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Carbon Dioxide Uptake from Natural Gas by Binary Ionic Liquid-Water Mixtures

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Carbon dioxide solubility in a set of carboxylate ionic liquids formulated with stoicheiometric amounts of water is found to be significantly higher than for other ionic liquids previously reported. This is due to synergistic chemical and physical absorption. The formulated ionic liquid/water mixtures show greatly enhanced carbon dioxide solubility relative to both anhydrous ionic liquids and aqueous ionic liquid solutions, and are competitive with commercial chemical absorbers, such as activated *N*-methyldiethanolamine or monoethanolamine.

Introduction: Current Carbon Capture Technologies

The separation of carbon dioxide from other gases, generally known as acid gas stripping, is currently of great industrial interest for natural gas processing and carbon capture. Once captured, the carbon dioxide may be stored (a process commonly known as carbon capture and storage, CCS), purified for sale or reprocessing, or used for enhanced oil recovery (EOR).[1-3] The economic implications of ignoring carbon dioxide releases have been emphasised elsewhere,[4] although the conclusions of that report have been heavily criticised.[5,6] In the case of EOR, typically carbon dioxide from either natural gas processing plants or CCS facilities is pressurised and pumped underground into oil reservoirs to force additional oil out of the porous formation.[7]

Presently, the favoured means of removing carbon dioxide from both raw natural gas and flue gas is by the use of an absorption tower containing an aqueous amine solution, normally the primary amine monoethanolamine (MEA; $HOCH_2CH_2NH_2$), or the tertiary amine *N*-methyldiethanolamine (MDEA; $(HOCH_2CH_2)_2NCH_3$) with an additional base, typically piperazine, often added as an activator ("activated" MDEA, or aMDEA).[1,8]

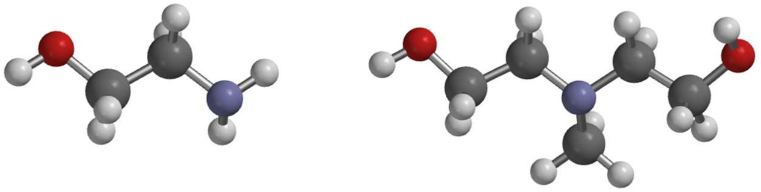

MEA MDEA

Figure 1. Structures of common amines used for CO_2 capture: monoethanolamine (MEA) and *N*-methyldiethanolamine (MDEA). Grey: carbon; white: hydrogen; red: oxygen; blue: nitrogen.

Although the capture of CO_2 with amines is the most widely implemented technology, this system is rife with both practical and political ramifications.[9] The amines used in practice are volatile, corrosive, and thermally labile, resulting in unwanted emissions from any practical process. In addition, thermal decomposition products enhance foaming, and the best commercial candidate, MDEA (see Figure 1), is a Schedule 3 compound under the Chemical Weapons Convention.[10] This will result in future difficulties in deploying these technologies in many oil-rich regions, particularly the Middle East. Despite the attractive qualities of these amines (cost and familiarity), the weight of negative issues stimulates the need for the development of safer, more efficient, CO_2 capture technologies.

Current common alternative technologies[11,12] to amine absorbers include, the Benfield, Catacarb®, Selexol™, Fluor®, Rectisol®, and Purisol® processes, as well as a range of less preferred technologies,[8] as depicted in Figure 2.[13] The Benfield process, a chemical absorber relying on hot aqueous potassium carbonate solution with vanadium(V) oxide,[8,11] and the related Catacarb[14] process which replaces the vanadium(V) oxide with alkali metal borates, are two such processes. The Benfield process suffers from potassium hydrogencarbonate precipitation when the carbonate concentration exceeds 35 wt %. In addition, the potassium carbonate methods all suffer from well-known corrosion issues.[15]

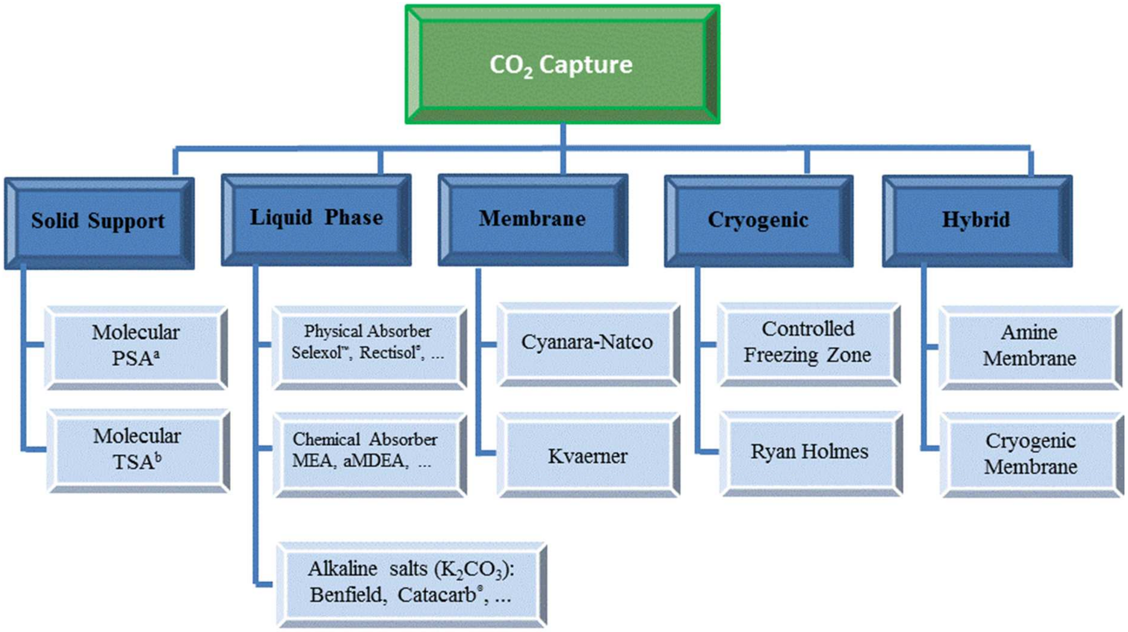


Figure 2 Carbon dioxide separation technologies currently available.[13] [a] PSA = pressure swing adsorption; [b] TSA= temperature swing adsorption.

It has been estimated that, in 1998, corrosion prevention expenditure in the USA petroleum refining industry alone was approximately US$3,700,000,000,[16] demonstrating that the use of corrosive solvent systems is a considerable expense. Although often overlooked in reviews, the Catacarb process also involves diethanolamine, $(HOCH_2CH_2)_2NH$, which ultimately led to the United States EPA citing Unocal for spill violations after the release of the Catacarb® absorption solvent, resulting in the loss of US$80,000,000 in a class action law suit.[17,18] The remaining solvent-based processes commonly utilise physical absorption, relying on a latent basicity for interaction with acid gases. These include Selexol™ (a mixture of dimethyl ethers of polyethylene glycols), the Fluor® process (which uses propylene carbonate), Rectisol® (methanol), and Purisol® (*N*-methyl-2-pyrrolidone). As physical absorbers, they all exhibit lower uptake than the chemical processes. Selexol™ and Purisol® both have a propensity for the uptake of hydrocarbons (particularly ethane and propane), whereas elastomers are also soluble in Purisol®. Fluor® and Rectisol® operate best at temperatures that require refrigeration. Moreover Purisol®, and particularly Rectisol®, have high volatility, which is a major drawback for both processes. In contrast to the solvent-based carbon dioxide capture methods, there are also methods based on solid physical adsorbers. These are largely limited to molecular sieves (zeolites)[19] and membrane separators.[20] The molecular sieves absorb several contaminants, but at different rates, and the spent sieves must be regenerated with the regeneration gas flared. Membrane separators have found use in situations where either the feed gas has a high carbon dioxide content and the gas separator must have a limited footprint (such as offshore platforms in high CO_2 fields), and or in circumstances where separation quality is less important (*e.g.* where the carbon dioxide is being produced for EOR). In the case where membrane separators are to be used for natural gas purification, the raw gas generally must undergo an additional polishing step with the use of a traditional amine, Benfield, or Selexol™ solvent.

State-of-the-Art Carbon Dioxide Capture with Ionic Liquids

Rationale

Despite the plethora of carbon dioxide capture technologies, deficiencies remain with regard to volatility, thermal stability, cost, and environmental issues. Perhaps it is not surprising, therefore, that the scientific community has turned to ionic liquids as potential CCS and gas processing media, with a concomitant explosion of papers and patents. The potential benefits of ionic liquids for the purpose of carbon dioxide capture (indeed, for most gas separation uses) are numerous. These fluids show quite high thermal, oxidative, and radiological stability relative to many molecular organic solvents.[21] Since they consist solely of ions, stable ionic liquids show negligible vapour pressure under typical industrial process conditions.[22] Ionic liquids show little tendency for causing corrosion of typical industrial materials, and may even inhibit corrosion.[23,24] In addition, contrary to many of the candidate amines, there is no expectation that useful ionic liquids will be prohibited under the Chemical Weapons Convention. As the custom design of the solvent is possible, one may optimise for the collection of properties desired for the purpose at hand (thermal stability, desirable physical properties, low cost, low toxicity, high biodegradability, *etc*.), thereby greatly increasing the probability of finding a successful, economic system. Indeed, it has been estimated that there are over a million simple ionic liquids possible.[25] The systems designed and described in this paper are targeted specifically at the high (10-90%) carbon dioxide levels found in submarine sources of natural gas, and not at power station emissions (which are at much lower partial pressures of carbon dioxide). Ionic liquids are a current hot topic in chemistry with over 20,000 papers and 4,000 patents published since 1996.[26] This has resulted in a wide range of reviews and books which summarise the properties, scope, and applications of these Coulombic fluids.[21,27-35]

Physisorption with Ionic Liquids

Capitalising on the features outlined above, Brennecke and coworkers[36] reported the physical solubility of supercritical carbon dioxide in $[C_4mim][PF_6]^{\S}$ ($[C_4mim]^+$ = 1-butyl-3-methylimidazolium),[37] and later demonstrated (see Figure 3)[38] the huge difference in solubilities between polar carbon dioxide and non-polar methane and ethane.

