial \ln p}{\partial(1/T)}\right)_x, \quad (2)$$

$$\Delta s = \overline{s} - s^{ig} = -R\left(\frac{\partial \ln p}{\partial \ln T}\right)_x, \quad (3)$$

where $\overline{h}$ and $\overline{s}$ and are partial molar enthalpy and partial molar entropy of a gas in the mixed liquid state, h^{ig} and s^{ig} are enthalpy and entropy of a pure (ideal gas state) gas, R is the universal gas constant, p stands for partial pressure of a gas and T is temperature.

Thus, Δh and Δs can be obtained by determining the pressure required to achieve a specified solubility at several different temperatures and constant composition x. In the Henry's law region, Δh and Δs can be found directly from the temperature dependence of the Henry's law constant, as given by van't Hoff equations:

$$\Delta h = R\left(\frac{\partial \ln H}{\partial(1/T)}\right)_p, \quad (4)$$

$$\Delta s = -R\left(\frac{\partial \ln H}{\partial \ln T}\right)_p. \quad (5)$$

The enthalpy and entropy of gas dissolution in the IL provide information about the strength of the interactions between the IL and the gas, and about the ordering which takes place in the gas–IL mixture, respectively.[62]

CO_2 has by far the highest solubility of all the tested gases (with the exception of water vapour), as can be seen below,[62] which gives the Henry's law constants of the various gases in [bmim][PF_6] at 298 K.[66] CO_2 solubilities reached values as high as 70 mol.% under high pressures.[68]

Gas	H/bar	Gas	H/bar
CO_2	53.4 ± 0.3	O_2	8000 ± 5400
C_2H_4	173 ± 17	Ar	8000 ± 3800
C_2H_6	355 ± 36	H_2	non-detectable (>1500)
CH_4	1690 ± 180	N_2	the same ($>20\,000$)
		CO	" ($>20\,000$)

The solubility of CO_2 was determined for MEA solution and the dependence of Henry's law constants for CO_2 and CH_4 can be represented by the following Eqns (6) and (7):[69–71]

$$\ln H_{CO_2} = 170.7126 - \frac{8477.711}{T} - 21.95743 \cdot \ln T + 0.005781 \cdot T, \quad (6)$$

$$\ln H_{CH_4} = 5.1345 + \frac{7837}{T} - \frac{1.5090 \times 10^6}{T^2} + \frac{2.060 \times 10^7}{T^3}. \quad (7)$$

It means that, at room temperature, the values of Henry's law constants for CO_2 and CH_4 are approximately 1604 bar and 2.387×10^{10} bar, respectively. Such calculations are indicative of better solubility of natural gas components in ionic liquids than in amine solutions.

Many ILs are suitable as solvents for gas separations since they are frequently non-volatile and, thus, cannot evaporate and cause contamination of the gas stream. This is important when selective absorbing media are used in conventional absorbers, or when ILs are used in supported liquid membranes. For conventional absorbers, the ability to separate one gas from another depends entirely on their relative solubilities (*i.e.* the ratio of Henry's law constants) in a liquid. In addition, ILs are particularly promising for supported liquid membranes, because they have the potential to be very stable. Supported liquid membranes containing conventional liquids will probably deteriorate because the liquid slowly evaporates.[72]

3. Types of ionic liquids used for CO_2 capture

There are different categories of ionic liquids, which will be described in more detail in the sequel:

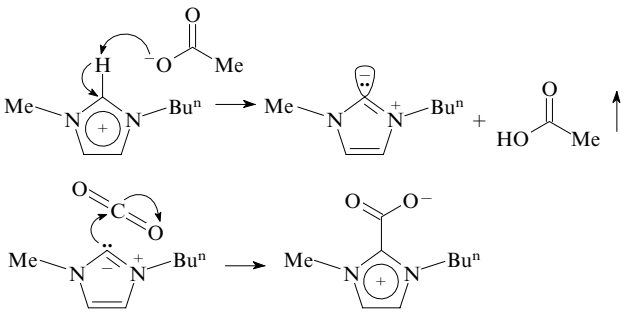
— room-temperature ionic liquids;
— task-specific ionic liquids;
— poly(ionic liquid)s;
— ionic liquids based on Jessop's 'switchable solvent'-concept.[73]

a. Room-temperature ionic liquids

Room-temperature ionic liquids (RTILs) are organic salts which melt near room temperature. RTILs generally include bulky low-symmetry organic cations with a delocalized charge, which causes their low melting points (see Fig. 12).[61] The ionic liquid anions are more symmetrical and generally smaller than the cations. Common anions include hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and [bis(trifluoromethylsulfonyl)imide] (Tf_2N^-), to mention a few.

RTILs are usually non-flammable, have high thermal stability, and a wide liquid range.[74,75] Furthermore, RTILs have negligible vapour pressure; therefore, they are considered to be 'green' solvents which could, in certain cases, replace conventional volatile organic solvents in many reaction and separation processes. The properties of RTILs, such as melting points, viscosity, density, and gas and liquid solubilities, can be adjusted *via* the appropriate choice of cation and anion.[76] The incorporation of this functionality should result into the salt with a capacity to behave not only as a reaction medium but also as a reagent or catalyst in some reactions or processes.

RTILs may be used for CO_2 separations, due to substantial solubility of CO_2 in RTILs.[77–79] The following mechanism for enhanced CO_2 solubility in imidazolium acetate ionic liquids was proposed.[77]



CO_2 solubility was studied for several ionic liquids containing alkylimidazolium cation and such anions as $[BF_4]^-$, $[PF_6]^-$, $[Tf_2N]^-$.[80] It appeared that the anion dominates the interaction with the CO_2, and the cation plays a secondary role. The major factor controlling CO_2 solubility in this class of ionic liquids is therefore the nature of the anion. The association of CO_2 with the anion is the best indicator of CO_2 solubility in alkylimidazolium-based

Table 2. Henry's law constants of CO_2 in different ionic liquids at different temperatures.[76]

Ionic liquid	Henry's law constant /bar					
	283 K	293 K	298 K	303 K	313 K	323 K
[bmim][Tf_2N]	28 ± 2	30.7 ± 0.3	34.3 ± 0.8	42 ± 2	45 ± 3	51 ± 2
[pmmim][Tf_2N]	29.6 ± 0.6	34 ± 3	38.5 ± 0.9	40.4 ± 0.6	46 ± 3	53 ± 2
[bmpy][Tf_2N]	26 ± 1	31.2 ± 0.1	33 ± 1	35 ± 2	41 ± 4	46 ± 1
[F-hmim][Tf_2N]	25.5 ± 0.2	29.2 ± 0.4	31 ± 2	32 ± 2	36 ± 4	42 ± 2
[bmim][BF_4]	41.9 ± 0.2	52 ± 2	56 ± 2	63 ± 2	73 ± 1	84 ± 4

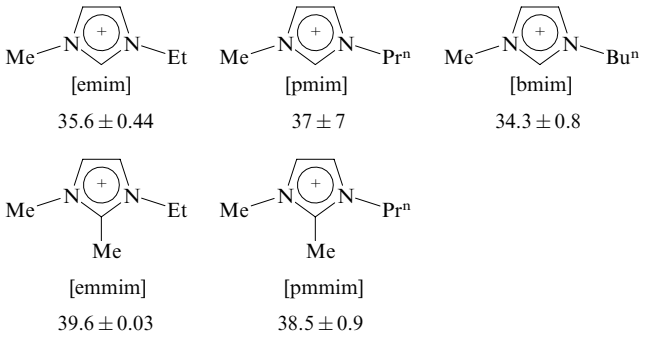
ILs.[80] Changes in the imidazolium cation involving alkyl groups are expected to have relatively little influence on CO_2 solubility.

Values for the Henry's law constants for CO_2 in the tested ionic liquids are listed in Table 2, where the ionic liquids are 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]), 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide ([pmmim].[Tf_2N]), 1-butyl-3-methylpyridinium bis(trifluoromethyl sulfonyl)imide ([bmpy][Tf_2N]), 1-methyl-3-(3,3,4,4,5,5,6,6-octafluorohexyl)imidazolium bis(trifluoromethyl sulfonyl)-imide ([F-hmim][Tf_2N]), and 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]).[76] Smaller values correspond to higher solubility of CO_2, at the same pressure. A comparison of CO_2 solubilities in [bmim][Tf_2N] and [bmim][BF_4] in Table 2 clearly illustrates that CO_2 is considerably more soluble in [bmim][Tf_2N] than in [bmim][BF_4]. Thus, CO_2 solubility is higher in ionic liquids with [Tf_2N] anions than in ionic liquids with [BF_4] anions. The results also show that ionic liquids with the [Tf_2N] anion have similar CO_2 solubilities, implying that the ionic liquid anion has a stronger effect on CO_2 solubility than the cation.[76] The CO_2 solubility for ionic liquids with [Tf_2N] anion increases in the following order:

[pmmim] < [bmim] < [bmpy] < [F-hmim].

CO_2 is more soluble in [bmim] compared to [pmmim] because of the combination of the steric factors. It was established that these weaker inter-ion interactions can increase interactions between CO_2 and the anion, resulting in an increase in CO_2 solubility.[76] As a consequence, the high CO_2 solubility in [bmpy] can be explained by the ability of the larger pyridinium ring to distribute and stabilize the cation charge better than the imidazolium ring.

The highest CO_2 solubility was observed for [F-hmim][Tf_2N]. It is currently not understood what is the ultimate reason for this behaviour. As has been reported in the literature, an increase in CO_2 solubility generally takes place when the length of the alkyl side chain on the cation is increased. The reason for this is the increased free volume available for CO_2, as well as a decrease in cation–anion interactions.[81,82] However, in the case of [F-hmim] cation, the increase in free volume resulting from the long alkyl side chain is counter-effected by the large F atoms in the side chain. It is possible that the fluorine atoms also have an impact on the distribution of charges in the cation, thus influencing the strength of the cation–anion interactions. A comparison of the effect of the number, size, and position of alkyl groups on CO_2 solubility in imidazolium-based ionic liquids (H_{CO_2}) with an anion [Tf_2N] at 298 K can be seen below:[76]



An additional methyl group in the imidazolium ring reduces the CO_2 solubility because of reducing the free volume available for CO_2, which can be noticed after the comparison of Henry's law constants for IL with [emim] to [emmim] and [pmim] to [pmmim], correspondingly. Taking into account the large uncertainty in the value reported for [pmim][Tf_2N], the results are generally consistent with the trends reported in the previous studies: CO_2 solubility increases as the length of the alkyl chain in [C*n*mim][Tf_2N] ionic liquids increases.[81,82] This observation can be explained by the increase in the free volume and the decrease in cation–anion interactions.

