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CO_2 Capture using Phenoxide Salts; Alternatives to Amine-based Capture Agents, and Comparative Speciation Studies as Components in Solvent Blends.

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ABSTRACT

Amine blends represent the leading absorbents for post-combustion CO_2 capture, yet they still have considerable issues associated with their use, such as high energy requirements, corrosivity, cost and toxicity. At least one amine component is usually considered to operate as base, and on this hypothesis phenol (pKa 9.95), as its conjugate base, can potentially act as an amine-free alternative in such blends. We report the first detailed study using phenoxide based capture reagents, including different blends of ethanolamine and potassium phenoxide. CO_2 absorption rate and speciation of these solutions was compared with that of comparable amine blends, and whilst potassium phenolate alone showed poor kinetics, its use in combination with monoethanolamine (MEA) showed interesting and potentially beneficial properties. This work is the first to use phenoxides as a base in CO_2 capture solvents and demonstrates the viability of this diverse family of compounds for industrially relevant CO_2 capture solvents.

Keywords: CO_2 capture; solvents; phenoxide; bicarbonate; amines; speciation.

Highlights.

- Aqueous potassium phenoxide captures CO_2 through bicarbonate formation.
- Rate of CO_2 capture is substantially enhanced using potassium phenoxide-MEA blends.
- Speciation in phenoxide-MEA and amine blends is compared.
- Potassium phenoxide-MEA blends give superior performance compared to the amine blends investigated.

1. Introduction

Amines have been extensively used for CO_2 removal from gas streams since the 1930s, mainly for use in natural gas sweetening. In more recent times, amine technology has been adapted to provide a leading technology for post-combustion CO_2 capture in power generation for carbon capture and storage (CCS). However it can suffer from issues such as amine degradation, high energy requirements and potential environmental hazards, which all become particularly acute once adopted on the scale required for CCS.[1] Improvements are therefore required in order to reduce cost of both capital and operating expenditure, and an important aspect of this is understanding the fundamental chemical processes operating during CO_2 capture, such that significant issues can be understood and where possible, addressed, and new opportunities identified.

Amines are most often used for CO_2 capture due to their low cost, high availability, and relatively high rate at which many primary and secondary amines react with CO_2. Ammonium carbamate salts are produced preferentially (Figure 1)[2,3] however in aqueous solution, ammonium bicarbonate salts can also be formed via base-promoted hydration of CO_2, however this reaction proceeds at a significantly slower rate than carbamate formation. The CO_2 capture solvent historically used as a baseline reference is 5 M aqueous monoethanolamine (MEA (1), see Figures 1 and 2).[4] In more recent times, other amines have also been developed,[5,6] which show significantly improved performance characteristics over aqueous MEA, including piperazine (PZ (2)), N-methyldiethanolamine (MDEA (3)) and 2-amino-2-methyl propan-1-ol (AMP (4)), particularly when used in amine blend formulations (Figure 2).[7,8]

CCS needs to be deployed on an enormous scale to have any significant impact on climate change. This presents major challenges to any chemical solvent based processes; capture must be highly efficient and reversible in order to minimise the amount of capture agent required, energy of solvent regeneration must be minimised, and solvent lifetime must be optimised to reduce waste and cost.

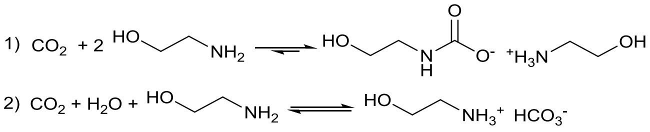

Figure 1. Reactions of CO_2 with aqueous monoethanolamine (MEA), to form either 1) ammonium carbamate or 2) ammonium bicarbonate salts.