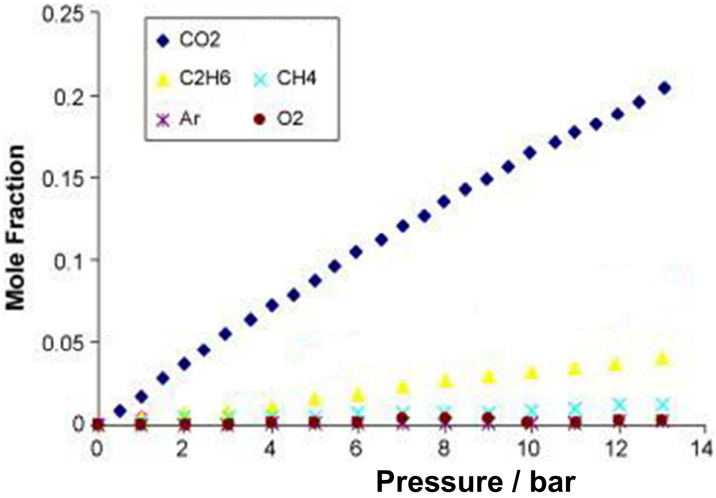


Figure 3. Uptake of various gases by $[C_4mim][PF_6]$.[38]

[§] Although not widely appreciated at the time, hexafluorophosphate ionic liquids hydrolyse in moist air to release five equivalents of hydrogen fluoride, and will have no practical industrial application.

However, it should be noted that the majority of the research on carbon dioxide solubility in ionic liquids to date has, curiously, neglected a major issue related to the way in which uptake is reported. For physical absorbers, carbon dioxide uptake is typically described in terms of Henry's constant, Equation (1).

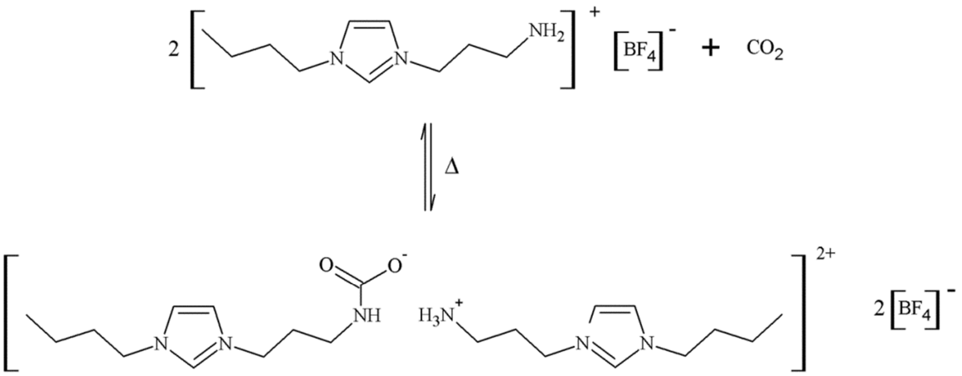
$$k_{\mathrm{H}} = \frac{p}{c} \qquad (1)$$

Here, p is the partial pressure of carbon dioxide, and c is concentration, typically expressed as mole fraction. When Henry's constant is expressed as a mole fraction, however, the molecular weight of the ionic liquid is not accounted for. As most of the ionic liquids extensively studied consist of relatively large organic cations paired with high molecular weight anions (often containing fluorine, oxygen, and/or sulfur atoms), the molecular weight of one ionic liquid "ion pair" is often much, much larger than the molecular weight of carbon dioxide. For example, one readily available ionic liquid is trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]amide, $[P_{6\,6\,6\,14}][NTf_2]$, with a molecular weight of 764.01 a.m.u., while the molecular weight of carbon dioxide is 44.01 a.m.u. Therefore, high uptake in terms of molar fraction corresponds to a much lower uptake in terms of weight fraction (approximately 17 times lower). From an industrial perspective, efficient uptake in terms of solvent weight or volume is far more important than uptake in terms of mole fraction; the important empirical ratio is the weight of carbon dioxide absorbed per litre of solvent. Most ionic liquid studies have reported uptake in terms of Henry's constant using mole fractions. This has inadvertently led to artificially inflated views on the carbon dioxide capacity of many ionic liquids.

To counteract the above problems, in this work it was decided to determine carbon dioxide solubility in terms of weight and volume of solvent. This allows a more industrially relevant measure for determining the relative value of ionic liquids as gas uptake solvents. In addition, ionic liquid design was redirected towards physically smaller cations paired with low molecular weight anions. In this way, carbon dioxide uptake may be maximised in terms of solvent weight or volume.

Chemisorption with Ionic Liquids

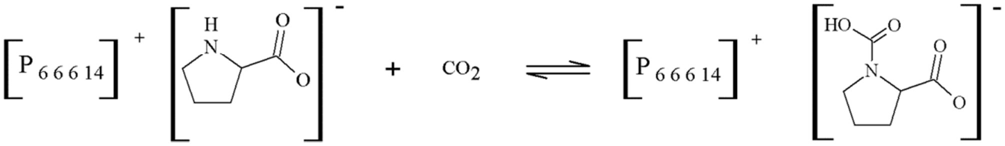
In 2002, Davis Jr. and co-workers proposed the concept of a "task-specific" ionic liquid, now preferably known as functionalised ionic liquids.[39] Initially, they incorporated an amine functionality onto the terminal end of the side chain of an imidazolium cation. Coupled with the tetrafluoroborate anion, this generated the functionalised ionic liquid shown in Scheme 1. This ionic liquid was shown to result in the chemisorption of carbon dioxide at a 1:2 CO_2:IL ratio in accordance with Scheme 1.[40]



Scheme 1. Reaction between original functionalised ionic liquid and carbon dioxide.[40]

Since these landmark publications on carbon dioxide absorption, there has been a flood of derivative publications, many of which have been reviewed elsewhere.[41-43] Although these papers largely play a variation on a known theme, many contained extremely reliable and valuable data on the physisorption of carbon dioxide in a wide range of ionic liquids.[42,44,45]

It rapidly became clear from the reported Henry's constants for CO_2 in a wide range of ionic liquids, from about 0.1 to 0.25 (mol CO_2) (kg IL)$^{-1}$ at 5 bar,[42] that a system based on physisorption alone would never be commercially viable, but that the systems based on chemisorption were constrained by a low molar uptake. Work from Notre Dame recognises this, resulting in new functionalised ionic liquid systems based on amino acids, which doubled the carbon dioxide uptake by operating on 1:1 stoicheiometry (Scheme 2, where $[P_{6\,6\,6\,14}]^+$ is the trihexyl(tetradecyl)phosphonium cation). In this, and many other papers, the authors stressed the importance of using dry ionic liquids.[46,47]



Scheme 2. Reaction between a functionalised amino acid anion and carbon dioxide.[48]

Here, we report the development of a new acid gas stripping solvent for removal of carbon dioxide from natural gas sources, based on ionic liquids with carboxylate anions, as reported in recent patents.[49,50] Unlike previous literature studies, the water content of these ionic liquids is carefully controlled at near equimolar amounts. The formulated ionic liquid/water mixtures show greatly enhanced carbon dioxide solubility relative to both anhydrous ionic liquids and aqueous ionic liquid solutions.

Equipment and Uptake Experiments

Ionic Liquid Selection

An important design factor that may be incorporated is dependent on ionic liquid basicity, as the mechanisms of carbon dioxide chemisorption involve nucleophilic attack. Typically, to generate strongly basic ionic liquids, a basic functional group has been appended to the side chain of the quaternising alkyl chain: see, for example, Scheme 1.[40] However, a facile consideration of electron density suggests that placing the basic group on the cation will reduce its basicity, while placing the basic group on the anion should enhance basicity. Bases are, more or less by definition, species with regions of high electron density. It makes little sense to append an electron-rich functional group to an inherently electron-poor species. To quantify this subjective argument, computational studies were performed on a cation and anion with basic functionalisation, using Spartan '10 with density functional theory (DFT) at the B3LYP level, and a 6-31G* basis set.[51] Figure 4 illustrates electrostatic potential maps for the [2-[2-(diisopropylamino)ethoxy]ethyl]-(ethyl)dimethylammonium cation (top) and the ethanoate anion (bottom). Electron density increases from the extremes of positive blue to negative red. On the cation, the lone pair on the nitrogen atom on the far right (green) is significantly less basic than the oxygen atoms (red) on the ethanoate anion. Hence, our ionic liquid design strategy was directed towards placing the nucleophilic site on the anion, rather than the cation. In addition, candidate cations and anions were also selected with an eye towards reducing molecular size and mass.

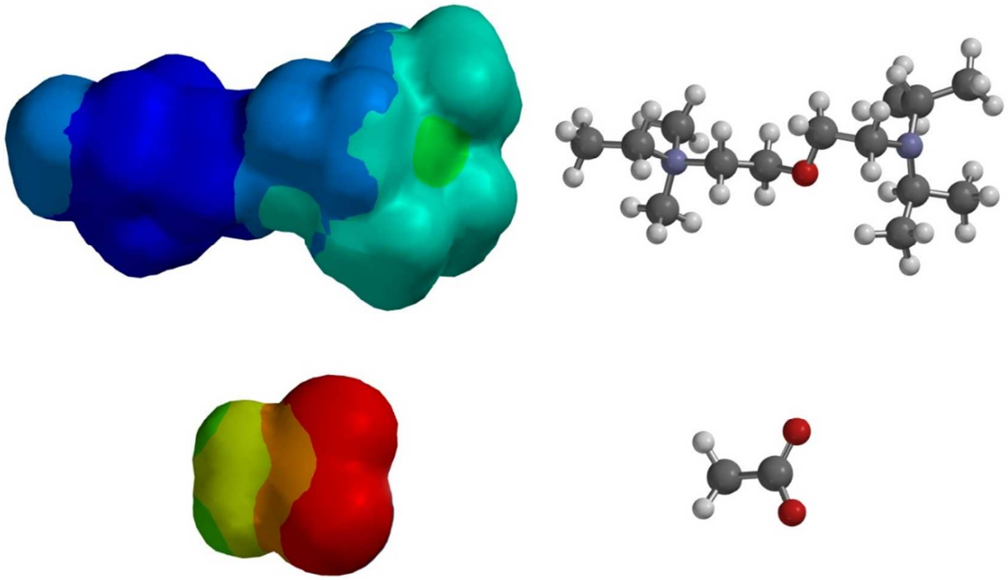


Figure 4. Potential energy mapped onto the electron density surface for (top) the [2-[2-(diisopropylamino)ethoxy]ethyl](ethyl)dimethylammonium cation and (bottom) the ethanoate anion. The colour scheme ranges from red as the most negative to blue as the most positive.