The effect of temperature on CO_2 solubility can be related to the partial molar entropy and partial molar enthalpy of dissolution (Eqns 4 and 5).[83] These values are listed in Table 3 and the values for CO_2 dissolution in ionic liquid containing [BF_4] were larger than those for ionic liquids with [Tf_2 N] anions, whereas solubility was the highest in the [Tf_2N] ionic liquids.

Table 3. Partial molar entropies and enthalpies of CO_2 dissolution, and Henry's law constants (H), in ionic liquids.[76]

Ionic liquid	$\Delta\bar{s}_{CO_2}$ /J mol^{-1} K^{-1}	$\Delta\bar{h}_{CO_2}$ /kJ mol^{-1}	H (298 K) /bar
[F-hmim][Tf_2N]	-29 ± 5	-9 ± 2	31 ± 2
[bmpy][Tf_2N]	-34 ± 3	-10.4 ± 0.9	33 ± 1
[bmim][Tf_2N]	-40 ± 13	-12 ± 4	34.3 ± 0.8
[pmmim][Tf_2N]	-36 ± 5	-11 ± 1	38.5 ± 0.9
[bmim][BF_4]	-44 ± 5	-14 ± 1	56 ± 2

It was revealed that the results with [pmmim][Tf_2N] are an exception to this trend. The feasible reason is the impact of the extra methyl group in the imidazolium ring on the ordering of CO_2 in the ionic liquid. The partial molar enthalpies of dissolution in [pmmim][Tf_2N] and [bmim].[Tf_2N] are quite similar, which indicates similar interaction forces between CO_2 and these ionic liquids. Since enthalpy

and entropy valves are rather uncertain, all conclusions drawn are rendered highly speculative.[76]

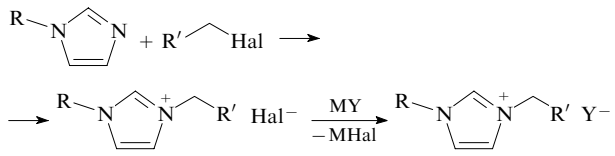
RTILs can be regenerated, which can be carried out *e.g.* by introducing N_2, followed by system evacuation at high temperature (343 K) to draw the absorbed CO_2 out of the ionic liquid. RTILs can, thus, be used for CO_2 separations. Technology utilizing RTILs for CO_2-based separations has not yet been adopted by industry. Feasibility reports have shown that CO_2 separations with RTILs may become economically viable processes in the future.[84]

b. Task-specific ionic liquids

Task-specific ionic liquids (TSILs) are ionic liquids in which a functional group is covalently combined into the cation or anion (or both) of the IL. The definition of TSILs extends to 'conventional' ionic liquids to which ionic solutes are dissolved introducing a functional group into the liquid. Therefore, when added to a 'conventional' ionic liquid, these solutes become integral elements of the overall ion mixture. They can be regarded as elements of the ionic liquid as a whole, making the resulting material a TSIL.

TSILs can be regarded as liquid versions of solid-supported reagents.

The structure of the TSIL can consist of two elements. The first element is a core, which bears the ionic charge; the second element contains the substituent group. On the contrary to the well documented chloroaluminate ionic liquids, established TSILs contain large species in which the functional group is cation-tethered. Consequently, TSIL synthesis is based on the synthesis of salts containing functionalized cations.[62]



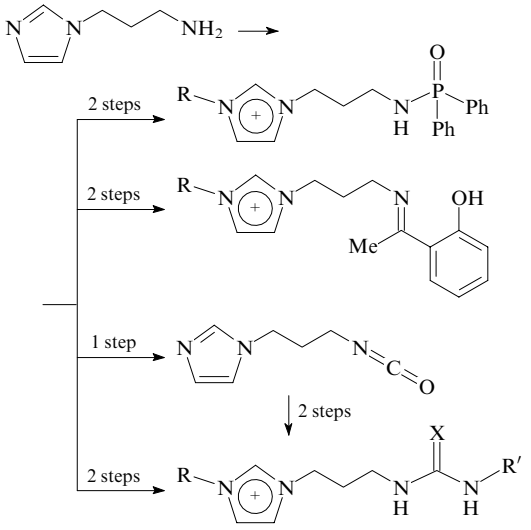
R = Me, Bu^n; R′ is functional group

The general principles outlined are pertinent to the synthesis of functionalized anions as well.[62]

The incorporation of functional groups into an ion selected for further use is often a multi-step process. Consequently, several aspects must be considered in planning the synthesis of the ion, like the choice of the cationic core. The core of a TSIL cation may be as simple as a single atom (N, P, or S) as found in ammonium, phosphonium, or sulfonium ions, respectively. Alternatively, it may be (and often is) a heterocycle (*e.g.* imidazole or pyridine). The choices play a large role in determining both the chemical and physical properties of the resulting salt. For example, ionic liquids formed with phosphonium cations generally exhibit the greatest thermal stability, but, at the same time, commonly possess melting points higher than those of salts of other cations.[85] Thus, if the desired ionic liquid is to be used in a process intended to be conducted at 273 K, it may be very challenging to build the cation around a phosphonium ion.

The synthesis usually consists of two steps (Scheme 1). Step one is the conversion of the primary moiety into the functional group of interest. Step two involves quaternization of imidazole ring by alkylation at N(3).[62]

Scheme 1



R, R′ = Alk; X = O, S

The types of functional groups incorporated into TSILs can often be based on *e.g.* nitrogen, oxygen, or phosphorus ionic liquids containing imidazolium cations with polyfluoroalkyl substitutes.

Although TSILs melt at high temperatures (333 – 423 K range), they exhibit interesting chemistry when combined with conventional ILs. Their solubility in conventional ionic liquids is rather limited (saturation concentrations of about 5 mmol litre^{-1}), but fluorous TSILs apparently form micelles in the ILs. A conventional ionic liquid doped with a fluorous TSIL can be mixed with perfluorocarbons and extremely stable emulsions can be formed. Consequently, these may then be of use in the development of two-phase fluorous/ionic liquid reaction systems.[65] As in the case of many other TSILs reported so far, these compounds are prepared by direct treatment of 1-alkylimidazoles with a (polyfluoro)alkyl iodide, followed by anion metathesis.

c. Poly(ionic liquid)s

The ionic liquids in polymeric forms are solid at room temperature. However, they exhibit significantly increased CO_2 sorption capacity compared to ionic liquids. For example, the polymers of tetraalkylammonium-based ionic liquids have CO_2 sorption capacities 6.0 – 7.6 times higher than room temperature ionic liquids. These polymers are very often used as sorbents and membrane materials for CO_2 separation.[86]

Poly(ionic liquid)s are typically synthesized by free radical polymerization of their corresponding ionic liquid monomers using AIBN (azobisisobutyronitrile) as an initiator.[72] The structure of the polymers, poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate] (P[VBTMA][BF_4]), poly[2-(methacryloyloxy)ethyltrimethylammonium tetrafluoroborate] (P[MATMA][BF_4]), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrafluoroborate](P[VBBI][BF_4]) or bis(trifluoromethylsulfonyl)imide (P[VBBI][Tf_2N]), and poly[1-(2- methacryloyloxy)ethyl-3-butylimidazolium tetrafluoroborate] (P[MABI][BF_4]) are depicted in Fig. 13.[86]

The CO_2 sorption kinetics of the polymers, their corresponding monomers and a room-temperature ionic liquid [bmim][BF_4] is shown in Fig. 14.[86] At equilibrium, the polymers took up 10.22 mol.% (P[VBTMA][BF_4]),

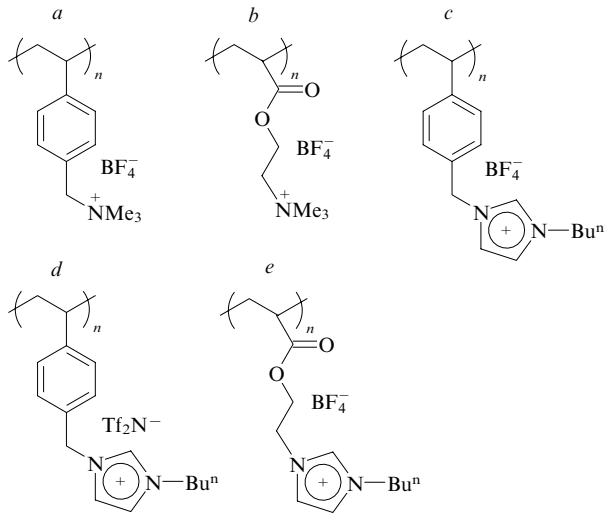


Figure 13. Structures of the poly(ionic liquid)s: P[VBTMA][BF_4] (*a*), P[MATMA][BF_4] (*b*), P[VBBI][BF_4] (*c*), P[VBBI][Tf_2N] (*d*), P[MABI][BF_4] (*e*).[86]

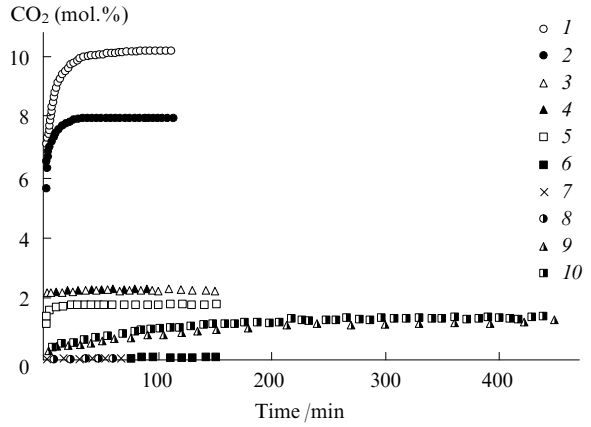


Figure 14. Sorption kinetics of CO_2 by the polymers in Figure 13 *a*–*e* (*1*)–(*5*), their corresponding monomers [VBTMA][BF_4] (*6*), [MATMA][BF_4] (*7*), [VBBI][BF_4] (*8*), ([MABI][BF_4] (*9*) and ionic liquid [bmim][BF_4] (*10*) as a function of time at 295 K and 0.8 bar CO_2.[86]

7.99 mol.% (P[MATMA][BF4]), 2.27 mol.% (P[VBBI]. .[BF_4] or P[VBBI][Tf_2N]), and 1.80 mol.% (P[MABI][BF_4]) of CO_2 in terms of their monomer units. Further, room temperature ionic liquid [bmim][BF_4] only absorbed 1.34 mol.% of CO_2 under the same conditions. Their monomers, [VBTMA][BF_4], [MATMA][BF_4] and [VBBI][BF_4] did not absorb CO_2 at all because of their crystalline structures. The [MABI][BF_4] monomer is a liquid at room temperature and has the same CO_2 absorption capacity as [bmim][BF_4]. This comparison shows that simply making the ionic liquids into polymeric forms can significantly increase the CO_2 sorption capacity. CO_2 sorption capacities are also significantly higher than those for other polymer solids such as polymethacrylates, polystyrene and polycarbonates.[87–89]

The type of cation plays a major role for the CO_2 sorption capacity. For example, tetraalkylammonium-based poly(ionic liquid)s (curves *1*, *2*) exhibit much higher CO_2 sorption capacity than the imidazolium-based poly(ionic liquid)s (curves *3*, *4*, *5*) (see Fig. 14). The tetraalkylammonium cation has a high positive charge density and thus strong interaction with CO_2. In contrast, the positive charge of the imidazolium is delocalized. The anions have little effect on the CO_2 sorption capacity. For example, the following poly(ionic liquid)s; P[VBBI][BF_4] and P[VBBI][Tf_2N] (curves *3*, *4*) had the same CO_2 sorption capacity.