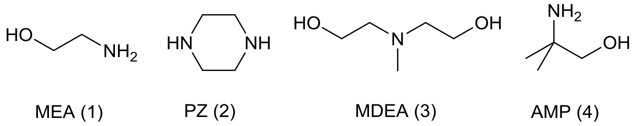

Figure 2. Structures of amines typically used in CCS, with their common abbreviations: (1) monoethanolamine (MEA); (2) piperazine (PZ); (3) N-methyldiethanolamine (MDEA); (4) 2-amino-2-methyl-propan-1-ol (AMP).

Solvents are typically exposed to CO_2 at low temperatures, leading to capture of the CO_2 by chemical reaction (Figure 1). This is then reversed by heating the loaded solvent to much higher temperatures, where the CO_2 is released and the lean solvent regenerated. However, regeneration must overcome the inherent thermodynamic stability of the CO_2-derived salts, which for carbamate salts are relatively high.[9] Hence regeneration is energy-intensive and involves high temperatures which leads to significant energy consumption, alongside oxidative and thermal degradation of the capture agent over time.

Ammonium carbamates are less-than-ideal CO_2 absorption products due to the stoichiometry of their formation, requiring two moles of amine for every mole of CO_2 captured. Since it is desirable to maximise the concentration of CO_2 absorbed in order to minimise the amount of solvent that needs to be regenerated, much better energetic performance can in principle be achieved by capturing CO_2 in an equimolar fashion, such as the formation of an ammonium bicarbonate salt (Figure 1). Bicarbonate is also thermodynamically less stable than typical carbamates so undergoes loss of CO_2 under milder conditions. Capture of CO_2 as bicarbonate may be achieved using an amine that does not easily undergo carbamate formation, such as a tertiary amine (e.g. MDEA (3)) or one which is particularly sterically hindered at the reacting nitrogen centre (e.g. AMP (4)).[10–12] Such amines react with CO_2 and water to form bicarbonate, however the rates of reaction are typically much slower than that of carbamate formation with primary amines.[13,14]

Much current research focuses upon blended solutions of one carbamate-forming amine and one non-carbamate forming amine, reporting improved performance by combining the beneficial properties of both: high rates of reaction due to carbamate formation; and easier regeneration due to the presence of bicarbonate.[15–17] Nevertheless, the practicality of amines as CO_2 capture agents remains a subject of some concern. Not only can they be corrosive to steel, necessitating the use of corrosion-resistant materials with commensurately high capital costs, but many have significant toxicity issues associated with them.[18,19–22] and it would be desirable to find non-amine alternatives if they offer improved (or even similar) capture performance.

Since non-carbamate-forming amines function solely as a Brønsted-Lowry base and no other particular reactivity appears to be necessary, in principle any other bases within a similar pK_a range (*ca.* 9-11) could give rise to bicarbonate formation in CO_2 capture solvents. Among the few other classes of compounds with basicities in this range, by far the most common are the phenoxides derived from phenol, which has a pK_a of 9.95.[23] Indeed, phenoxides were considered alongside amines as CO_2 capture agents for gas sweetening applications from relatively early on, but were discounted due to the superior performance of amines.[24] Hence, they have received relatively little attention since then, but being both inexpensive and now available in the large quantities that CCS would require, notwithstanding potential hazards arguably comparable with some amine components under serious consideration, their use as capture agents is worth revisiting to understand the potential of such amine free components in more detail.

Phenoxides have previously received attention primarily in the context of CO_2 utilisation, as their potassium or sodium salts can be converted to aryl carboxylic acids in the Kolbe-Schmitt process (Figure 3). This classic reaction is a source of numerous important compounds in the chemical industry, most notably salicylic acid, although the overall scale is small when considered in terms of CO_2 utilisation impact.[25] Barbarossa *et al.*[26] recently reported reversible CO_2 capture into alkaline resorcinol solutions, employing a variant of this reaction to produce β-resorcylic acid as the capture product. Other past work on phenoxides in carbon capture has considered their potential as anions within an ionic liquid.[27,28] Due to the usually low water content of ionic liquids, bicarbonate is not expected and reaction with CO_2 reportedly produces phenyl carbonate anions.