All ionic liquids in this study have been synthesised from aqueous or methanolic solutions containing the cation of interest paired with the methyl carbonate, hydroxide, or hydrogencarbonate anions. In all cases, the conjugate acid of the anion of interest, typically a carboxylic acid or an amino acid, is added slowly to the aqueous or methanolic solution in sub-equivalent amounts (normally up to 80% of the required amount). The solution was stirred with mild heating, resulting in reaction to form water (hydroxide and hydrogencarbonate), methanol (methyl carbonate), or carbon dioxide (hydrogencarbonate and methyl carbonate). Where carbon dioxide is produced, greater heating and longer reaction times were required, as the carbon dioxide buffers the solution and must be released. The reaction is allowed to proceed until carbon dioxide is no longer generated (in the case of hydroxide solutions, the reaction shows no visible indication of completion but is quite rapid). The pH of the reaction mixture was then monitored as additional acid was added to the equivalence point of that particular species. Hydrogencarbonate and some hydroxide solutions were purchased from chemical supply companies, while most hydroxide and methyl carbonates were generated in-house using previously published methodologies.[52,53] Some of the tributylmethylphosphonium methyl carbonate in methanol was received as a gift from Cytec Canada.

Anhydrous Carboxylate Ionic Liquids

The absorption of carbon dioxide by ionic liquids has recently been reviewed.[43] The authors concluded that "the overall tendency is that adding a certain amount of water into the pure ionic liquids will slightly decrease the absorption capacity of CO_2, but the lower viscosity of the mixture is favourable as it can promote gas diffusion in the solvent and reduce operational constrains on the use of ionic liquids fluids".[43] There have been many studies published on carboxylates, and especially on the $[C_n\text{mim}][CH_3CO_2]$-$CO_2$ ($n = 2$ or 4) system,[45,46,54-63] but the focus has largely been upon a possible interaction between the carbon dioxide and the anion; two groups have noted a positive effect of the presence of water, but ascribed it to a lower viscosity of the system.[62,64] Of the multitude of papers on carbon dioxide solubility in ionic liquids, those that mention water content, with very few exceptions, state that the ionic liquids must be as dry as possible.[46,47] When considering physical absorbers, this is a sensible precaution. Although carbon dioxide is significantly more soluble in water than most other gases,[65] solubility is still quite low (Henry's constant on the order of 1640 bar) relative to "good" physical solvents such as methanol (on the order of 100 bar), used in the Rectisol process.[66] Thus, addition of water is expected to effectively dilute the uptake solvent and reduce solubility.

Table 1. The solubility of CO_2 in trihexyl(tetradecyl)phosphonium carboxylate ionic liquids at 25 °C and 5 bar.

Ionic Liquid	Henry's Constant / bar	CO_2 solubility /mol kg^{-1}	/mol l^{-1}
$[P_{6\,6\,6\,14}][HCO_2]$	19.4	0.58	0.66
$[P_{6\,6\,6\,14}][CH_3CO_2]$	23.7	0.44	0.50
$[P_{6\,6\,6\,14}][C_2H_5CO_2]$	25.2	0.40	0.45
$[P_{6\,6\,6\,14}][C_3H_7CO_2]$	29.2	0.33	0.36
$[P_{6\,6\,6\,14}][C_5H_{11}CO_2]$	28.1	0.34	0.37
$[P_{6\,6\,6\,14}][C_7H_{15}CO_2]$	24.7	0.36	0.41
$[P_{6\,6\,6\,14}][Me_2CHCO_2]$	32.2	0.30	0.33
$[P_{6\,6\,6\,14}][MeCH(OH)CO_2]$	23.9	0.42	0.46
$[P_{6\,6\,6\,14}][HOCH_2CO_2]$	27.2	0.38	0.42

To establish the viability of carboxylate anions for carbon dioxide uptake, a series of ionic liquids containing carboxylate anions of varying alkyl chain length and branching, paired with the trihexyl(tetradecyl)phosphonium cation, were prepared. This initial series was generated because the chloride form of the cation is readily available, and easily converted to the hydroxide using the reported method.[53] The solubility of carbon dioxide in this ionic liquid series, at 25 °C and 5 bar, is presented in Table 1. This reveals excellent uptake in terms of Henry's constant (19-32 bar), with reasonably good uptake in both weight and volume terms – an uptake of 0.30-0.58 (mol CO_2) (kg IL)$^{-1}$. Buoyed up by these results, it was decided to determine if altering the cation size would significantly change the carbon dioxide uptake in terms of weight and volume. These studies included symmetrical cations: Table 2 shows an uptake of 0.36-0.58 (mol CO_2) (kg IL)$^{-1}$ for the methanoate anion, and 0.39-0.50 (mol CO_2) (kg IL)$^{-1}$ for the ethanoate anion. The effect of cation chain length is detailed in Table 3 for the alkyltrioctylphosphonium cation series, showing an uptake of 0.28-0.48 (mol CO_2) (kg IL)$^{-1}$ for the methanoate anion, and 0.39-0.43 (mol CO_2) (kg IL)$^{-1}$ for the ethanoate anion. Finally, Table 4 shows an uptake of 0.37-0.45 (mol CO_2) (kg IL)$^{-1}$ for the methanoate anion, 0.35-0.39 (mol CO_2) (kg IL)$^{-1}$ for the ethanoate anion, for the alkyltributylphosphonium cation series. Curiously, changes in cation size, even quite large changes, showed little effect on the CO_2 uptake. In addition, the changes in uptake across series that did occur were inconsistent and difficult to explain in physical terms. As these ionic liquids all show at least a degree of hygroscopicity, it was thought that small variations in adventitious water content (due to subtle handling differences prior to uptake experiments) may have been responsible. This was one rationale for the water content studies outlined later.

Ionic Liquids based on Amino Acids

Alkaline metal amino acid salts are the primary component of an industrial CO_2 absorption system known as the DECAB process.[67] Thus, in a parallel study to the carboxylates above, ionic liquids with anions based on amino acids were explored as a potentially useful set of chemical absorbers.[68,69]

Table 2. Solubility of CO_2 in symmetrical tetraalkylphosphonium methanoates and ethanoates at 25 °C and 5 bar.

Ionic Liquid	Henry's Constant	CO_2 solubility	
	/ bar	/ mol kg^{-1}	/ mol l^{-1}
$[P_{5\,5\,5\,5}][HCO_2]$	38.5	0.38	0.41
$[P_{6\,6\,6\,6}][HCO_2]$	24.0	0.58	0.64
$[P_{8\,8\,8\,8}][HCO_2]$	29.0	0.36	0.40
$[P_{5\,5\,5\,5}][CH_3CO_2]$	34.7	0.42	0.45
$[P_{6\,6\,6\,6}][CH_3CO_2]$	26.4	0.50	0.55
$[P_{8\,8\,8\,8}][CH_3CO_2]$	26.0	0.39	0.44

Table 3. Solubility of CO_2 in $[P_{8\,8\,8\,n}][HCO_2]$ and $[P_{8\,8\,8\,n}][CH_3CO_2]$ (n = 4, 6, 8, 10, 12 or 14) at 25 °C and 5 bar.

Ionic Liquid	Henry's Constant	CO_2 solubility	
	/ bar	/ mol kg^{-1}	/ mol l^{-1}
$[P_{8\,8\,8\,4}][HCO_2]$	29.0	0.40	0.44
$[P_{8\,8\,8\,6}][HCO_2]$	37.5	0.28	0.31
$[P_{8\,8\,8\,8}][HCO_2]$	29.0	0.36	0.40
$[P_{8\,8\,8\,10}][HCO_2]$	25.4	0.39	0.44
$[P_{8\,8\,8\,12}][HCO_2]$	21.0	0.48	0.53
$[P_{8\,8\,8\,14}][HCO_2]$	29.7	0.30	0.33
$[P_{8\,8\,8\,4}][CH_3CO_2]$	28.2	0.40	0.44
$[P_{8\,8\,8\,6}][CH_3CO_2]$	25.2	0.43	0.48
$[P_{8\,8\,8\,8}][CH_3CO_2]$	26.0	0.39	0.44
$[P_{8\,8\,8\,10}][CH_3CO_2]$	24.6	0.40	0.45
$[P_{8\,8\,8\,12}][CH_3CO_2]$	24.4	0.38	0.43
$[P_{8\,8\,8\,14}][CH_3CO_2]$	22.9	0.40	0.45

Table 4. Solubility of CO_2 in $[P_{4\,4\,4\,n}][HCO_2]$ and $[P_{4\,4\,4\,n}][CH_3CO_2]$ (n = 6, 8, 10, 12 or 14) at 25 °C and 5 bar.