The sorption rates of these polymer particles are very fast (Fig. 15).[86] In a few minutes these polymers reached 95% of their sorption capacities. In contrast, more than 400 min were needed for room temperature ionic liquids [MABI][BF_4] and for [bmim][BF_4] to reach the equilibrium state.[86]

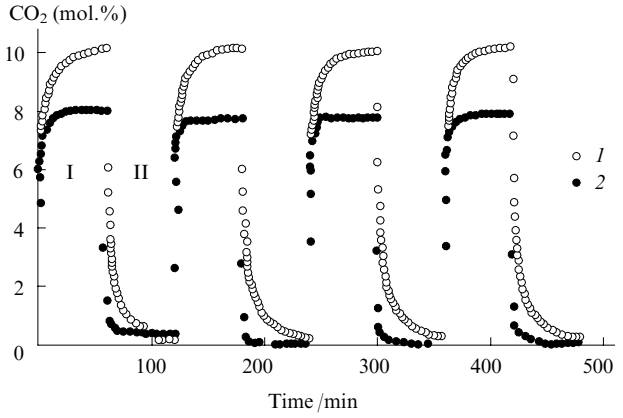


Figure 15. Sorption kinetics of CO_2 (I) (0.8 bar CO_2, 295 K) and its release under vacuum (II) of following poly(ionic liquid)s P[VBTMA][BF_4] (*1*) and P[MATMA][BF_4] (*2*).[86]

The desorption of carbon dioxide from poly(ionic liquid)s is also fast (see Fig. 15). Under vacuum, the polymers released CO_2 in less than 15 min. The desorption was complete, and no changes in sorption–desorption kinetics and sorption capacity were observed after four cycles of sorption–desorption experiments, suggesting that the sorption–desorption was completely reversible. In contrast, the desorption of ionic liquids (*e.g.* [bmim][BF_4]) was very slow (Fig. 16).[86]

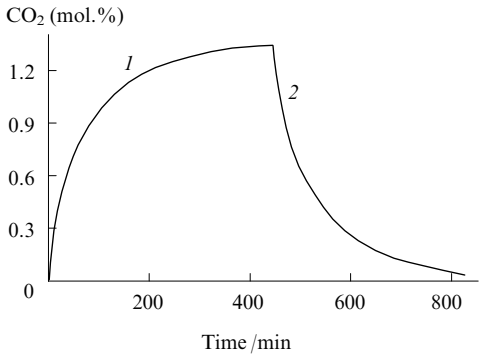


Figure 16. CO_2 sorption (*1*) and desorption (*2*) of [bmim][BF_4].[86] (*1*) 0.8 bar CO_2, 295 K; (*2*) under vacuum.

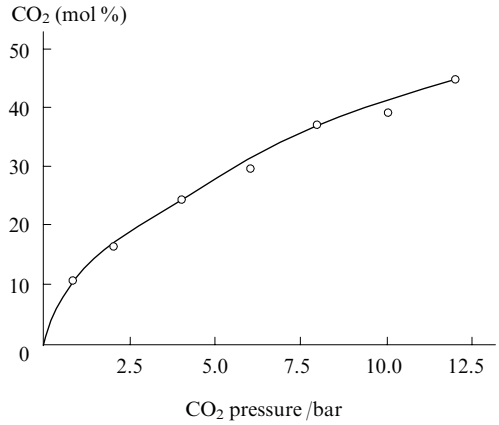


Figure 17. CO_2 loading of P[VBTMA][BF_4] at different CO_2 pressures (295 K).[86]

The CO_2 sorption of P[VBTMA][BF_4] as a function of pressure is shown in Fig. 17. The sorption capacity increased with the increase of the CO_2 pressure. For example, P[VBTMA][BF_4] absorbed 44.8 mol.% of CO_2 (in terms of its monomer units), at 12 bar of CO_2 pressure. This value is much higher than that of monomeric room temperature ionic liquids.[86]

The fast absorption–desorption rates suggest that the diffusion of CO_2 inside the polymer solids is very fast. The bulk of the polymer particles plays a major role in the CO_2 sorption. Therefore, the CO_2 sorption of the polymer particles involves stronger absorption in the bulk but less adsorption on the surface.

The CO_2 absorption of the polymers is very selective (Fig. 18). No weight gain was observed when the polymers were exposed to N_2 or O_2 under similar conditions.[72]

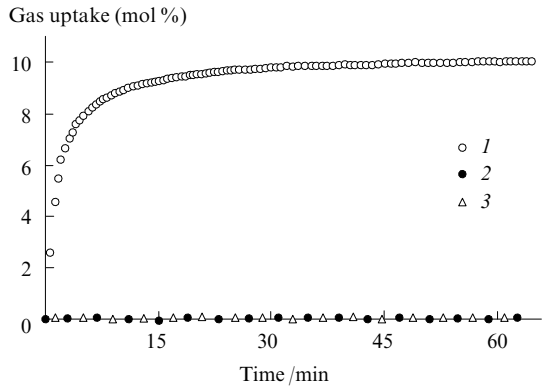


Figure 18. Gas sorption of P[VBTMA][BF_4] as a function of time at 0.8 bar, 295 K.[72]
(*1*) CO_2, (*2*) N_2, (*3*) O_2.

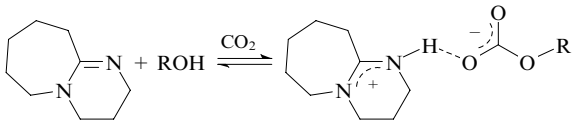
Presence of moisture could slightly decrease the CO_2 absorption capacity. For example, wet P[VBTMA][BF_4] with 13.8 mol.% water had a CO_2 absorption capacity of 7.9 mol.%, which was lower than that of dry P[VBTMA][BF_4] (10.22 mol.%).[86]

The poly(ionic liquid)s are a class of novel polymer materials, which selectively absorb CO_2 with higher absorption capacity and faster absorption–desorption rates than classical room temperature ionic liquids. These characteristics properties make these polymers exceptionally promising as absorbents and membrane materials for CO_2 separation.

d. Ionic liquids based on Jessop's 'switchable solvent' concept

A switchable solvent is a solvent in which one of its physical characteristics can be switched from one form to another.[90] CO_2 binding organic liquids (CO_2BOLs) based on Jessop's 'switchable solvents' — mixtures of an alcohol[91–97] and an amidine such as diazabicyclo[5.4.0]-undec-7-ene (DBU) or guanidine base — chemically bind CO_2 to form an amidinium or guanidinium alkyl carbonate salt[90,98,99] (Scheme 2).

Scheme 2



Novel CO_2BOLs bind chemically CO_2 with high volumetric and gravimetric capacity and become ionic liquids after bonding the CO_2. Carbon dioxide is chemically bound in CO_2BOLs as an alkyl carbonate salt rather than as bicarbonate or, carbamate salts used in conventional aqueous amine CO_2 scrubbing systems.[73]

Carbamate and bicarbonate salts contain CO_2 with high hydrogen bonding. CO_2 is weakly bound in an alkyl carbonate salt, perhaps because of decreased hydrogen bonding. For this reason, minor amount of energy is required to thermally strip the CO_2 from the liquid. Furthermore, in certain cases CO_2BOLs exhibit a higher CO_2 capacity than conventional solvents. For the sake of comparison these values are presented below, *e.g.* the CO_2 capturing capacities of CO_2BOL based on DBU and hexan-1-ol mixture and of aqueous 30 wt.% MEA are 147 g CO_2 litre^{-1} liquids (19 wt %) and 108 g CO_2 litre^{-1} liquid (7 wt %), respectively.[73] Therefore, it can be suggested that this type of solvents can compete with aMDEA in terms of CO_2 loading capacity.

The ability of DBU or polymer-bound DBU to capture CO_2 will be limited to the amount of CO_2 which can be physically adsorbed or dissolved. The amount of CO_2 which is trapped can, however, be increased because CO_2 may be trapped as bicarbonate in the presence of water. The CO_2BOLs that contain a stoichiometric amount of an alcohol should be superior in chemically binding CO_2 since no water is required.

The switchable solvents can be used as reaction media. CO_2BOLs are liquids before and after reacting with CO_2, eliminating the need for superfluous inert solvents which reduce the weight and volumetric capacity of the trapping agent. Moreover, the physical and chemical properties of CO_2 BOLs can be adjusted by changing alcohol–base pairs, as well as by chemically modifying the alcohol–base pairs.

The reaction energetics depends strongly on the choice of the base. ΔH_{sol} and ΔG_{sol} values are almost independent of the choice of the primary alcohol (Table 4).[73] Table 4 reflects the approach to equilibrium (Scheme 2). If binding of CO_2 is complete, then the value of CO_2 absorbed would be 100%. Due to thermodynamic restrictions, the values

Table 4. Thermodynamics of CO_2 capture by using CO_2BOLs in MeCN-d_3, estimated by NMR spectroscopic determination of equilibrium constants.[73]

Base – alcohol	ΔH_{sol} (see [a])	ΔS_{sol} (see [b])	ΔG_{sol} (see [a])	CO_2 absorption (%) in MeCN-d_3 at 298 K
TMG – n-$C_6H_{13}OH$	−160	−530	1.6	42
Barton's base – n-$C_6H_{13}OH$	−83	−250	−11.0	90
DBU – n-$C_6H_{13}OH$	−140	−440	−9.4	87
DBU – n-$C_5H_{11}OH$	−120	−390	−7.5	82
DBU – Bu^nOH	−140	−450	−9.7	88
DBU – Pr^nOH	−130	−420	−7.8	83
DBU – Pr^iOH	−140	−450	−5.7	76

Note. Data rounded to two significant figures. Calculated at 298 K from NMR integrations using equations

$$\Delta G = -RT\ln K_{eq},\ K_{eq} = \frac{[BaseH^+][ROCO_2^-]}{p_{CO_2}[Base][ROH]},\ \Delta G = \Delta H - T\Delta S.$$

[a] In kJ mol^{-1}, [b] J mol^{-1} K^{-1}.

reported in Table 4 are lower depending on the alcohol used.