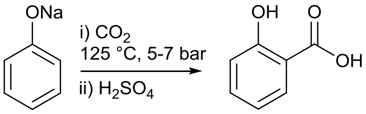

Figure 3. Kolbe-Schmitt carboxylation of sodium phenoxide to produce salicylic acid.

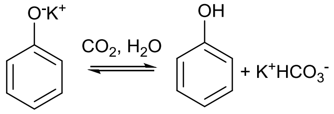

Figure 4. Hydration of CO_2 by potassium phenoxide.

Our work seeks to employ phenoxide solely as a Brønsted-Lowry base, and side-reactions such as these would be undesirable unless they can be easily reversed. Hence we explore the effectiveness of phenoxide as a CO_2 capture agent in aqueous solution, both alone and in conjunction with carbamate-forming amines, in compositions similar in principle to contemporary amine blends. The study places particular emphasis upon the speciation within CO_2-loaded solvents, the importance of which has been more greatly appreciated in recent years. Methods employing NMR have proven particularly effective due to the ease of obtaining quantitative information with ^{1}H NMR,[29–31] although more time-consuming quantitative ^{13}C NMR has often been considered necessary in order to measure the concentrations of carbonates that lack non-exchanging protons.[6,32–35] In this work a combination of ^{1}H NMR and vapour-liquid equilibrium (VLE) cell measurements are employed in order to develop a greater understanding of the chemistry underlying the CO_2 absorption behaviour of phenoxide-based capture solvents.

2. Materials and methods.

2.1. General Information

Phenol (Sigma Aldrich) was supplied as a liquid saturated with 9.9 wt% water, and used as received. The alkanolamines (monoethanolamine (MEA), 2-methyl-2-amino-1-propanol (AMP) and N-methyldiethanolamine (MDEA)) were supplied by Sigma Aldrich, distilled over 3Å molecular sieves and stored over 3Å molecular sieves. Potassium hydroxide (Sigma Aldrich), piperazine (Sigma Aldrich), sodium 4,4-dimethyl-4-silapentane-1-sulfonate (Sigma Aldrich), acetic acid (Sigma Aldrich) and CO_2 (BOC) were used as received. pH measurements were carried out using a Jenway 3540 meter calibrated with standard buffer solutions at pH 4, 7 and 10.

^1H and $^{13}C\{^1H\}$ NMR spectra were measured using a Bruker 300MHz spectrometer, and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) used as an internal reference for all reported chemical shift values.

Further experimental data is provided in the supplementary material, specifically ^1H NMR data and tables of speciation for all capture agents compositions discussed.

2.2. Preparation of capture solvents

The following amine solutions were required: 5 M MEA; 1 M MEA/3 M MDEA; 1 M MEA/3 M AMP; 1 M PZ/3 M AMP. For each of these compositions, a 250 mL stock solution was prepared from the requisite amount of each amine, to which was added DSS (0.27g, 1.25 mmol), the mixture dissolved in distilled water (18 MΩ) and diluted up to a volume of 250 mL.

The following phenoxide solutions were required: 1 M KOPh; 1 M MEA/1 M KOPh; 1 M MEA/2 M KOPh; 2 M MEA/1 M KOPh; 1 M MEA/3 M KOPh; 2 M MEA/2 M KOPh. For each of these compositions, a 250 mL stock solution was prepared. Potassium hydroxide was dissolved in water (30 mL) and neutralised by an equimolar amount of phenol (9.9 wt% water) at 0 °C. This mixture was warmed up to room temperature, DSS (0.27g, 1.25 mmol) and MEA added, and the whole was diluted up to 250 mL with distilled water.

2.3. Gasometric measurement of CO_2 loading using the carbonate bomb method.

A known volume of CO_2-loaded solution (typically 5 mL) was injected into the cell (Figure 5, volume 400 mL), followed by a known excess of acetic acid (typically 5 mL) in order to regenerate CO_2 from acid-sensitive CO_2 salts, producing a pressure increase in the sealed cell. Pressure (0-5 bar Omega transducer) and temperature within the cell were continuously monitored. From this pressure change the amount of CO_2 released, and thus the concentration of CO_2 in solution was accurately determined on the basis of the ideal gas law.