Ionic Liquid	Henry's Constant	CO_2 solubility	
	/ bar	/ mol kg^{-1}	/ mol l^{-1}
$[P_{4\,4\,4\,6}][HCO_2]$	43.1	0.37	0.40
$[P_{4\,4\,4\,8}][HCO_2]$	33.7	0.45	0.49
$[P_{4\,4\,4\,10}][HCO_2]$	35.3	0.39	0.42
$[P_{4\,4\,4\,12}][HCO_2]$	32.5	0.40	0.44
$[P_{4\,4\,4\,14}][HCO_2]$	28.5	0.43	0.48
$[P_{4\,4\,4\,6}][CH_3CO_2]$	43.4	0.35	0.38
$[P_{4\,4\,4\,8}][CH_3CO_2]$	39.8	0.35	0.39
$[P_{4\,4\,4\,10}][CH_3CO_2]$	35.7	0.37	0.41
$[P_{4\,4\,4\,12}][CH_3CO_2]$	32.5	0.39	0.43
$[P_{4\,4\,4\,14}][CH_3CO_2]$	30.8	0.39	0.43

Indeed, the tetrabutylphosphonium salts of amino acids prepared here show excellent carbon dioxide uptake (with the exceptions of the two amino acids with tertiary amine groups), achieving approximately 1:1 molar absorption (Table 5). Unfortunately, as pure, anhydrous compounds, these ionic liquids solidify or form thick pastes upon CO_2 uptake, rendering them unsuitable for real world applications.

Table 5. Solubility of CO_2 in tetrabutylphosphonium ionic liquids with anions[a] derived from amino acids at 25 °C and 5 bar.

Ionic Liquid		CO_2 solubility	
	/mol l^{-1}	/mol kg^{-1}	mol CO_2/mol IL
$[P_{4444}]$[Gly]	2.93	3.04	1.02
$[P_{4444}]$[Ala]	3.00	3.16	1.10
$[P_{4444}]$[Val]	2.70	2.85	1.07
$[P_{4444}]$[Ile]	2.60	2.75	1.07
$[P_{4444}]$[Pro]	2.61	2.70	1.01
$[P_{4444}]$[Bic]	1.05	1.04	0.44
$[P_{4444}]$[Dmg]	0.65	0.67	0.24

[a] [Gly] = glycinate, [Ala] = alaninate, [Val] = valinate, [Ile] = isoleucinate, [Pro] = prolinate, [Bic] = bicinate, 2-(bis(2-hydroxyethyl)amino)ethanoate, [Dmg] = dimethylglycinate

Effect of Water on Carbon Dioxide Uptake

The solubility of carbon dioxide in water as a function of temperature (see Figure 5) and pressure is well known.[70] It can be seen that the solubilities in water are three orders of magnitude lower than those in simple ionic liquids (see Tables 1-5). It is perhaps not surprising, therefore, that the literature has emphasised the need for the ionic liquids to be dry.

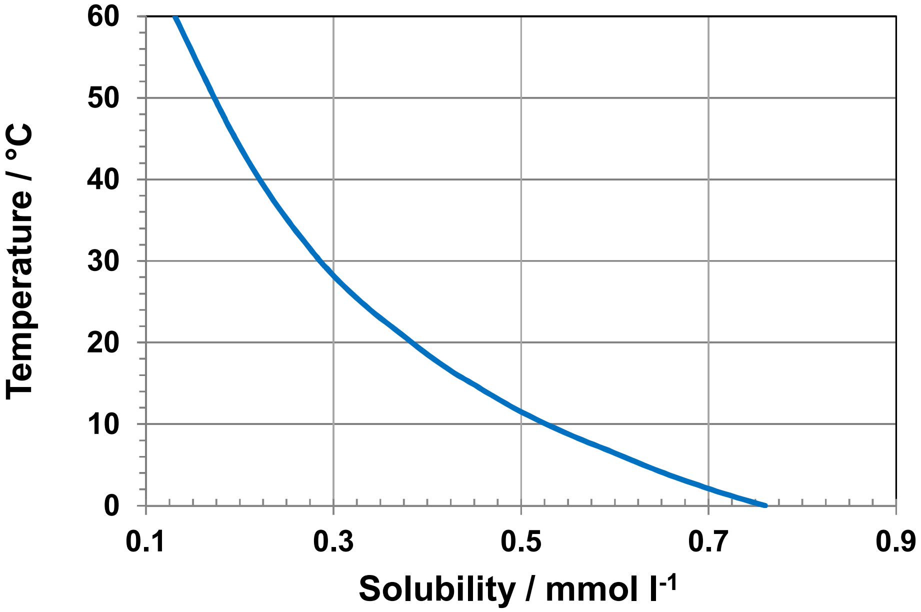


Figure 5. The temperature-dependent solubility of carbon dioxide in water at atmospheric pressure.[70]

Our initial observations of carbon dioxide solubility in "dry" carboxylate ionic liquids showed a scatter over and above that expected for the experimental design. This suggested that it would be prudent to determine the effect of water on carbon dioxide uptake, as these ionic liquids are particularly hygroscopic. In addition, both raw natural gas and flue gas are saturated with water, and hence (during any industrial process) it would be expected that ionic liquids would absorb water if used as CO_2 absorbers.

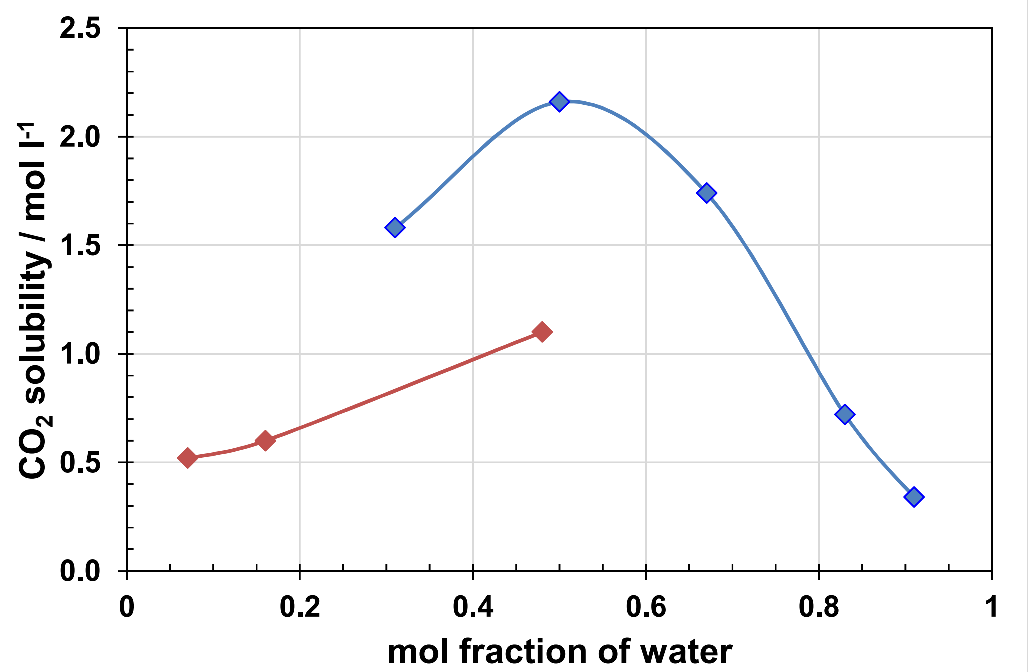


Figure 6. Carbon dioxide uptake of mixtures of water and the ionic liquids $[P_{4\,4\,4\,4}][HCO_2]$ (blue) and $[P_{6\,6\,6\,14}][HCO_2]$ (red), at 25 °C and 5.00±0.02 bar.

To determine the effect of low levels of water on these carboxylate ionic liquids, initially noted on exposure to ambient air, two ionic liquids were chosen for uptake trials. The liquid trihexyl(tetradecyl)phosphonium methanoate, $[P_{6\,6\,6\,14}][HCO_2]$, and the low melting solid tetrabutylphosphonium methanoate, $[P_{4\,4\,4\,4}][HCO_2]$, were dried by heating *in vacuo*, and a series of ionic liquid:water mixtures were prepared. In the case of $[P_{4\,4\,4\,4}][HCO_2]$, the water content ranged from about 30 mol% to 90 mol%, while the water content of $[P_{6\,6\,6\,14}][HCO_2]$ ranged from *ca*. 0 mol% to 50 mol%. The $[P_{4\,4\,4\,4}][HCO_2]:H_2O$ system is solid below 30 mol% at 25 °C, while $[P_{6\,6\,6\,14}][HCO_2]$ reaches water solubility limits at 50 mol%. Figure 6 displays the carbon dioxide solubility of each ionic liquid:water mixture studied, resulting in curves that increase with increasing water content until a maximum is reached, followed by a reduction in uptake in the case of $[P_{4\,4\,4\,4}][HCO_2]$. In each case, carbon dioxide solubility is at a maximum at a 1:1 molar ratio of ionic liquid:water, suggesting that the water is bound to the anion with a structure similar to that illustrated in Figure 7. Interestingly, and significantly, Kazarian and coworkers found that 1-alkyl-3-methylimidazolium ionic liquids with eight varied and different anions, X^- (including $[CF_3CO_2]^-$, but no other carboxylates), formed hydrated complex anions of the general formula $[X\cdots H\text{-}O\text{-}H\cdots X]^{2-}$ when exposed to water.[71]

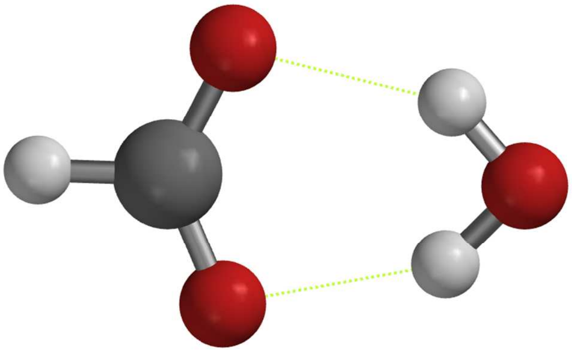


Figure 7. Optimised geometry (DFT; B3LYP; 6-31G*) of the stoicheiometric hydrogen-bonded anion, $[HCO_2(H_2O)]^-$

On exposure to low levels of water and carbon dioxide, tetrabutylphosphonium methanoate forms a crystalline solid that may be separated from the solution (*vide infra*). The crystallographic structure of this solid reveals (Figure 8) that it is tetrabutylphosphonium hydrogencarbonate, containing hydrogen-bonded dimeric dianions (the common form of this ion in the solid state).[72,73]