The average enthalpy values for each base combined with linear alcohols are given in Table 4, in which the following decreasing order of exothermicity is shown: TMG > DBU > Barton's base, where TMG is 1,1,3,3-tetramethylguanidine. The weakest base of these three is TMG, which exhibited the least favourable ΔG_{sol} of the reaction and therefore the weakest ability to capture CO_2. CO_2 capture by TMG and alcohol had, however, the most favourable reaction enthalpy, presumably because the salt $[TMGH^+][ROCO_2^-]$ is more capable of hydrogen bonding interactions than the corresponding DBU and Barton's salts (Table 4). The very low ΔS_{sol} was achieved in TMG/alcohol mixtures, which had the weak capturing capacity of CO_2, whereas the low ΔS_{sol} was responsible for the positive ΔG_{sol}. Extensive hydrogen bonding would be expected to lower the entropy. DBU, an intermediate strength base (pK_{aH} in MeCN is 24.3)[73] and Barton's base, the strongest of the three bases (estimated pK_{aH} in MeCN is 25.3),[100] exhibited almost identical abilities to bind CO_2 but DBU had a more favourable reaction enthalpy. Barton's base, on the other hand, diplays a more favourable reaction entropy compared to the DBU (−390 J mol^{-1} K^{-1} for DBU *vs.* −185 J mol^{-1} K^{-1} for Barton's). The enthalpy of Barton's base is also comparable to that of a 30 wt % of MEA solution in water at 313 K (−80 kJ mol^{-1} CO_2).[94] Thus, termodynamic data explain the behaviour observed in terms of CO_2 binding.

The amidine and guanidine bases and alkyl carbonate salts form CO_2BOLs which contain highly delocalized charges. This weakens the attractions between the ions. It was suggested that the delocalization (protonated amidines and guanidines) plays a vital role for the chemical properties (reversibility of CO_2 binding and release) of CO_2BOLs, as well as the physical properties (*e.g.* melting point or viscosity).[73]

However, the efficiency of the switchable mixture is related not only to the base but also to the alcohol. There is a clear relationship between CO_2 capturing efficiency and alcohol structure. Several papers discovered the effect of the chain length, an increase in the number of the functional groups as well as the influence of the nature of the side chain.[101,102] In most of the cases, the increase of the chain length resulted in a decrease of the absorption rate but in an increase in the capturing efficiency. Moreover, the presence of an additional amine group also contributes to the increased CO_2 capturing efficiency.[101]

For industrial applications, a CO_2 capturing agent must be recyclable. In order to quantify this, a series of capture and release cycles with DBU – hexan-1-ol was performed.[73] The mixture of DBU and hexan-1-ol was sparged with CO_2 for five minutes at room temperature to form the alkyl carbonate salt $[BaseH^+][ROCO_2^-]$ and then placed into a hot oil bath at 363 K and measured for CO_2 release (Fig. 19).

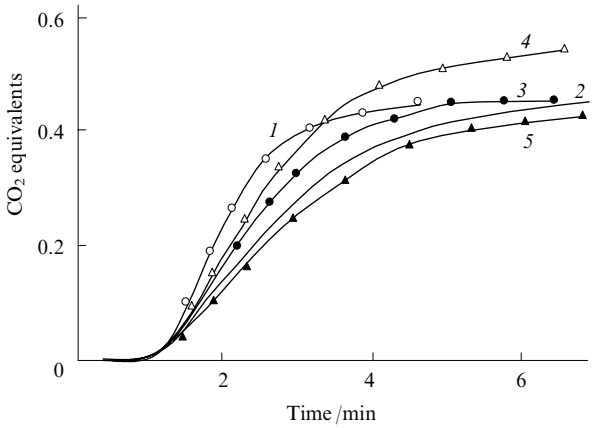


Figure 19. Five cycles (*1–5*) of CO_2 release from carboxylated mixture of DBU and hexan-1-ol at 363 K. Heating begins after one minute.[73]

As a result, it was shown that DBU and hexan-1-ol were carboxylated and decarboxylated five times with any visible loss of activity.[93] Probably DBU and hexan-1-ol CO_2BOL could be recycled indefinitely as long as the gas stream would be anhydrous and the evaporative losses would remain low. Thus, CO_2BOLs have tremendous potential to be energy efficient industrial liquids for CO_2 capture.[73]

4. Immobilized ionic liquids

a. Supported ionic liquid membranes

Several strategies have been proposed to improve the performance of ionic liquid solutions. One of the innovative developments is new types of membrane systems (Section I.5.a) such as immobilized ionic liquid membranes or supported ionic liquid membranes (SILM).

Immobilized (or supported) ionic liquid membranes consist of an ionic liquid immobilized in a supporting porous membrane by capillary forces.[103] Gas transport in supported liquid membranes occurs through the dissolution – diffusion mechanism. Gas molecules on the inlet absorb into the liquid, diffuse across the membrane, and desorb at the permeate site.[104]

The traditional liquid membranes with an organic solvent despite the high separation capability have some essential drawbacks namely rupturing of the membrane due to evaporation of the liquid phase into the gas

stream,[105,106], and lack of long-term stability. This results in membrane degradation and a loss of selectivity.[107]

In order to overcome the drawback of volatile organic solvents, ionic liquids are applied. Thermal stability, low volatility and high surface tension make membranes containing ionic liquids more stable than supported liquid membranes. Moreover, they can be regenerated and reused.

For immobilization purposes, not only traditional ionic liquids [108] but also amine-terminated ionic liquids can be applied.[109] Particularly, the amine moiety of these task-specific ionic liquids facilitates selective transport of CO_2.[109] Among the most common anions of task-specific ionic liquid are bis(trifluoromethylsulfonyl)imide $[Tf_2N]$,[108–111] tetrafluoroborate $[BF_4]$ [108] and trifluoromethanesulfone $[CF_3SO_3]$.[109]

The support can vary from polymeric hollow fibre membranes made of poly-vinylidene fluoride (PVDF) [110] to different inorganic supports such as α-Al_2O_3,[108] mesoporous materials SBA-15 or Al-SBA-15.[112]

Substantial research efforts have lately been devoted to ascertain the support – liquid relations, correlations between the membrane tortuosity and performance, the various preparation parameters, *etc*.[110] To evaluate the performance of a SILM, parameters such as permeability, diffusivity, gas selectivity and operational conditions have to be addressed.

The evaluation of the permeability (P) of the membrane can be expressed by the following equation:

$$P = \frac{Q_{STP} l}{A \Delta p}, \tag{8}$$

where Q_{STP} is the flow rate of permeation, l stands for the thickness of the selective layer, A is the effective sectional area of the ionic liquid membrane, Δp is the pressure drop across the membrane.[110]

There is another way to calculate the permeability (P) of bulk ionic liquid, which is related to the values of the permeance of supported ionic liquids membrane (P_{SILM}), the effect of membrane porosity (φ), membrane tortuosity (τ), and membrane thickness (d):[109]

$$P = \left(\frac{\tau d}{\varphi}\right) P_{SILM}\,. \tag{9}$$

High permeability decreases the required surface area to perform expected gas separation. There are no direct correlations between gas permeability and the ionic liquid viscosity. For example, considering the ionic liquids on α-Al_2O_3 it can be noticed that 1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and 1-butyl-4-methylpyridinium tetrafluoroborate showed similar CO_2 permeance, although their viscosity differs two-fold, being 100 mPa s and 203 mPa s, respectively.[108]

Nevertheless, in open literature one can find an equation suggested by Scovazzo [113] to estimate the CO_2 permeability in imidazolium, ammonium, and phosphonium-based ionic liquids:

$$P = \frac{4953}{(\mu_{IL})0.388 \pm 0.03}, \tag{10}$$

where μ_{IL} is the viscosity of an ionic liquid.

Besides viscosities, the permeability of ionic liquids membranes can be affected by CO_2 diffusivity *i.e*., how fast the gas is able to pass through the ionic liquid. At low pressures, the relations between diffusivity (D) and the permeability can be expressed according to the following equation:[111]

$$D = \frac{H M_w P}{\rho_{IL}}, \tag{11}$$

where H stands for Henry's law constant, M_w is a neat ionic liquid molecular mass, ρ_{IL} is a neat ionic liquid density.

Moreover, a relation between the viscosity and the gas diffusivity ($cm^2\,s^{-1}$) was proposed in Ref. 114 based on pure ionic liquid viscosity (mPa s) and the permeate gas liquid molar volume at normal boiling point (v_{NBP} /$cm^3\,mol^{-1}$):

$$D = 2.66 \times 10^{-3} \frac{1}{\mu_{IL}^{0.66 \pm 0.33}\, v_{NBP}^{1.04 \pm 0.08}}\,. \tag{12}$$

To perform separation of gas mixtures, the supported ionic liquid membranes (SILMs) must be selective to these gases. The SILMs containing amine functional groups experience high $CO_2 - CH_4$ selectivity due to higher affinity existing between IL and CO_2 compared to CH_4.