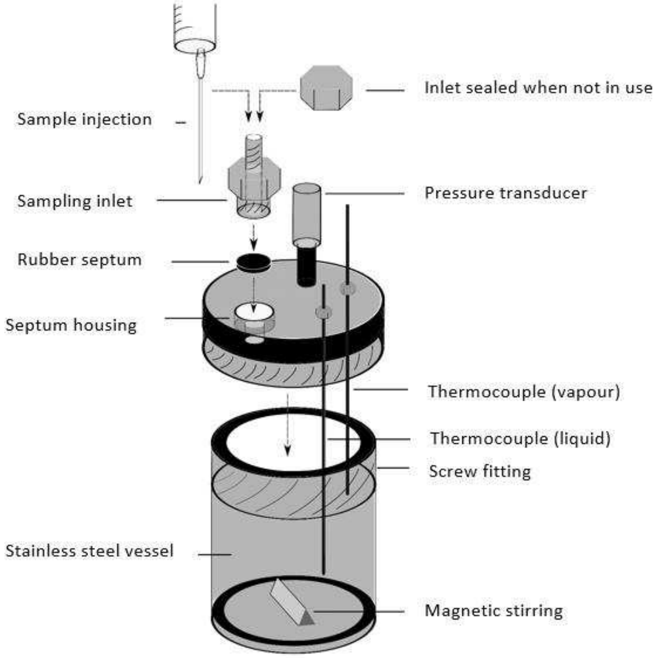

Figure 5. Diagram (not to scale) of cell used in carbonate bomb method for determination of the concentration of absorbed CO_2 in various capture solvents.

2.4. Procedure for loading solvent samples with CO_2.

To a graduated cylinder (50 mL) was added a sample of the capture solvent (30 mL) and the whole maintained at 25 °C with constant magnetic stirring. A steady flow of CO_2 (0.3 L min^{-1} was introduced at the base of the cylinder via a 19 gauge needle for a specified time (for each composition studied, samples loaded over 1, 5, 10, 15, 30, 60 and 90 mins were prepared). The phase behaviour of the resulting loaded solution was observed. In the case of homogeneous solutions, one sample (0.5 mL) was removed, slightly diluted with D_2O (75 µL) and the ^{1}H NMR spectrum recorded. An additional sample (5 mL) was withdrawn for total CO_2 determination.

If a precipitate was formed, the supernatant was carefully decanted into a second cylinder, and the precipitate dried over H_2SO_4 for 72 hours. The CO_2 content of this precipitate was measured using the carbonate bomb method. The supernatant was then treated as described below.

In the case of heterogeneous solutions, a sample (5 mL) of the combined phases was withdrawn with rapid stirring. A small portion (25 µL) was dissolved in D_2O (0.5 mL) and the ^{1}H NMR spectrum recorded. The total CO_2 concentration was determined using the carbonate bomb method. From the remainder of the CO_2-loaded mixture, the stir bar was removed and the phases allowed to separate until two completely distinct layers were present. Samples were carefully withdrawn from each phase by syringe, and the total CO_2 concentration of each measured using the carbonate bomb. From the upper (organic) phase, a small portion (25 µL) was dissolved in D_2O (0.5 mL) and the ^{1}H NMR spectrum recorded. From the lower (aqueous) phase a portion (0.5 mL) was slightly diluted with D_2O (75 µL) and the ^{1}H NMR spectrum recorded.

2.5. Speciation of homogeneous solutions

The concentration of carbamate in each sample was determined as a fraction of the total concentration of the parent amine, based on the integral values of the relevant peaks in the ^{1}H NMR spectrum. The concentration of bicarbonate was then deduced as the difference between the total absorbed CO_2 concentration as measured by the carbonate bomb method, and the concentration of carbamate species.