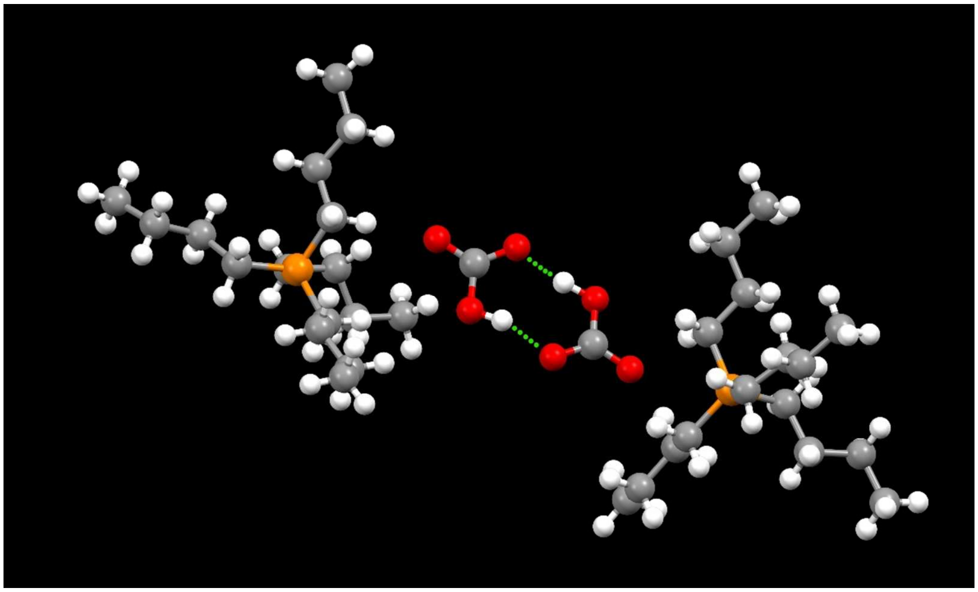


Figure 8. Partial crystal structure of solid tetrabutylphosphonium hydrogencarbonate, $[P_{4\,4\,4\,4}][HCO_3]$, formed on exposure of tetrabutylphosphonium methanoate, $[P_{4\,4\,4\,4}][HCO_2]$, to atmospheric water and carbon dioxide.

This structure, in conjunction with the carbon dioxide solubility maximum seen in the 1:1 $[P_{4\,4\,4\,4}][HCO_2]$:H_2O mixture (Figure 6) suggests the reactions illustrated in Scheme 3:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 + [P_{m\,m\,m\,n}][RCOO] \rightleftharpoons RCOOH + [P_{m\,m\,m\,n}][HCO_3]$$

Scheme 3. Proposed reactions between a tetraalkylphosphonium carboxylate ionic liquid, water, and carbon dioxide. “H_2CO_3” is a convenient shorthand, and makes no assumption about the correct speciation of this moiety, which may be simply hydrated CO_2; whichever extreme is nearest to the correct formulation, it does not alter the overall equilibria described.

To determine if this was indeed the reaction taking place, $^{13}C\{^1H\}$ nuclear magnetic resonance studies of water-formulated $[P_{4\,4\,4\,4}][CH_3CO_2]$, before and after exposure to carbon dioxide, were undertaken, with comparison to aqueous sodium hydrogencarbonate solutions, as depicted in Figure 9. Figure 9 focusses on the ^{13}C chemical shift range between 150 and 215 p.p.m., and so does not reveal the observed peaks due to dissolved CO_2 (δ_C = 125 p.p.m.), the phosphonium cation (δ_C = 10-35 p.p.m.),[74] or the CH_3 resonance of the ethanoate group; it does encompass the resonances of hydrogencarbonate and the carboxylate group of ethanoate. Figure 9(a) defines the ^{13}C chemical shift of the carboxylate function of ethanoate in water, at δ_C = 176.5 p.p.m., and Figure 9(d) shows the same mixture saturated with carbon dioxide, with a peak around 160 ppm. Figure 9(c) defines the ^{13}C chemical shift of the hydrogencarbonate anion in water, at δ_C = 161.5 p.p.m, very close to the new peak in Figure 9(d). The ^{13}C NMR spectrum, Figure 9(b), of an aqueous mixture of $[P_{4\,4\,4\,4}][CH_3CO_2]$ and sodium hydrogencarbonate reveals that the chemical shifts of both the carboxylate and the hydrogencarbonate anions move to lower field, suggesting that they are involved in a dynamic equilibrium such as that illustrated in Scheme 4.

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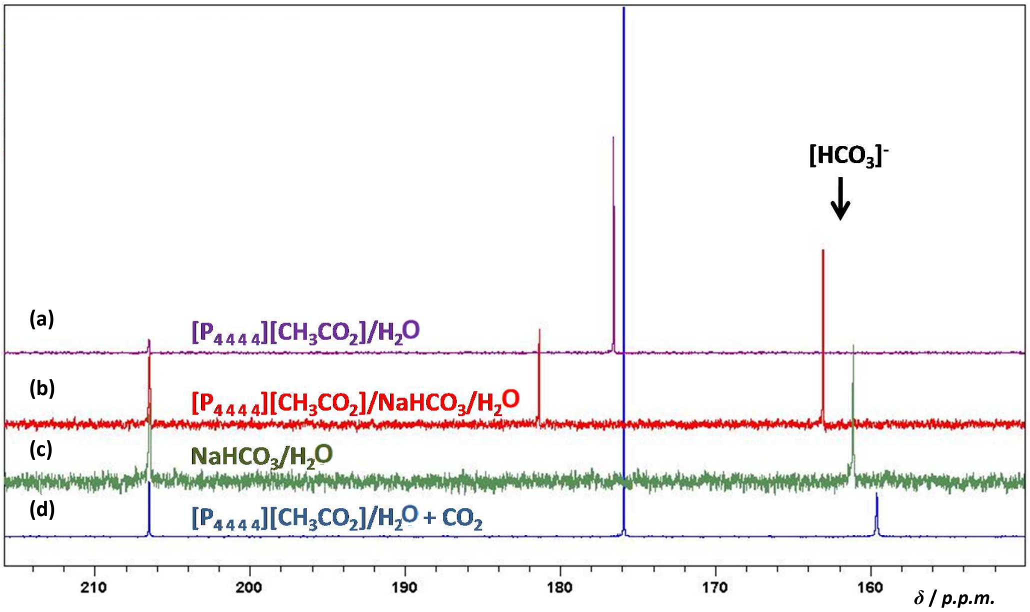
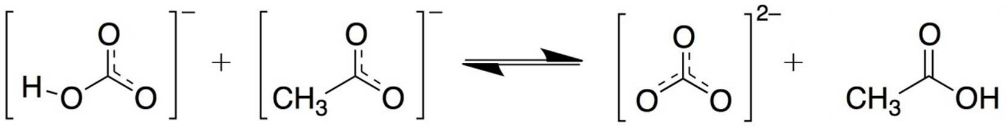


Figure 9. $^{13}C[^1H]$ NMR spectra (75 MHz) of a series of solutions: (a) $[P_{4\,4\,4\,4}][CH_3CO_2] + H_2O$ (purple trace), before CO_2 exposure, (b) $[P_{4\,4\,4\,4}][CH_3CO_2] + Na[HCO_3] + H_2O$ (red trace), (c) $Na[HCO_3] + H_2O$ (green trace), and (d) $[P_{4\,4\,4\,4}][CH_3CO_2] + H_2O$ (blue trace) after CO_2 absorption. Solutions were measured in NMR tubes with an inserted capillary tube containing propanone-d_6 as an external reference (δ_C = 206.7 p.p.m.).[75]



Scheme 4. Equilibrium between hydrogencarbonate and ethanoate resulting in the averaged signals in the $^{13}C\{^1H\}$ NMR spectra (Figure 9).

The $^{13}C\{^1H\}$ NMR results (Figure 9) suggest that Scheme 4 accurately represents the reaction with carbon dioxide taking place in this series of ionic liquids. This also explains the reduction of carbon dioxide uptake as the water content is increased past the 50 mol% ratio. When it is added in greater than equimolar amounts, water simply acts as a diluent, decreasing the uptake.

Crystal structure of $[P_{4\,4\,4\,4}][HCO_3]$

Single crystals of $[P_{4\,4\,4\,4}][HCO_3]$ were harvested from a bulk wet sample of $[P_{4\,4\,4\,4}][HCO_2]$ under atmospheric air. First, the solid methanoate salt became liquid by absorption of atmospheric moisture, and after several weeks, abundant crystals had formed. Crystals of the methanoate salt were not found: only the hydrogencarbonate salt crystallised. It should be noted that the sample from which single crystals of tetrabutylphosphonium hydrogencarbonate grew had not been used for CO_2 absorption experiments (*i.e.* they were never in contact with pure commercial CO_2), and hence, the origin of the hydrogencarbonate anions forming the crystalline material must have been atmospheric CO_2. Crystal growth was also attempted under a dinitrogen atmosphere from either pure or hydrated $[P_{4\,4\,4\,4}][HCO_2]$, but no signs of crystallisation were observed under such conditions. The fact that only tetrabutylphosphonium hydrogencarbonate crystals grew from wet tetrabutylphosphonium methanoate under atmospheric air confirms the high affinity for, and capacity of, phosphonium carboxylate salts for CO_2 in the presence of water.

Crystal data for $[P_{4\,4\,4\,4}][HCO_3]$ were collected using a Bruker kappaCCD diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at *ca.* 150 K in a dinitrogen stream. Lorentz and polarisation corrections were applied. The structure was solved by direct methods and the non-hydrogen atoms were refined with anisotropic thermal parameters, with the exceptions of the disordered carbon atoms in one of the butyl chains. Hydrogen-atom positions were added at idealised positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for methyl)), was used for subsequent refinements. The function minimised was $\Sigma[w(|F_0|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_0|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_0|^2 + 2|F_c|^2]/3$. The SHELXTL package [76] was used for structure solution and refinement.