Ideal selectivity is represented by the ratio between the permeabilities of permeate A and permeate B:[110]

$$S = \frac{P_A}{P_B}\,. \tag{13}$$

The best values for $CO_2 - CH_4$ ionic liquids membranes found in literature are about 50: for example, 55 for 1-(3-aminopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (the porous hydrophilic polytetrafluoroethylene membrane as a support) [109] and 52 for the mixture of 1-butyl-4-methylpyridinium tetrafluoroborate with 1-aminopyridinium iodide (apir) on α-Al_2O_3.[108] Ionic liquids immobilized on α Al_2O_3 with the anion $[Tf_2N]$ and different cations gave approximately the same permeance but different selectivity in the following order [hmim] > [bmpy] > $MeOct_3N$ ([hmim] is 1-n-hexyl-3-methylimidazolium, Oct is n-octyl). Probably, the quaternary ammonium ions residing in the ring structure interact more easily with CO_2 than tetrahedrally coordinated ions.[108]

Supported ionic liquid membranes are most effective at lower pressures,[108] and the $CO_2 - CH_4$ selectivity gradually decreases as temperature increases.[109] Moreover, the performance of ionic liquids depends not only on the above-mentioned properties and operational conditions but also on immobilization methods.[110]

Consequently, supported ionic liquid membranes have to be used at certain, well defined conditions. The selectivity issue has to be still improved. The properties of these membranes were reported to improve significantly by addition of an organic salt with amine group functionality.[108]

b. Ionic liquids on metal organic frameworks

Metal organic frameworks (MOFs) (Section II.5.b) seem to be promising supports for ionic liquids leading to their wider application and increasing their efficiency for CO_2 capture. However, the research in this area is so far quite limited. The impregnation of ionic liquids in porous support

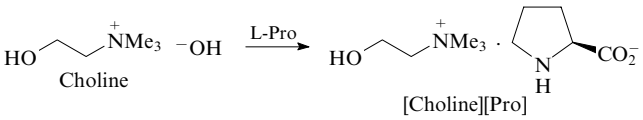
in part eliminates their drawbacks related to high viscosity and high costs in the same way as for supported membrane ionic liquids.[115] Moreover, due to porosity ionic liquids impregnated on MOFs exhibit improved mass transfer and, consequently, high separation efficiency.[116]

The first attempt to study MOF-supported IL was performed by Chen *et al.* by means of computational methods.[116] The focus of research was devoted to the [bmim][PF_6] impregnated in different ratios over $Zn_4O(BDC)_3$, where BDC is 1,4-benzenedicarboxylate. It was observed that with increasing concentration of IL the molecules come to the pores more uniformly and ordered. Thereby, for such aggregates with increasing IL : MOF ratio the amount of ionic absorption sites is increasing providing better selectivity. Since a great number of ILs as well as MOFs exist, this research area has a great potential in terms of identifying a proper CO_2 capturing adsorbent.

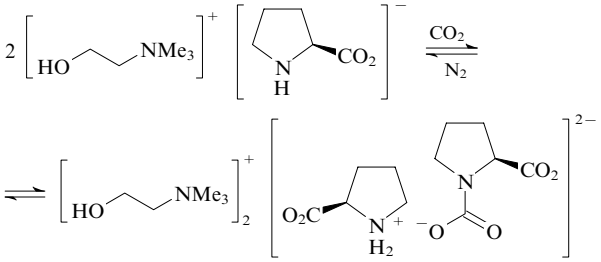
5. Mixtures of ionic liquids with different additives for CO_2 removal

a. Ionic liquid – polyethylene glycol mixture

In the recent years, synthesis of ILs using renewable raw materials has become an attractive goal.[117–121] ILs were synthesized from (2-hydroxyethyl)-trimethyl-ammonium (*S*)-2-pyrrolidinecarboxylate ([Choline][Pro]).[2, 121]



This IL contains both cation and anion from renewable materials. The following reaction of [Choline][Pro] with CO_2 was proposed:[2]



Polyethylene glycols (PEGs), with the molecular formula $HO(CH_2CH_2O)_nH$, have also been used as environmentally benign solvents to replace volatile organic solvents in different processes.[122, 123] PEG has some unusual properties, being non-volatile, non-toxic, biodegradable, inexpensive, widely available, and in addition their properties can be tuned by changing molecular weight.

Both the neat IL and the IL/PEG200 mixture were very efficient in capturing CO_2. The regeneration can be easily performed under vacuum or, alternatively, by bubbling an inert gas through the solution (Fig. 20).[2] The process was claimed to be reversible, since the recovered ionic liquid was used repeatedly without visible losses of efficiency.[2]

Chemically, one mole of IL can absorb 0.5 mole of CO_2.[124] The molar ratio CO_2 : IL could, however, exceed 1/2 (see Fig. 20), suggesting that physical absorption also contributes in part to the uptake of CO_2.

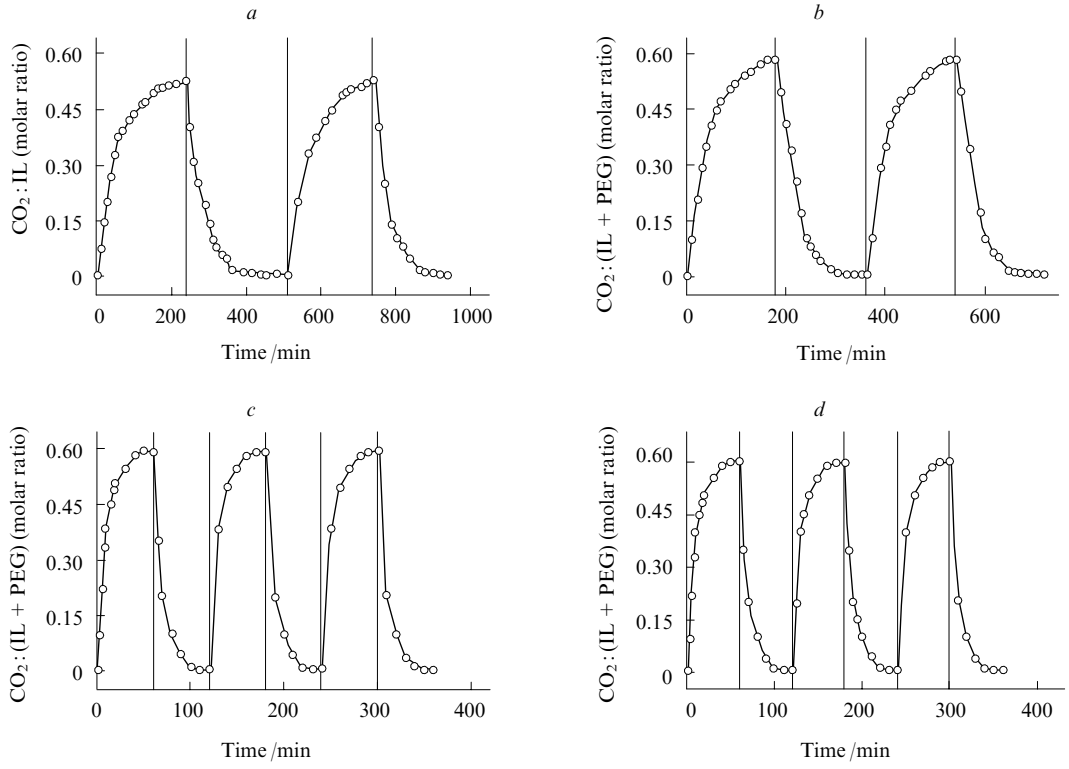


Figure 20. Sorption – desorption cycles of CO_2 by ionic liquid [Choline][Pro] (323.15 K) (*a*) and [Choline][Pro] – PEG200 mixtures (308.15 K) at [Choline][Pro] : PEG200 (weight ratio) 2 : 1 (*b*), 1 : 1(*c*), 1 : 3 (*d*).[2]

The absorption and desorption rates of CO_2 in IL can be significantly enhanced by adding PEG 200 into IL. The contribution of PEG 200 to the uptake of CO_2 is, however, very limited, because the solubility of CO_2 in PEG 200 at ambient pressure is very small.[125] Therefore, PEG 200 enhanced CO_2 absorption acting as a solvent for the IL.

The solubility of CO_2 in the mixtures increased with increasing pressure, being more sensitive to pressure in the low-pressure range. The solubility of CO_2 in this mixture also decreased with increasing temperature (Fig. 21).[2]

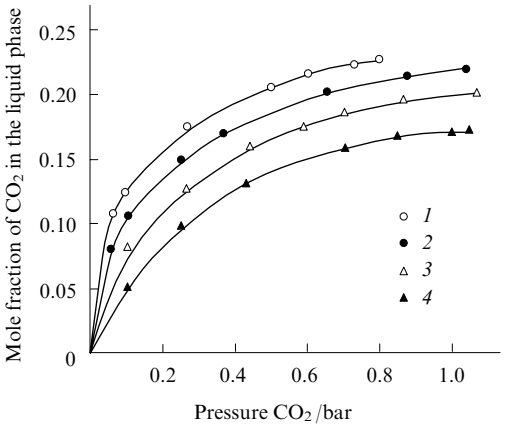


Figure 21. Dependence of solubility of CO_2 in [Choline][Pro]/PEG200 mixture as a function of pressure at the following temperatures and weight ratio of [Choline][Pro] : PEG200 = 1 : 1; 308.15 K (*1*), 323.15 K (*2*), 338.15 K (*3*), 353.15 K (*4*).[2]

The enthalpy and entropy of solutions are important parameters of the system because they are related to the strength of interactions between the liquid and the gas. The enthalpy of solution is a large negative value, *i.e.*, a large amount of heat is released during the absorption process indicating that the interactions between the IL and CO_2 are very strong (Table 5).[2] The entropy of the solution is also negative (indicating a high ordering so that the molecules CO_2 in the liquid can be solubilized.

Table 5. Partial molar enthalpy (kJ mol^{-1}) and entropy (J mol^{-1} K^{-1}) of CO_2 absorption in [Choline][Pro]/PEG200 ionic liquids mixtures at $T = 308-353$ K.[2]

IL : PEG = 1 : 1 (by mass)			IL : PEG = 1 : 2 (by mass)		
x (see [a])	$-\Delta\overline{h}$	$-\Delta\overline{s}$	x (see [a])	$-\Delta\overline{h}$	$-\Delta\overline{s}$
0.108	40.3	121.9	0.073	40.3	122.0
0.125	31.7	96.1	0.085	30.4	92.2
0.150	24.8	75.2	0.100	26.2	79.6
0.170	25.5	77.4	0.115	25.3	76.7

x stands for mole fraction of CO_2 in the liquid phase.

It can be concluded that, the IL synthesized from renewable materials [Choline][Pro] and the [Choline][Pro]/PEG200 mixture could absorb CO_2 effectively with the molar ratio of CO_2 and the IL reaching 0.6.[2]

b. Ionic liquids with chitin and chitosan

A novel application of chitin and chitosan as substitutes for amino-functionalized synthetic polymers for capturing and releasing CO_2 was also explored by using the 1-butyl-3-methylimidazolium chloride ([bmim]Cl) ionic liquid as the solvent for the aforementioned bio-polymers.

Chitosan, a natural biomaterial, is an *N*-deacetylated product of chitin, which is the second most abundant natural polymer after cellulose and it has a similar structure to cellulose.[126] Chitin has two hydroxyl groups while chitosan has one amino group and two hydroxyl groups in the repeating hexosaminide residue.[127]

Chitosan can be considered as a natural polyamine, and it could be a suitable alternative amino-functionalized polymer to fix CO_2. The drawbacks of the traditional dissolving processes using aqueous acids restrict its applications. The ability of [bmim]Cl to destroy hydrogen bonds makes the amino group in chitosan free from the intermolecular hydrogen bonds. This makes it possible for the amine group to react with other chemical reagents easily.