2.6. Speciation of heterogeneous solutions

In situations where heterogeneous biphasic solutions were observed, the phases were separated and quantified individually, and a sample of mixed phases (before allowing to separate) was also analysed. The composition of the aqueous phase was determined exactly as described above for homogeneous solutions. ^{1}H NMR of the organic phase gave the molar ratio of phenolic to amine derivatives in that phase based on integration of the spectra. Comparison to the same ratio in the aqueous phase allowed calculation of the amount of each phase as a mole fraction of total capture agent, since the (known) molar ratio of phenoxide to amine in the total solution is an average of the same ratio in each phase (known), weighted by the amount of each phase. Given the amount of each phase, the mole fraction of each component species in the aqueous phase could be converted into a total concentration in the overall solution by simple multiplication.

Further details of specific compositions are provided in the supplementary material.

3. Results and discussion

3.1. Potassium phenoxide as a CO_2 capture agent.

As an initial experiment, a 1 M aqueous solution of potassium phenoxide was prepared *in situ* from phenol and potassium hydroxide. The potassium salt was chosen due to the particularly favourable aqueous solubility of potassium bicarbonate, in order to avoid excessive precipitation. A controlled stream of pure CO_2 was bubbled through 30 ml samples of this solution for a set time span, with separate samples being exposed to CO_2 for 1, 5, 10, 15, 30, 60 and 90 minutes. This provided samples with a range of CO_2 loadings. ^{13}C NMR spectra of the resulting solutions showed a peak corresponding to bicarbonate/carbonate (a single peak representing both species is observed due to rapid exchange in solution) and no other additional compounds, confirming the absence of any measurable Kolbe-Schmitt-type carboxylation, as would be expected due to the relatively mild conditions of this current study.[26]

The amount of CO_2 absorbed into the solution was measured using a sealed vapour-liquid equilibrium cell, following a gasometric method similar to those published in prior literature.[36,37] Quenching of a known volume of CO_2-loaded solution using excess acetic acid led to a pressure increase in the VLE cell due to released CO_2, and the amount of CO_2 produced calculated based on the ideal gas law.

Application of this method to 1 M aqueous KOPh showed that CO_2 absorption is stoichiometric, approaching a maximum of 1 mol L^{-1} of absorbed CO_2, behaviour consistent with the hydration of CO_2 to bicarbonate (Figures 6 and 7).

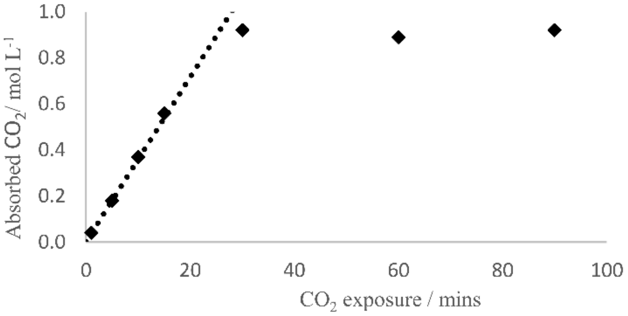

Figure 6. CO_2 absorption into 1 M aqueous KOPh, with linear trendline showing the initial rate of absorption. Concentration of absorbed CO_2 measured via the carbonate bomb method.

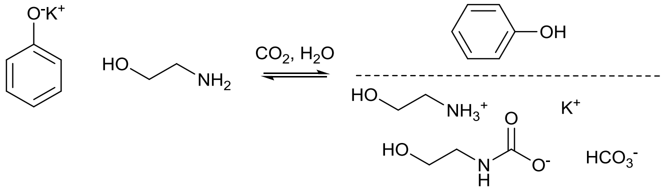

Figure 7. CO_2 absorption products in aqueous blends of KOPh and ethanolamine, and approximate distribution between two phases during capture.