Search procedures in the Cambridge Structural Database (CSD) were carried out using ConQuest 1.15.[77] The CSD (version 5.34, updated November 2012) was examined using the following criteria: 3D coordinates determined, with no errors and no powder structures.

Single crystals of $[P_{4\,4\,4\,4}][HCO_3]$ grew from a sample of $[P_{4\,4\,4\,4}][HCO_2]$ under atmospheric air after standing for approximately three weeks at ambient temperature (*ca.* 20 °C). Crystal data for $[P_{4\,4\,4\,4}][HCO_3]$: $C_{17}H_{37}O_3P$, $T = 150(2)$ K, monoclinic, $P2_1/c$, $a = 10.569(5)$, $b = 11.627(5)$, $c = 31.826(5)$ Å, $\beta = 90.812(5)$, $V = 3911(3)$ Å^3, $Z = 4$, $D_c = 1.089$ Mg m^{-3}, reflections collected/unique = 28489/9503 ($R_{int} = 0.0651$), $\mu = 0.149$ mm^{-1}, $S = 0.880$, $R_1 = 0.0567$ ($I > 2\sigma$), $wR_2 = 0.1331$ (all data).

The case of $[P_{4\,4\,4\,4}][HCO_3]$, as crystallised from $[P_{4\,4\,4\,4}][HCO_2]$, was unique among a range of tetraalkylphosphonium carboxylate salts studied. None of a series of salts, including $[P_{2\,2\,2\,6}][HCO_2]$, $[P_{2\,2\,2\,8}][HCO_2]$ or $[P_{2\,2\,2\,6}][CH_3CO_2]$, showed any sign of crystal growth under similar conditions to those described. However, analogous experiments performed using hydrated (*ca.* 20% water by weight) $[P_{4\,4\,4\,4}][CH_3CO_2]$ led to the growth of a crystalline material (large plates) in the bulk viscous liquid medium after several days under atmospheric air. A sample of that material was successfully analysed by single crystal X-ray diffraction (data not presented here). Surprisingly, the actual composition of the crystals was $[P_{4\,4\,4\,4}][H(CH_3CO_2)_2]$, where an ethanoate anion forms an adduct with an ethanoic acid molecule. This is in accord with Scheme 3, where the liberated ethanoic acid is reacting with the excess of ethanoate to form the stable protonated dimeric anion. This structure has been previously described, although no details on crystal growth were given.[78] It should be also noted that the crystal structure of tetramethylphosphonium hydrogencarbonate

([$P_{1\,1\,1\,1}$][HCO_3]) is known;[79] single crystals of [$P_{1\,1\,1\,1}$][HCO_3] were obtained on exposure to air but the origin of the hydrogencarbonate anion was not discussed in that report. In addition, and regarding the ammonium analogues, only a few hydrates (clathrates), *i.e.* [$N_{2\,2\,2\,2}$][HCO_3]·H_2O,[80] [$N_{2\,2\,2\,2}$][HCO_3]·$3H_2O$[81] and [$N_{4\,4\,4\,4}$][HCO_3]·$32H_2O$,[82] have been crystallographically studied. Moreover, the crystal structure of the cyclic 1,1-dimethylpyrrolidinium hydrogencarbonate ([C_1C_1pyrr][HCO_3]) has also been reported,[83] and very recently the anhydrous salt 1-ethyl-3,4,5-trimethylimidazolium hydrogencarbonate was determined.[84]

The asymmetric unit of [$P_{4\,4\,4\,4}$][HCO_3] consists of one hydrogencarbonate dimer and two tetrabutylphosphonium cations. In the refined structure, disorder is found for one of the butyl chains in one of the cations over two positions, with a 50:50 occupancy factor ratio. When comparing both disordered butyl chains, it is observed that one of them is in all-*trans* conformation, whereas the second one is in a distorted *gauche*-*trans* conformation as revealed by its torsion angles (90.1 and 176.1 ° for P-C_α-C_β-C_γ and C_α-C_β-C_γ-C_δ, respectively). On the other hand, the average P-C bond distance in the [$P_{4\,4\,4\,4}$][HCO_3] structure is 1.80 ± 0.01 Å, in good agreement with known quaternary phosphonium salts, 1.80 ± 0.02 Å. [NOTE: Searches on the CSD for any phosphonium cations where the phosphorus atoms is bonded to four carbon atoms; 4453 hits found.] Furthermore, the arrangement around the central phosphorus atom in [$P_{4\,4\,4\,4}$][HCO_3] is tetrahedral (average C-P-C angle = 109.6 ± 3.6 °), with a slight deviation due to the distorted geometry of the disordered butyl chains.

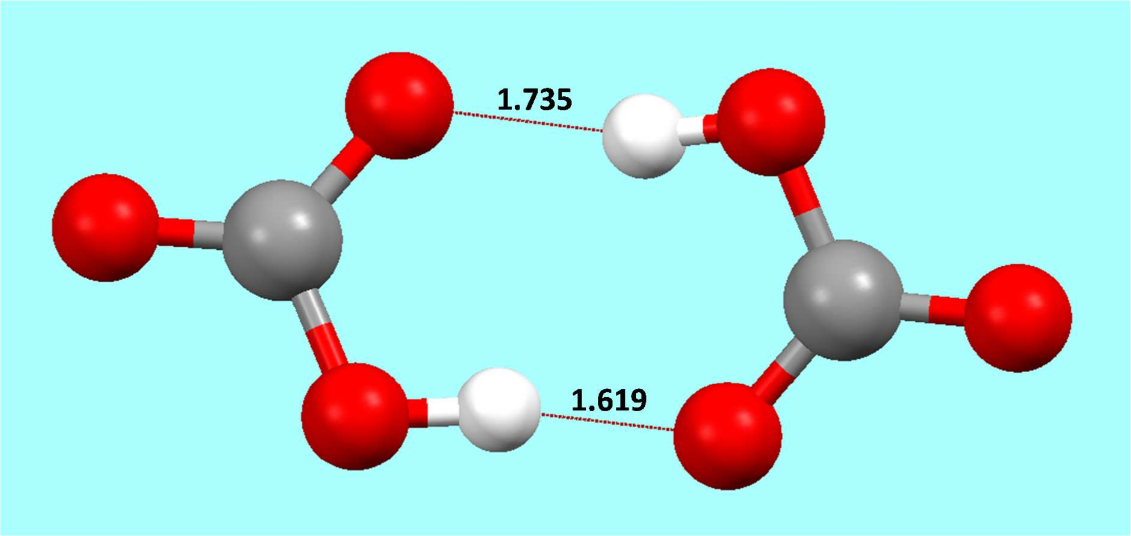


Figure 10. A perspective of the dimers formed by two hydrogencarbonate anions in the crystal structure of [$P_{4\,4\,4\,4}$][HCO_3]. The O-H···O hydrogen bonds are represented by dark red dashed lines, and the corresponding distances (Å) are shown in black. Grey = carbon, white = hydrogen; red = oxygen.

The hydrogencarbonate dimers in the crystal structure of [$P_{4\,4\,4\,4}$][HCO_3] are surrounded by five [$P_{4\,4\,4\,4}$]$^+$ cations. A number of short interionic contacts have been found between hydrogen atoms in the cations and anion oxygen atoms, being the mean C-H···O distance 2.49±0.17 Å. Such contacts, although considerably longer than those for the strong hydrogen bonds responsible for holding the [HCO_3]$^-$ dimers together (*vide supra*), are still shorter than the sum of the Van der Waals radii (2.70 Å).[85,86] Therefore, in addition to the electrostatic attraction between tetrabutylphosphonium cations and hydrogencarbonate anions, the sum of a number of weak cation-anion hydrogen bonds should also be significant in determining the solid state structure of [$P_{4\,4\,4\,4}$][HCO_3]. These data, and analogous C-H···O distances for the related (non-hydrated) [$P_{1\,1\,1\,1}$][HCO_3][79] and

$[C_1C_1pyrr][HCO_3]$,[83] are listed in Table 6. In all cases, a number of weak hydrogen bonds around the anion dimers was found.

Table 6. Average interionic distances in the crystal structure of $[P_{4\,4\,4\,4}][HCO_3]$ and in related fully alkylated phosphonium or ammonium (pyrrolidinium) hydrogencarbonates.

	$d(CH\cdots O)/Å^{a,b}$	$d(P\cdots O)/Å^{b,c}$	$d(N\cdots O)/Å^{b,c}$	minimum $d(E\cdots O)/Å^{b,d}$
Σ(VdW radii)[b]	2.72	3.32	3.07	
$[P_{4\,4\,4\,4}][HCO_3]$	2.49(17)	4.03(42)		3.418(2)
$[P_{1\,1\,1\,1}][HCO_3]$[e,f]	2.53(9)	3.94(42)		3.358(1)
$[C_1C_1pyrr][HCO_3]$[e,g]	2.55(9)		4.08(38)	3.537(1)

[a] Distances averaged for all contacts shorter than the sum of Van der Waals radii. [b] Van der Waals radii taken from ref.[85,86]. [c] Distances averaged for all contacts shorter than the sum of Van der Waals radii plus 1.2 Å (arbitrary limit, see text). [d] Closest approach of an oxygen atom to a phosphorus or nitrogen atom (E = P, N). [e] Data retrieved from the CSD, referred to by their six-letter code. [f] #UGUKAI, ref.[79]. [g] #LUQFUZ, ref.[83].