CO_2 fixation and release were performed using chitin/IL and chitosan/IL solutions (10%) at 303 K and under 1 bar CO_2.[128] Fixing efficiency [(mmol of CO_2/mmol of ionic liquid × 100%] was estimated from the weight increase in the reaction mixture. Ionic liquid [bmim]Cl and chitosan powder have almost no ability to absorb CO_2 (Fig. 22, curves *3* and *4*), but 10 wt % chitin/IL or chitosan/IL solutions both demonstrated good capacity to capture CO_2 (Fig. 22, curves *1* and *2*). For example, at equilibrium, the chitosan/IL and chitin/IL solutions exhibited approximately 8.1% and 3.8% CO_2 fixing efficiency, respectively.

This further strengthens the evidence towards the important effect of chitin and chitosan in CO_2 absorption process. The sorption efficiency of chitosan/IL solution is much higher than that of chitin solution (Fig. 22, curves *1* and *2*). This is probably due to the presence of substantial amounts of amino groups in chitosan contrary to chitin. It is reasonable to assume that physically dissolved carbon dioxide is responsible for the CO_2 sorption capacity of chitin/IL solution, while both physically dissolved CO_2 and chemically bound carbon dioxide are responsible for the effective CO_2 sorption capacity of chitosan/IL solution. The amount of chemically bound carbon dioxide should

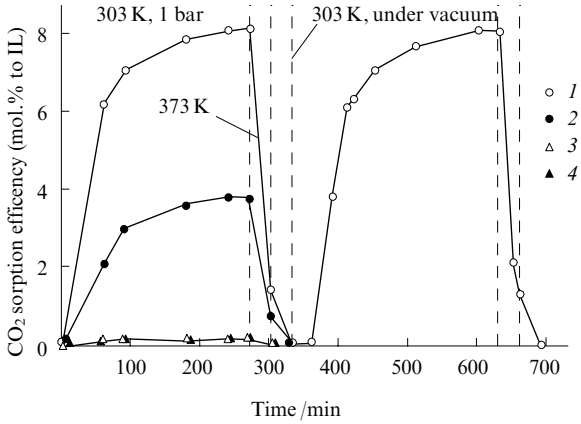


Figure 22. CO_2 absorption – release by 10 wt % chitosan/IL solution (*1*), 10 wt % chitin/IL (*2*), IL [bmim]Cl (*3*) and 1 g chitosan powder (*4*) under 1 bar CO_2.[128]

correspond to a sequestration efficiency of 4.5%. The CO_2 sequestration efficiency of 10 wt % chitosan/IL solution is, in reality, 8.1% and, therefore, the 'extra' CO_2 sorption capacity of chitosan/IL solution should be attributed to physical dissolution.[128]

It can be also seen that the amount of physically dissolved CO_2 (3.8%) in a 10 wt % chitin/IL solution is equal to that of a 10 wt % chitosan/IL solution under the same conditions (Fig. 22, curve *2*). The highest CO_2 sorption capacity (10 wt% chitosan/IL) is almost equal to the amount of the physically dissolved CO_2 added to the theoretical chemically bound CO_2 (4.5%). It seems that almost all the amino groups in the chitosan/IL solution (which have higher activity) participate in this CO_2 capture-release cycle. CO_2 desorption was achieved at high temperature (373 K) at which the CO_2 level decreased from 8.1% to 1.4% (Fig. 22, curve *1*) and CO_2 was completely released under vacuum.[128]

In summary, chitin and chitosan are biologically renewable, biodegradable, biocompatible, almost non-toxic, and biofunctional materials. However, the overall biocompatibility of these systems depends on the dissolution media (ionic liquid) applied.

c. Ionic liquids and amine solutions

Eventually, the presence of amine group in ionic liquids generates a rise in CO_2 capturing efficiency. However, the production of amine-functionalized imidazolium ionic liquids requires sophisticated synthesis and purification.[124] An attractive mixing approach is a cost-competitive method allowing application of many potential advantages of ionic liquid–amine solvents over aqueous amines based. Thus, the implementation of ionic liquids for CO_2 capture can be enhanced by combination with amines.[124, 129, 130]

$$2\,HO(CH_2)_2NH_2 + CO_2 \overset{\text{IL, solvent}}{\rightleftharpoons} \rightleftharpoons HO(CH_2)_2NH{-}CO_2^- \;\; H_3\overset{+}{N}(CH_2)_2OH$$

Moreover, CO_2 can be released by either heating or implying reduced pressure.[129]

Beneficial properties of ionic liquids can be combined with the advantages of amines. Whilst, the high viscosity and high initial costs impede wide application of ionic liquids, the IL–amine mixtures solve these questions and expand versatile applications.

For this approach, well-known amines (primary, secondary and tertiary alkanolamines) and imidazolium-based ionic liquids with anion [Tf_2N] have been used. The conditions of the CO_2 capture are related to the amine structure as MEA and triethanolamine (TEA) are used at low and high pressure, respectively. For example, a mixture of aqueous 20 wt % bis(2-hydroxyethyl)ammonium acetate [bheaa] and 20 wt % MEA provided, at high pressure (12 bar), about four times higher loading (0.95 mol CO_2/mol IL) than pure IL.[131] Similar tendency was reported for the mixture of MDEA and tetramethylammonium glycinate (Fig. 23).[132] Under similar conditions, an addition of 30 wt % of MDEA provided an about 4-fold increase in CO_2 uptake.[133]

Therefore, these solvent systems are expected to be efficient in a wide range of pressures. They perform similarly to the aqueous amine solutions and possess, at the same time, significant advantages in terms of the amount of energy consumed in the process.[129]

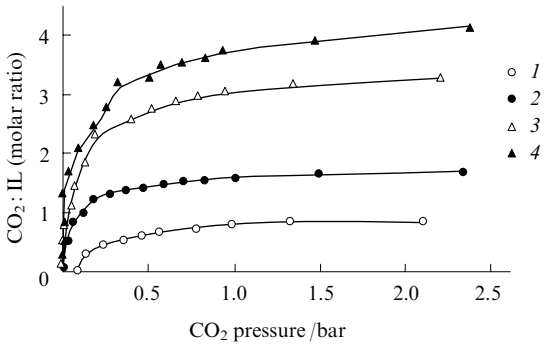


Figure 23. Influence of *N*-methyldiethanolamine on CO_2 loading of aqueous 15 wt % tetramethylammonium glycinate.[132]
MDEA (%): 0 (*1*), 15 (*2*), 30 (*3*), 40 (*4*).

A detailed investigation of hydroxyl imidazolium based ionic liquid solutions mixed with amines based on kinetic and thermodynamical data was reported.[133] The viscosity increase of those mixtures was reported after CO_2 capture. Hereby, the viscosity increase slows down the transport of CO_2 and more time is needed to reach equilibrium. However, a rise in temperature provides a significant viscosity decrease.

Since these ILs are non-volatile, the mixtures (IL–amine) exhibited lower weight losses than water–amine solutions caused by amine evaporation. Moreover, after CO_2 saturations the mixtures exhibited only small changes in response to vacuum heating. The thermal stability increased significantly, thus providing practical significance for a new strategy for stabilization of amine solutions.[133]

6. Quality aspects and other questions related to commercial ionic liquid production

a. Purification of ionic liquids

The synthesis of ionic liquids is basically quite simple organic chemistry, while the preparation of ionic liquids of a certain quality requires certain know-how and experience. Commercial producers try to make ionic liquids that meet the highest quality at reasonable costs. Some ionic liquids exhibit high purity (>99%), whereas others contain more impurities.

The lack of significant vapour pressure prevents the purification of typical ionic liquids by distillation. On the other hand, any volatile impurity can, in principle, be separated from an ionic liquid by distillation. However, it is better to remove as many impurities as possible from the starting materials. Synthetic methods which generate few side products or allow their easy separation from the final ionic liquid product are also favoured.[62]

The development of the purification methods for ionic liquids is, however, still needed. During the purification of ionic liquids, volatile impurities can easily be removed from the non-volatile ionic liquid by simple evaporation. This process is, however, quite slow. Factors that influence the time required for the removal of all volatiles from an ionic liquid (at a given temperature and pressure) are: amounts of volatiles, boiling points of molecular species present, spe-

cific interactions with the ionic liquid, viscosity of the ionic liquid, the surface tension of the ionic liquid.

Water in an ionic liquid may be a problem for some applications and its content should be known. Furthermore, water in an ionic liquid may not be inert and, thus, it can significantly influence the physicochemical properties of ionic liquids or their stability. For example, some ionic liquids can be hydrolyzed in the presence of water.[49]

b. Purification of commercial ionic liquids

For research carried out with commercial ionic liquids it is recommended to check quality of the product prior to work. Commercial ionic liquids may have colour pointing to impurities and may contain some traces of water. However, it should be free of organic volatiles, halides (if not a halide ionic liquid), and of all ionic impurities.

To remove water in laboratory research, commercial ionic liquids are usually dried at 333 K in vacuum overnight. The water content in any ionic liquid should be checked prior to its use (infrared spectroscopy, cyclic voltammetric measurements, Karl Fischer titration) and should always be mentioned in all descriptions and documentation of the experiments.

IV. Comparison of classical and novel solutions in terms of CO_2 capture

During the last few decades a lot of research effort was devoted to the development of new CO_2 absorption media. Even if an ideal absorbent to replace the current ones used in CO_2 scrubbing technologies has not yet been found, significant progress has been achieved in this area. Plausible examples of promising new solvents are summarized in Table 6.

At atmospheric pressure amines are still difficult to compete with (Table 6, No. 6). However, one can notice from Table 6 that 'switchable ionic liquids' and 'chemical' ionic liquids can potentially become plausible alternatives (Nos 5 and 2, respectively). Ionic liquid [bmim][BF_4] as a representative of 'physical' ionic liquids family, possesses really low CO_2 capacity at low pressure. However, as mentioned above, elevated pressures significantly boost its efficiency. A pressure increase of 10 bar resulted in seven times higher value of CO_2 loading (Table 6, Nos 1 and 7). Pressure rise can affect 'chemical' ionic liquids (No. 10) and poly(ionic liquid)s (No. 11), while for amine solutions capacity remains the same. Further pressure increase enhanced CO_2 capturing capacity leading to surprisingly high CO_2 capturing efficiency (Table 6, Nos 15 – 17).

However, to estimate the advantages from replacement of current amine solvents with ionic liquids, detailed feasibility calculations are required.