It is well known that the rate of bicarbonate formation mediated by amines is usually slow compared to that for carbamate formation. Reaction rates are very important for CCS applications as a low absorption rate leads to excessive size requirements for absorber columns. Approximate rate data has been obtained in order to assess the impact of different components on the rate of reaction, as well as capture capacity and speciation. The initial rate of absorption was estimated from a linear extrapolation of the initial data points in a plot of absorbed CO_2 against contact time (Figure 6). Pure CO_2 was used for the loading experiments in an effort to avoid mass transfer limitations on the absorption rate.

The observed rate of absorption for 1 M KOPh with 100% CO_2 was 0.036 mol CO_2 L^{-1} min^{-1}, which was approximately an order of magnitude slower than MEA alone (0.32 mol CO_2 L^{-1} min^{-1} for 5 M MEA), which is also confirmed by prior studies of amine solutions.[38] Although of interest, this was deemed too slow to have practical application as a single component capture solvent, but could have the potential to replace bicarbonate forming amines such as MDEA in an amine blend, when used alongside a faster reacting primary amine such as MEA. Hence, we began to investigate blends of KOPh with MEA, with the aim of understanding the effects of phenoxide upon capture performance, particularly reaction rate, speciation and loading.

3.2. Investigation of MEA-potassium phenoxide blends.

Speciation of MEA-potassium phenoxide blends is complex due to the variety of species that can be formed. Measurement of the concentration of the MEA-derived carbamate in solution is pivotal to understanding the behaviour of the capture solvent. This was measured using ^1H NMR by integration of the carbamate peak relative to the total (known) concentration of amine, a method also used in previously published studies.[35,39,40] The concentration of bicarbonate could then be calculated as the difference between the total concentration of absorbed CO_2 detected using the gasometric method, and the concentration of carbamate measured by ^1H NMR. This assumes that bicarbonate is the sole other CO_2-derived species in solution, which is not strictly true as carbonate (CO_3^{2-}), carbonic acid (H_2CO_3) and dissolved CO_2 would also be present. However prior speciation studies have shown that they are present only in very small proportions (0.1 mol% or less) under the pH and solvent conditions common to CO_2 capture solvents, and therefore are insignificant to the capture performance of the solution as a whole.[35]

The accuracy of this approach was verified by assessing CO_2 absorption into 5 M MEA, as this is a very widely-studied capture solvent. Numerous speciation studies have been reported, and our observations showed very good agreement with these.[29,35,41] CO_2 was captured almost exclusively as the carbamate below *ca.* 50% CO_2 loading, and then bicarbonate formation becomes the dominant process for additional CO_2 capture (see Figure 8). This is consistent with the understanding that a primary driving force for bicarbonate formation is the advantageous stoichiometry of this process.