In the structure of $[P_{4\,4\,4\,4}][HCO_3]$, hydrogencarbonate anions form dimers whereby the two anions are bound together by two O-H···O hydrogen bonds, effectively forming a dianion, as seen in Fig. 10. The arrangement of the dimers is asymmetric, with the anion planes rotated relative to each other by *ca.* 14 °. The H···O distances are 1.619 and 1.735 Å, and the corresponding O-H···O angles are 170.3 and 158.2 °, respectively. These values confirm that the hydrogen bonds are remarkably strong (distances are around 1 Å shorter than the sum of Van der Waals radii, *i.e.* 2.70 Å),[85,86] as expected for a hydrogencarbonate dimer of this sort. The dimer motif is frequent in structures containing $[HCO_3]^-$; a search on the CSD resulted in a total of 145 crystal structures, among which 74 (51%) contained dimers similar to the ones occurring in the structure of $[P_{4\,4\,4\,4}][HCO_3]$. In the structures where no dimers are found, hydrogencarbonate anions are efficiently coordinated in all directions by solvent molecules, metal cations, or bulky organic ligands. Hydrogencarbonate anions in $[P_{1\,1\,1\,1}][HCO_3]$,[79] $[N_{2\,2\,2\,2}][HCO_3]\cdot H_2O$,[80] $[N_{2\,2\,2\,2}][HCO_3]\cdot 3H_2O$[81] and $[C_1C_1pyrr][HCO_3]$,[83] are also assembled as dimers.

Further analysis was focussed on the interionic E···O (E = P or N) distances (see Table 6). It was observed that the oxygen atoms not taking part in the formation of the hydrogencarbonate dimers are, in general, closer to the central phosphorus (or nitrogen) atoms, whereas several other contacts exist involving all oxygen atoms. Due to the ubiquity of such contacts, statistical analyses become ambiguous. For that reason, only the contacts for the first sphere of coordination were considered (arbitrary limit set below the sum of Van der Waals radii plus 1.2 Å). The resulting average E···O distances were marginally shorter for the smaller and less hindered tetramethylphosphonium cation than for the tetrabutyl analogue, although within a wide distribution (see Table 6). Minimum E···O distances are more informative about the degree of cation-anion interaction. The minimum P···O distance in $[P_{4\,4\,4\,4}][HCO_3]$ is *ca.* 3.42 Å, slightly longer than that found in $[P_{1\,1\,1\,1}][HCO_3]$ (3.36 Å), owing to the lower steric encumbrance of the cation in the latter. Both are slightly longer than the sum of Van der Waals radii. This, in combination with the tetrahedral arrangement around the central phosphorus, is indicative of very weak P-O interactions. Notably, the minimum N···O distance in $[C_1C_1pyrr][HCO_3]$ is longer (3.54 Å) than P···O for the phosphonium salts, and considerably longer than the sum of Van der Waals radii, indicating a clearly decreased anion-cation interaction in the ammonium (pyrrolidinium) salt. This is in agreement with our previous study on halide structures,[74] where it was shown that the smaller size of nitrogen is responsible for a more crowded environment around the central atom in ammonium cations as compared to phosphonium. Therefore, the more open structure around the phosphorus allows a deeper penetration of the anion through the protective "shrubbery" of the alkyl groups. This trend is confirmed here for hydrogencarbonates, thus demonstrating the validity of the reasoning for a wider range of anions.

Regeneration experiments

A comparative study of the recyclability towards CO_2 capture of some selected ionic liquid:water (for $[P_{4\,4\,4\,4}][HCO_2]$ or $[P_{2\,2\,2\,8}][CH_3CO_2]$) systems and the commercially used aqueous MEA absorber has been carried out. These systems were chosen for their high capacity to dissolve CO_2. As can be seen in Figure 11, the $[P_{4\,4\,4\,4}][HCO_2]$ system recovers essentially 100% of its CO_2 capacity at as low as 70 °C, over two consecutive recycles. The $[P_{2\,2\,2\,8}][CH_3CO_2]$ system recovers *ca.* 90% of its capacity by recycling at 70 °C. Finally, the industrially used chemical absorbent (MEA/H_2O) only recovers *ca.* 82% at temperatures as high as 120 °C, using the same experimental set-up. These results prove that the regeneration conditions for the tetraalkylphosphonium carboxylate ionic liquid systems for CO_2 absorption might be much less energetically demanding than those for aqueous amine systems. In addition, the $[P_{4\,4\,4\,n}]^+$ cations (and, indeed, their hexyl and octyl analogues) have been shown, by us, elsewhere[87-89] to be thermally and chemically stable under much harsher than those used here. These carboxylate anions, of course, are well recognised to be stable in aqueous conditions below 100 ºC. As a general trend, they may also indicate that methanoate systems might be easier to regenerate as compared to ethanoate ones, which would be consistent with the lower basicity of the former anion. These conditions need to be optimised in order to determine the practical recycling conditions for other compositions of ionic liquid absorbents. In addition, if water is to be removed in the same stripping unit, the corresponding temperatures should be further determined.

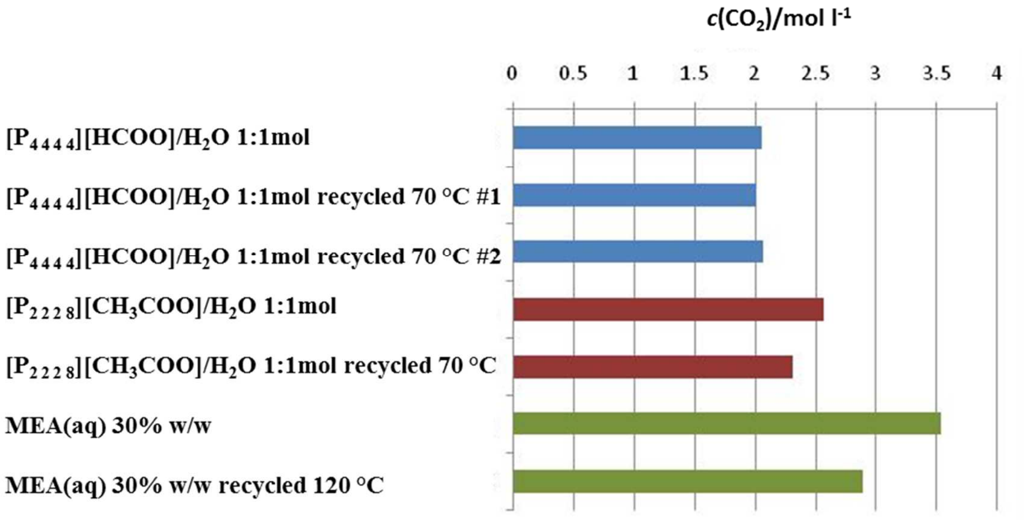


Figure 11. CO_2 solubility data on fresh and recycled liquid absorbents, both ionic liquid:water (1:1) and MEA:water solutions. All recycles were done by sparging a dry gas (N_2 or air) through the stirred liquids for 15 min. Water content was determined by Karl-Fischer titration after the stripping step, and corrected in accordance before subsequent CO_2 absorption measurements. Mole ratio of the recycled absorbents might have an associated error of ±0.3.

Selection of the Best System

On establishment of the reaction mechanism, several carboxylate ionic liquids were generated to improve this system. As the ionic liquids based on the tetrabutylphosphonium cation were either solid at room temperature when dry, or produced solids on exposure to carbon dioxide, it was decided to use the lower symmetry tributylmethylphosphonium cation for further studies. The methanoate, ethanoate, propanoate, 2-methylpropanoate, butanoate, hexanoate, octanoate, lactate, or glycolate anions, paired with either the tributylmethylphosphonium or tributylmethylammonium cation, formed the initial ionic liquids synthesised and formulated with 50 mol% water. Initial carbon dioxide uptake was determined at five bar CO_2 pressure and 25 °C, followed by a second study at 40 °C. The most common commercial chemical absorber (MEA in water) and physical absorber (Genosorb®) were trialled in the same manner, as both a test of the methodology and to generate a realistic baseline. Tables 7 and 8 present the results of these initial single point experiments. Under these conditions, the commercial chemical absorber shows the best performance (30 wt% MEA in water, 3.58 mol l^{-1}), followed closely by tributylmethylphosphonium ethanoate, propanoate, and 2-methylpropanoate. The pK_a values of the conjugate acids of the ethanoate, propanoate, and 2-methylpropanoate anions (4.76, 4.87, and 4.86) are quite close to each other, while significantly higher than the conjugate acid of the methanoate anion (3.75). Thus, it would be expected that these anions would show similar basicity to each other, while acting as stronger bases than the methanoate. High base strength is expected to enhance the reactions shown in Scheme 4, as can be observed in Table 7.

Table 7. CO_2 solubility for equimolar tributylmethylphosphonium carboxylate-water systems at 5 bar.

Ionic Liquid	CO_2 solubility at 25 °C		CO_2 solubility at 40 °C	
	/mol l^{-1}	/mol kg^{-1}	/mol l^{-1}	/mol kg^{-1}
$[P_{4\,4\,4\,1}][HCO_2]$	2.11	2.18	1.56	1.63
$[P_{4\,4\,4\,1}][CH_3CO_2]$	2.78	2.83	2.29	2.42
$[P_{4\,4\,4\,1}][C_2H_5CO_2]$	2.60	2.64	2.53	2.66
$[P_{4\,4\,4\,1}][C_3H_7CO_2]$	2.28	2.32	2.05	2.10
$[P_{4\,4\,4\,1}][C_5H_{11}CO_2]$	2.24	2.25	1.91	2.03
$[P_{4\,4\,4\,1}][C_7H_{15}CO_2]$	2.17	2.18	1.87	2.04
$[P_{4\,4\,4\,1}][Me_2CHCO_2]$	2.55	2.71	2.30	2.46
$[P_{4\,4\,4\,1}][MeCH(OH)CO_2]$	1.12	1.14	0.68	0.70
$[P_{4\,4\,4\,1}][HOCH_2CO_2]$	1.22	1.22	0.84	0.85

Table 8. CO_2 solubility for equimolar tributylmethylammonium carboxylate-water systems at 5 bar.