V. Conclusions

Nowadays, amine scrubbing is most widely applied for CO_2 separation. In the present review, different upgrading systems, including traditional solvents are compared from technological, economic and environmental viewpoints. It was shown that aMDEA system is an excellent choice for new plants as well as revamping CO_2 removal sections in existing ones. The modern CO_2 capture technologies have, however, several disadvantages calling for the search of new technological solutions.

As an emerging alternative, ionic liquids are described in this review as a group of very promising materials with unique sets of properties not achievable by means of any other materials. They are designer solvents, since their properties can be adjusted to suit the requirements. In addition, ILs can be recycled and they are non-volatile. This opens up opportunities for a great variety of industrial applications. High-efficient separation performance coupled to a low charge of the sequestration media is the obvious goal.

However, cost issues remain as some of the main drawbacks of ionic liquids currently often preventing their successful commercialization; it can be, partly, offset through simplifying their synthesis. Among other disadvantages of ILs, high viscosity and frequently uncontrolled (and low) purity can be mentioned. Moreover, the lack of

Table 6. CO_2 capacity of selected, high-performance solvents at 298 K.

No.	Solvent type	Solvent	CO_2 pressure /bar	Mole fraction of CO_2	Ref.
1	IL	[bmim][BF_4]	1	< 0.02	117
2	the same	[emim]OAc	1	0.27	134
3	IL mixtures	[Choline][Pro] – PEG 200	1	0.23	2
4	polymeric liquid	P[VBTMA][BF_4]	1	0.10	86
5	CO_2BOL	DBU – n-C_6H_{13}OH	1	0.31	73
6	aqueous amine solutions	MEA (30 wt %)	1	0.41	12
7	IL	[bmim][BF_4]	10	0.15	117
8	the same	[emim][Tf_2N]	10	0.20	135
9	"	[bmim]OPh	10	0.25	136
10	"	[emim]OAc	10	0.35	134
11	polymeric liquid	P[VBTMA][BF_4]	10	0.40	86
12	IL	[bmim]OTf	40	0.50	82
13	the same	[bmim][Tf_2N]	40	0.60	82
14	"	[bmim]OPh	40	0.70	136
15	"	[bmim]OTf	60	0.65	82
16	"	[bmim][Tf_2N]	60	0.70	82
17	"	[bmim][CTf_3]	60	0.75	82

knowledge about their toxicity is the main barrier to fully recognize them as absolutely green solvents.

In the current review, the most important research on ionic liquids as a media for CO_2 separation was summarized. This review focuses not only on the properties of pure ionic liquids but also on their mixtures which are aimed to improve their performance and CO_2 capturing efficiency. Moreover, ionic liquids have advantages compared to amines with respect to carbon reclaim. Ionic liquids, as amines, can be reused and provide the application of released CO_2 for the synthesis of fine chemicals.[133]

Thereby, the usefulness of ionic liquids has been demonstrated. ILs have already replaced volatile, polluting hydrocarbon solvents in some industrial processes. Thus, it can be expected that approaches based on ionic liquids will be a realistic choice for CO_2 capture as well as for other applications.

References

1. N MacDowell, N Florin, A Buchard, J Hallett, A Galindo, G Jackson, C S Adjiman, C K Williams, N Shah, P Fennell *Energy Environ. Sci.* **3** 1645 (2010)
2. X Li, M Hou, Z Zhang, B Han, G Yang, X Wang, L Zou *Green Chem.* **10** 879 (2008)
3. J Anderson, J Chiavari, H de Coninck, S Shackley, G Sigurthorsson, T Flach, D Reiner, P Upham, P Richardson, P Curnow *Energy Procedia* **1** 4649 (2009)
4. J C Peebles *Furnace Efficiency, Combustion and Flue Gases* (Charleston, SC: BiblioLife, 2009)
5. F A Tobiesen, H F Svendsen *Ind. Eng. Chem. Res.* **45** 2489 (2006)
6. A Kohl, R Nielsen *Gas Purification* (Houston, TX: Gulf Publishing, 1997)
7. A Meisen, X Shuai *Energy Convers. Manage.* **38** S37 (1997)
8. R Idem, M Wilson, P Tontiwachwuthikul, A Chakma, A Veawab, A Aroonwilas, D Gelowitz *Ind. Eng. Chem. Res.* **45** 2414 (2006)
9. U Desideri, A Paolucci *Energy Convers. Manage.* **40** 1899 (1999)
10. J D Figueroa, T Fout, S Plasynski, H McIlvried, R D Srivastava *Int. J. Greenhouse Gas Control* **2** 9 (2008)
11. R T Bailey, M M McDonald *Energy Convers. Manage.* **34** 1145 (1993)
12. Appl. US 2006/0251558 (2006)
13. B Wang, H Jin, D Zheng *Int. J. Energy Res.* **28** 521 (2004)
14. S K Furukawa, R K Bartoo *Improved Benfield Process for Ammonia Plants* (Des Plaines, IL: UOP, 1997)
15. G R Maxwell *Synthetic Nitrogen Products: a Practical Guide to the Products and Processes* (New York: Kluwer Academic, 2004)
16. R K Bartoo *Chem. Eng. Prog.* **80** 35 (1984)
17. M J Mitariten, C W Wolf, T J DePaola *Recent Developments in the Benfield Process for the Purification of Hydrogen* (Chicago, IL: ICI Katalco/KTI/UOP Hydrogen Plant Seminar, 1995)
18. M Appl *Ammonia. Principles and Industrial Practice* (Weinheim: Wiley-VCH, 1998)
19. A E Comyns *Encyclopedic Dictionary of Named Processes in Chemical Technology* (3rd Ed.) (Boca Raton, FL: Taylor and Francis, 2007)
20. S Paul, A K Ghoshal, B Mandal *Chem. Eng. Sci.* **64** 1618 (2009)
21. A Habibullah *Oil Gas J.* **100** (22) 46 (2002)
22. T L Huurdeman, S Goole, in *Ammonia Plant Safety Related Facilities* Vol. 43 (New York: American Institute of Chemical Engineers, 2002) p. 90
23. R E Meissner *Energy Prog.* **4** 17 (1984)
24. *The Rectisol Process. Lurgi's Leading Technology for Purification and Conditioning of Synthesis Gas* (Frankfurt am Main: Lurgi GmbH, 2007)
25. B Burr, L Lyddon *A Comparison of Physical Solvents for Acid Gas Removal* (Bryan, TX: Bryan Research and Engineering, 2008)
26. G Hochgesand *Ind. Eng. Chem.* **62** 37 (1970)
27. G Ranke, V H Mohr, in *Acid and Sour Gas Treating Processes* (Ed. S A Newman) (Houston, TX: Gulf Publishing Company, 1985) p. 80
28. J Sipilä, S Teir, R Zevenhoven *Carbon Dioxide Sequestration by Mineral Carbonation (Literature Review Updates 2005–2007. Report 2008-1)* (Turku: Åbo Akademi University, 2008)
29. R Zevenhoven, S Eloneva, S Teir *Catal. Today* **115** 73 (2006)
30. S Teir, R Kuusik, C-J Fogelholm, R Zevenhoven *Int. J. Miner. Process.* **85** 1 (2007)
31. F Goff, K S Lackner *Environ. Geosci.* **5** (3) 89 (1998)
32. Y Soong, A L Goodman, J R McCarthy-Jones, J P Baltrus *Energy Convers. Manage.* **45** 1845 (2004)
33. *Carbon Sequestration Research and Development* US Department of Energy. DOE.report DOE/SC/FE-1 (Washington, DC: US Government Printing Office, 1999)
34. S Bachu *Energy Convers. Manage.* **41** 953 (2000)
35. B Hitchon, W D Gunter, T Gentzis, R T Bailey *Energy Convers. Manage.* **40** 825 (1999)
36. P D Bergman, E M Winter *Energy Convers. Manage.* **36** 523 (1995)
37. E Favre *J. Membr. Sci.* **294** 50 (2007)
38. Y-S Bae, R Q Snurr *Angew. Chem., Int. Ed.* **50** 11586 (2011)
39. E van Jarwaarde *Benchmarking Novel Membrane Processes for CO_2 Removal from Contaminated Natural Gas* (Eindhoven: Technical University of Eindhoven, 2007)
40. J J Gassensmith, H Furukawa, R A Smaldone, R S Forgan, Y Y Botros, O M Yaghi, J F Stoddart *J. Am. Chem. Soc.* **133** 15312 (2011)
41. R Krishna, J M van Baten *J. Membr. Sci.* **277** 249 (2011)
42. Y Zhao, J Zhang, B Han, J Song, J Li, Q Wang *Angew. Chem., Int. Ed.* **50** 636 (2011)
43. J -R Li, Y Ma, M C McCarthy, J Sculley, J Yu, H-K Jeong, P B Balbuena, H-C Zhou *Coord. Chem. Rev.* **255** 1791 (2011)
44. S Choi, J H Drese, C W Jones *ChemSusChem.* **2** 796 (2009)
45. A R Millward, O M Yaghi *J. Am. Chem. Soc.* **127** 17998 (2005)
46. T Remy, G V Baron, J F M Denayer *Langmuir* **27** 13064 (2011)
47. Q Yang, A D Wiersum, H Jobic, V Guillerm, C Serre, P L Llewellyn, G Maurin *J. Phys. Chem. C* **115** 13768 (2011)
48. A Torrisi, R G Bell, C Mellot-Draznieks *Cryst. Growth Des.* **10** 2839 (2010)
49. Z Xiang, X Peng, X Cheng, X Li, D Cao *J. Phys. Chem. C* **115** 19864 (2011)
50. D Bonenfant, M Kharoune, P Niquette, M Mimeault, R Hausler *Sci. Technol. Adv. Mater.* **9** 013007 (2008)
51. D P Bezerra, R S Oliveira, R S Vieira, C L Cavalcante, D C S Azevedo *Adsorption* **17** 235 (2011)
52. S Zulfiqar, F Karadas, J Park, E Deniz, G D Stucky, Y Jung, M Atilhan, C T Yavuz *Energy Environ. Sci.* **4** 4528 (2011)
53. Appl. WO 2008/024329 (2008)
54. E Gallei, G Stumpf *J. Colloid Interface Sci.* **55** 415 (1976)
55. J-S Lee, J-H Kim, J-T Kim, J-K Suh, J-M Lee, C-H Lee *J. Chem. Eng. Data* **47** 1237 (2002)
56. G Calleja, J Pau, J A Calles *J. Chem. Eng. Data* **43** 994 (1998)
57. B Guo, L Chang, K Xie *J. Nat. Gas Chem.* **15** 223 (2006)
58. R V Siriwardane, M-S Shen, E P Fisher, J A Poston *Energy Fuels* **15** 279 (2001)
59. J A Thote, K S Iyer, R Chatti, N K Labhsetwar, R B Biniwale, S S Rayalu *Carbon* **48** 396 (2010)