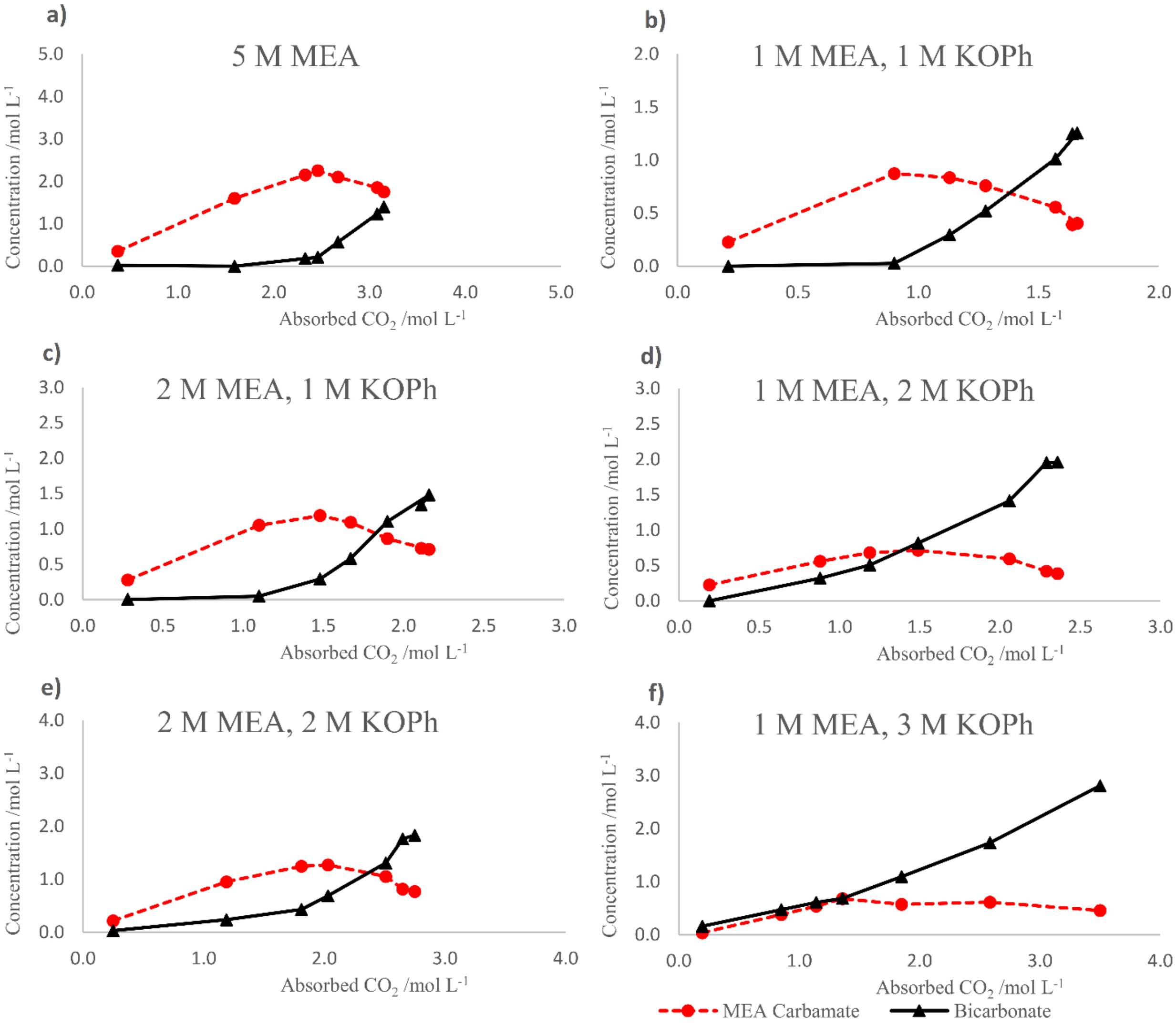

Figure 8. Species formed by absorption of CO_2 into aqueous solutions containing: a) 5 mol L^{-1} MEA; b) 1 mol L^{-1} MEA and 1 mol L^{-1} KOPh; c) 2 mol L^{-1} MEA and 1 mol L^{-1} KOPh; d) 1 mol L^{-1} MEA and 2 mol L^{-1} KOPh; e) 2 mol L^{-1} MEA and 2 mol L^{-1} KOPh; f) 1 mol L^{-1} MEA and 3 mol L^{-1} KOPh. All

solution were studied at 25°C and contained 1-5 mmol L^{-1} 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal ^{1}H NMR standard.

In order to determine the effect of KOPh upon CO_2 capture by aqueous MEA, a variety of possible combinations of the two capture agents was screened (Table 1). Owing to the formation of phenol during CO_2 loading, which has low (*ca.* 1 mol L^{-1}) aqueous solubility, a two-phase system (phenol top layer, aqueous lower layer) was formed as a consequence of CO_2 absorption for all compositions but the least concentrated (entry 3). The volume balance of the two phases was approximately proportional to the concentration of KOPh in the starting solution, with more KOPh producing a correspondingly larger organic phase.

Table 1. Summary of the rate and capacity for CO_2 absorption into aqueous solutions containing varying concentrations of MEA and KOPh.