Ionic Liquid	CO_2 solubility at 25 °C		CO_2 solubility at 40 °C	
	/mol l^{-1}	/mol kg^{-1}	/mol l^{-1}	/mol kg^{-1}
$[N_{4\,4\,4\,1}][HCO_2]$	2.26	2.37	1.78	1.88
$[N_{4\,4\,4\,1}][CH_3CO_2]$	Solid		Solid	
$[N_{4\,4\,4\,1}][C_2H_5CO_2]$	2.79	2.96	2.56	2.75
$[N_{4\,4\,4\,1}][C_3H_7CO_2]$	2.60	2.74	2.34	2.50
$[N_{4\,4\,4\,1}][C_5H_{11}CO_2]$	2.51	2.63	2.20	2.40
$[N_{4\,4\,4\,1}][C_7H_{15}CO_2]$	2.31	2.41	2.02	2.23
$[N_{4\,4\,4\,1}][Me_2CHCO_2]$	1.96	2.02	1.83	1.90
$[N_{4\,4\,4\,1}][MeCH(OH)CO_2]$	1.25	1.28	0.89	0.91
$[N_{4\,4\,4\,1}][HOCH_2CO_2]$	0.84	0.83	0.66	0.67

Table 9. Solubility of CO_2 in tetrabutylphosphonium ionic liquids with amino acid based anions with varying amounts of added water at 5 bar.

Ionic Liquid		CO_2 solubility			
	mol H_2O / mol IL	/mol l^{-1}	/mol kg^{-1}	mol CO_2/mol IL	mol CO_2/mol H_2O
$[P_{4\,4\,4\,4}]$[Gly]	0.06	2.93	3.04	1.02	17
	0.91	3.76	3.88	1.36	1.49
	1.83	3.77	3.87	1.42	0.77
	2.94	3.33	3.40	1.31	0.45
$[P_{4\,4\,4\,4}]$[Ala]	0.03	3.00	3.16	1.10	36.7
	0.73	1.97	2.06	0.74	1.01
	1.44	1.44	1.50	0.56	0.39
	2.06	1.35	1.40	0.54	0.26
$[P_{4\,4\,4\,4}]$[Val]	0.03	2.70	2.85	1.07	36
	0.97	3.23	3.41	1.34	1.38
	2.19	3.28	3.43	1.42	0.65
$[P_{4\,4\,4\,4}]$[Ile]	0.02	2.60	2.75	1.07	36
	1.04	3.07	3.24	1.32	1.27
	1.81	3.08	3.23	1.36	0.75
$[P_{4\,4\,4\,4}]$[Pro]	0.02	2.61	2.70	1.01	50.5
	0.75	3.20	3.29	1.27	1.69
	1.74	3.12	3.19	1.29	0.74
	2.41	2.78	2.83	1.18	0.49
$[P_{4\,4\,4\,4}]$[Bic]	0.04	1.05	1.04	0.44	11
	0.83	2.63	2.61	1.14	1.37
	1.34	3.27	3.23	1.44	1.07
	1.50	3.38	3.33	1.49	0.99
	1.80	3.19	3.15	1.43	0.79
	2.34	2.72	2.68	1.24	0.53
$[P_{4\,4\,4\,4}]$[Dmg]	0.01	0.65	0.67	0.24	24
	1.22	2.81	2.99	1.15	0.94
	1.55	3.31	3.51	1.37	0.88
	2.34	2.72	2.68	1.24	0.53

In the case of the tributylmethylammonium cation, the ethanoate immediately forms a solid. The results show that the propanoate, butanoate, and 2-methylpropanoate salts exhibit the highest carbon dioxide solubility, whereas the methanoate and octanoate show significantly lower uptake. The ammonium based ionic liquids, shown in Table 8, had a tendency to form solids on carbon dioxide exposure, and were generated from a less thermally stable cation than the phosphonium series; they were therefore not considered further.

The ionic liquids derived from amino acids (see Table 5) were also mixed with varying levels of water, in a bid to establish carbon dioxide uptake behaviour as a function of water content (Table 9). Here, it can be seen that addition of water results in a similar improvement in carbon dioxide uptake, with up to 1.5 moles of carbon dioxide absorbed per mole of ionic liquid, although the alaninate ionic liquid showed a reduction in CO_2 uptake. Addition of water did not prevent solidification, however, resulting in these systems being abandoned. Brennecke and coworkers have also reported similar results with these systems.[48]

The ionic liquids tributylmethylphosphonium ethanoate and tributylmethylphosphonium 2-methylpropanoate show some solid formation on exposure to carbon dioxide, leaving tributylmethylphosphonium propanoate as the preferred choice for further studies. As this research is industrially oriented, it was decided to further study both the pressure and temperature dependence of carbon dioxide solubility in the formulated ionic liquid. In this particular case, the water content was increased to 60 mol%, partly to ensure enough water was available for reaction, and partly to allow for water uptake from the inlet gas stream. Inlet temperatures of both raw natural gas and flue gas are expected to be 40 °C and above, while regeneration temperatures may be as high as 150 °C. In natural gas processing, inlet pressures may be in the range of 50 to 70 bar, while carbon dioxide content may be 2 vol% or higher (typical sales gas contains less than 2 vol% CO_2). Thus, carbon dioxide partial pressures range from *ca.* 1 bar to 20 bar or higher (depending on the quality of the natural gas field). To establish a reasonable operational range of the formulated ionic liquid, it was decided to test carbon dioxide pressures between about 0.5 bar and 20 bar and temperatures between 40 °C and 150 °C. The results of this study are included in Figure 12, where some striking features may be seen. At 40 °C, the carbon dioxide uptake is consistent with chemical absorbers up to pressures between 8 and 10 bar, where uptake is equivalent to *ca*. 1 mol CO_2 per mol IL (discounting the moles of water). At this point, the mixture continues to behave in the manner of a good physical absorber, showing an uptake that is equivalent to 2 mol CO_2 per mol IL at 20 bar partial pressure carbon dioxide. As the temperature is increased, the chemical absorption becomes less prominent until the formulated ionic liquid behaves principally as a weak physical absorber at 150 °C. This indicates that regeneration by temperature–pressure swing is feasible for these systems.[56,90]

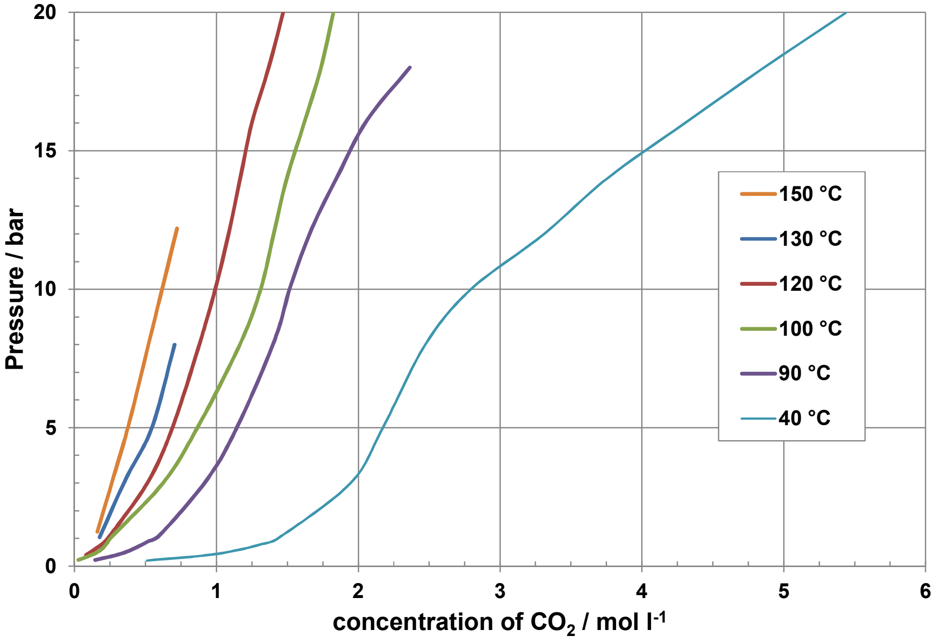


Figure 12. Carbon dioxide uptake *vs*. pressure for tributylmethylphosphonium propanoate (0.6 mole fraction water) at six temperatures.

Conclusions

We have described a series of ionic liquids based on carboxylate anions formulated with water with a high chemical absorption (up to a 1:1 mole ratio of carbon dioxide:IL), followed by high physical absorption. The basicity of the ionic liquid anions activates the reaction between water and carbon dioxide to form the hydrogencarbonate anion and the conjugate acid of the anion (Scheme 4), which appears to exist as a complex within the ionic liquid solution. The resulting mixture of ionic liquid cation, water, hydrogencarbonate anion, and carboxylic acid behaves as a strong physical absorber for carbon dioxide, resulting in CO_2 uptake that is comparable to commercial chemical absorbers at relatively low carbon dioxide partial pressure, while exceeding them at higher pressures. Regeneration methodology is indicated by the dependence of carbon dioxide uptake on temperature and pressure. These studies show the importance of careful control of water content for these systems.

A detailed engineering analysis for this project was performed by Worley-Parsons, and the main points are summarised in Table 10. It was found that, relative to a traditional absorber tower utilising activated methyl diethanolamine (aMDEA is MDEA (see Figure 1), containing up to 10 wt% of corrosive and volatile piperazine),[91,92] tributylmethylphosphonium propanoate (non-corrosive and involatile) with 60 mol% water required 5% less CAPEX and 22% less OPEX. Although costs vary unpredictably with time, this system is undoubtedly the best known based on ionic liquids, and is competitive with the best of the amine systems. There is much flexibility for further optimisation of this system (improvements in viscosity will lead to even better economics), which will be particularly attractive for implementation in areas of the world where the use of amines is sensitive or impractical.

Table 10. A summary of the main conclusions of the engineering analysis of the tributylmethylphosphonium propanoate with 60 mol% water system, compared with activated methyl diethanolamine (aMDEA)

	Propanoate	**aMDEA**
Low vapour pressure	Much better	Worst
High selectivity for acid gases	Equivalent	Equivalent
Low viscosity	Worst	Best
Heat stability at process temp	Equivalent	Equivalent
Non – corrosive	A million times better	Worse
Relative heat input to process	0.6	1
Relative power consumption	1.4	1
Relative CO_2 solubility in solvent on a mass basis	0.6	1

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Notes and references

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