60. K E Zanganeh, A Shafeen, M Gupta, C Salvador, in *Proceedings of the 31st International Technical Conference on Coal Utilization and Fuel Systems* Vol. 1 (Clearwater, FL: Coal Technology Association, 2006) p. 193
61. *Ionic Liquids: Industrial Application to Green Chemistry (ACS Symp. Ser.)* Vol. 818 (Eds R V Rogers, K R Seddon) (Washington, DC: American Chemical Society, 2002)
62. *Ionic Liquids in Synthesis* (Eds P Wasserscheid, T Welton) (Weinheim: Wiley-WCH, 2003)
63. D F Evans, A Yamauchi, G J Wei, V A Bloomfield *J. Phys. Chem.* **87** 3537 (1983)
64. P Bonhôte, A-P Dias, K Papageorgiou, K Kalyanasundaram, M Grätzel *Inorg. Chem.* **35** 1168 (1996)
65. N Karodia, S Guise, C Newlands, J-A Andersen *Chem. Commun.* 41 (1998)
66. P B Hitchcock, K R Seddon, T Welton *J. Chem. Soc. Dalton Trans.* **26** 39 (1993)
67. P B Hitchcock, R J Lewis, T Welton *Polyhedron* **12** 2039 (1993)
68. L A Blanchard, Z Gu, J F Brennecke *J. Phys. Chem. B* **105** 2437 (2001)
69. D M Austgen, G T Rochelle, C C Chen *Ind. Eng. Chem. Res.* **30** 543 (1991)
70. C C Chen, H I Britt, J F Boston, L B Evans *AIChE J.* **25** 820 (1979)
71. J J Carroll, A E Mather *Chem. Eng. Sci.* **52** 545 (1997)
72. J Tang, H Tang, W Sun, M Radosz, Y Shen *Polymer* **46** 12460 (2005)
73. D J Heldebrant, C R Yonker, P G Jessop, L Phan *Energy Environ. Sci.* **1** 487 (2008)
74. K R Seddon, A Stark, M J Torres *ACS Symp. Ser.* **819** 34 (2002)
75. R Fortunato, C M A Afonso, M A M Reis, J G Crespo *J. Membr. Sci.* **242** 197 (2004)
76. Y Hou, R E Baltus *Ind. Eng. Chem. Res.* **46** 8166 (2007)
77. E J Maginn *Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents* DOE report (Award Number: DE-FG26-04NT42122) (Notre Dame, Indiana: University of Notre Dame, 2005)
78. G Gurau, H Rodríguez, S P Kelley, P Janiczek, R S Kalb, R D Rogers *Angew. Chem., Int. Ed.* **50** 12024 (2011)
79. C A Ober, R B Gupta *Ind. Eng. Chem. Res.* **51** 2524 (2012)
80. C Cadena, J L Anthony, J K Shah, T I Morrow, J F Brennecke, E J Maginn *J. Am. Chem. Soc.* **126** 5300 (2004)
81. R E Baltus, B H Culbertson, S Dai, H M Luo, D W DePaoli *J. Phys. Chem. B* **108** 721 (2004)
82. S N V K Aki, B R Mellein, E M Saurer, J F Brennecke *J. Phys. Chem. B* **108** 20355 (2004)
83. J H Hildebrand, J M Prausnitz, R L Scott *Regular and Related Solutions* (New York: Van Nostrand Reinhold, 1970)
84. J E Bara, S Lessmann, C J Gabriel, E S Hatakeyama, R D Noble, D L Gin *Ind. Eng. Chem. Res.* **46** 5397 (2007)
85. T L Merrigan, E D Bates, S C Dorman, J H Davis Jr *Chem. Commun.* 2051 (2000)
86. J Tang, H Tang, W Sun, H Plancher, M Radosz, Y Shen *Chem. Commun.* 3325 (2005)
87. S Kato, Y Tsujita, H Yoshimizu, T Kinoshita, J S Higgins *Polymer* **38** 2807 (1997)
88. Z Mogri, D R Paul *Polymer* **42** 7781 (2001)
89. J L Budzien, J D McCoy, D H Weinkauf, R A LaViolette, E S Peterson *Macromolecules* **31** 3368 (1998)
90. P G Jessop, D J Heldebrant, X Li, C A Eckert, C L Liotta *Nature (London)* **436** 1102 (2005)
91. P Adams, F A Baron *Chem. Rev.* **65** 567 (1965)
92. K Adamczyk, M Prémont-Schwarz, D Pines, E Pines, E T J Nibbering *Science* **326** 1690 (2009)
93. D J Heldebrant, P G Jessop, C A Thomas, C A Eckert, C L Liotta *J. Org. Chem.* **70** 5335 (2005)
94. E R Pérez, M O da Silva, V C Costa, U P Rodrigues-Filho, D W Franco *Tetrahedron Lett.* **43** 4091 (2002)
95. T Endo, D Nagai, T Monma, H Yamaguchi, B Ochiai *Macromolecules* **37** 2007 (2004)
96. E R Pérez, R H A Santos, M T P Gambardella, L G M de Macedo, U P Rodrigues-Filho, J C Launay, D W Franco *J. Org. Chem.* **69** 8005 (2004)
97. E Haruki, in *Organic and Bio-Organic Chemistry of Carbon Dioxide* (Eds S Inoue, N Yamazaki) (Tokyo: Kodansha, 1982)
98. Y Liu, P G Jessop, M Cunningham, C A Eckert, C L Liotta *Science* **313** 958 (2006)
99. L Phan, D Chiu, D J Heldebrant, H Huttenhower, E John, X W Li, P Pollet, R Wang, C A Eckert, C L Liotta, P G Jessop *Ind. Eng. Chem. Res.* **47** 539 (2008)
100. E D Raczyńska, P-C Maria, J-F Gal, M Decouzon *J. Phys. Org. Chem.* **7** 725 (1994)
101. P Singh, J P M Niederer, G F Versteeg *Int. J. Greenhouse Gas Control* **1** 5 (2007)
102. Y Tao, T Yamada, G C Gaviola, R G Weiss *Chem. Mater.* **20** 5337 (2008)
103. N M Kocherginsky, Q Yang, L Seelam *Sep. Purif. Technol.* **53** 171 (2007)
104. P Scovazzo, J Kieft, D A Finan, C Koval, D DuBois, R D Noble *J. Membr. Sci.* **238** 57 (2004)
105. Q Gan, D Rooney, M Xue, G Thompson, Y Zou *J. Membr. Sci.* **280** 948 (2006)
106. F F Krull, C Fritzmann, T Melin *J. Membr. Sci.* **325** 509 (2008)
107. M Teramoto, Y Sakaida, S S Fu, N Ohnishi, H Matsuyama, T Maki, T Fukui, K Arai *Sep. Purif. Technol.* **21** 137 (2000)
108. D D Iarikov, P Hacarlioglu, S T Oyama *Chem. Eng. J.* **166** 401 (2011)
109. S Hanioka, T Maruyama, T Sotani, M Teramoto, H Matsuyama, K Nakashima, M Hanaki, F Kubota, M Goto *J. Membr. Sci.* **314** 1 (2008)
110. D-H Kim, I-H Baek, S-U Hong, H-K Lee *J. Membr. Sci.* **372** 346 (2011)
111. M Adibi, S H Barghi, D Rashtchian *J. Membr. Sci.* **371** 127 (2011)
112. W Dai, S Luo, S Yin, C Au *Front. Chem. Eng. China* **4** 163 (2010)
113. P Scovazzo *J. Membr. Sci.* **343** 199 (2009)
114. D Morgan, L Ferguson, P Scovazzo *Ind. Eng. Chem. Res.* **44** 4815 (2005)
115. L J Lozano, C Godínez, A P de los Ríos, F J Hernández-Fernández, S Sánchez-Segado, F J Alguacil *J. Membr. Sci.* **376** 1 (2011)
116. Y Chen, Z Hu, K M Gupta, J Jiang *J. Phys. Chem. C* **115** 21736 (2011)
117. L M Galvnd Svnchez, G W Meindersma, A B de Haan *Chem. Eng. Res. Des.* **85** 31 (2007)
118. M Avalos, R Babiano, P Cintas, J L Jimgnez, J C Palacios *Angew. Chem., Int. Ed.* **45** 3904 (2006)
119. K Fukumoto, M Yoshizawa, H Ohno *J. Am. Chem. Soc.* **127** 2398 (2005)
120. G Tao, L He, N Sun, Y Kou *Chem. Commun.* 3562 (2005)
121. S Hu, T Jiang, Z Zhan, A Zhu, B Han, J Song, Y Xie, W Li *Tetrahedron Lett.* **48** 5613 (2007)
122. J Chen, S K Spear, J G Huddleston, R D Rogers *Green Chem.* **7** 64 (2005)
123. Z Hou, N Theyssen, A Brinkmann, W Leitner *Angew. Chem., Int. Ed.* **44** 1346 (2005)
124. E D Bates, R D Mayton, I Ntai, J H Davis Jr *J. Am. Chem. Soc.* **124** 926 (2002)
125. M Q Hou, S Q Liang, Z F Zhang, J Y Song, T Jiang, B X Han *Fluid Phase Equilib.* **258** 108 (2007)
126. A B Foster, J M Webber *Adv. Carbohydr. Chem. Biochem.* **15** 371 (1960)

127. E Khor *Chitin: Fulfilling a Biomaterials Promise* (Amsterdam: Elsevier, 2001)
128. H Xie, S Zhang, S Li *Green Chem*. **8** 630 (2006)
129. D Camper, J E Bara, D L Gin, R D Noble *Ind. Eng. Chem. Res*. **47** 8496 (2008)
130. J E Bara, D E Camper, D L Gin, R D Noble *Acc. Chem. Res*. **43** 152 (2010)
131. M M Taib, T Murugesan *Chem. Eng. J*. **181** – **182** 56 (2012)
132. F Zheng, J-W Ma, Z Zhou, Y-T Wu, Z-B Zhang *Chem. Eng. J*. **181** – **182** 222 (2012)
133. Q Huang, Y Li, X Jin, D Zhao, G Z Chen *Energy Environ. Sci*. **4** 2125 (2011)
134. M B Shiflett, A Yokozeki *J. Chem. Eng. Data* **54** 108 (2009)
135. Y S Kim, W Y Choi, J H Jang, K-P Yoo, C S Lee *Fluid Phase Equilib*. **228** – **229** 439 (2005)
136. J K Sung, S H Kim, M Cheong, I Baek *Bull. Korean Chem. Soc*. **31** 2797 (2010)