	MEA (mol L^{-1})	KOPh (mol L^{-1})	Abs. %[a]	Initial rate[b]	Absorbed CO_2 (mol L^{-1})[c]
1	5	0	63	0.32	3.15
2	0	1	92	0.036	0.92
3	1	1	82	0.18	1.66
4	1	2	79	0.18	2.36
5	1	3	88	0.17	3.50
6	2	1	70	0.22	2.16
7	2	2	66	0.24	2.65

[a] Maximum mol% CO_2 absorbed relative to capture agent used.

[b] mol L^{-1} min^{-1}. Calculated from a linear extrapolation of initial slope of a plot of absorbed CO_2 against CO_2-liquid contact time.

[c] Maximum CO_2 concentration measured via carbonate bomb method. CO_2 loading conditions: 25 °C, 30 mL sample volume, CO_2 flow 0.3 L min^{-1} for 90 min.

^1H NMR analysis of the two phases showed that the upper phase consisted mostly of phenol along with a small quantity of MEA and derivatives (from 2-8 mol% of total MEA depending upon composition), with an overwhelming majority (>95%) of CO_2-derived salts being present in the lower aqueous lower phase (Figure 7). This biphasic behaviour complicated species determination somewhat as satisfactory ^1H NMR requires homogeneous solutions. Hence, each phase was separated and analysed individually, and their amounts relative to one another calculated based on integration of the ethanolamine- and phenoxide-derived peaks in the NMR spectra. Since the ratio of these in the total solution is known from the initially prepared composition, and is approximately invariant (as neither compound is especially volatile), this may be defined as the average of the same ratio in each phase, weighted by the amount (mole fraction) of each phase. Hence, these observed ratios could be used to calculate the mole fraction that each phase contributes toward the total, and therefore the amount of each species in each phase.

Precipitation of $KHCO_3$ was observed in the two most concentrated solutions (Table 1, entries 5 and 7) after particularly long exposure to CO_2. The identity of this precipitate was implied by the lack of visible organic species in a quantitative ^1H NMR spectrum (D_2O), and confirmed by both the ^{13}C NMR spectrum and use of the VLE to measure the mass fraction of acid-sensitive bicarbonates in a standard aqueous solution prepared from the precipitate. The concentration at which $KHCO_3$ began to precipitate (*ca.* 3 mol L^{-1}) is broadly consistent with its reported aqueous solubility.[42] The amount of CO_2 that could be absorbed was shown to vary based on the concentration and composition of the capture solvent (Table 1). Increases in the concentration of capture agent generally resulted in diminishing returns. For example, comparison of the two equimolar mixtures containing 1 M and 2 M of each base, respectively (entries 3 and 7) shows that although a higher concentration of CO_2 was absorbed when more capture agent was present, the amount of CO_2 absorbed in proportion to the amount of capture agent used was reduced from 82% to 66%.

Compositions in which the concentration of KOPh was greater than that of MEA (entries 4 and 5) exhibited superior performance. Conversely, the initial rate of absorption appears to be dependent almost exclusively on the concentration of MEA in solution, and is unaffected by changes in KOPh concentration. This is consistent with previously published kinetic studies into CO_2 capture by MEA, which showed that the rate of carbamate formation, which is dependent upon MEA concentration, is the fastest pathway of CO_2 absorption and would therefore be expected to dominate the initial rate of absorption.[9]

Closer examination of the species formed by loading with CO_2 (Figure 8) shows a broadly similar pattern to that observed in 5 M MEA, but with important differences in detail. Generally speaking, carbamate was found to be the principal CO_2-derived species when relatively little CO_2 had been absorbed, but the concentration of bicarbonate became significant as more and more CO_2 was absorbed. However it was particularly noticeable that formulations which contained an excess of KOPh over MEA showed much greater amounts of bicarbonate in the early phases of the reaction, and bicarbonate was noted to be a significant absorption product over the entire range of CO_2 concentrations. This behaviour is likely to be beneficial for CCS applications, since liberation of CO_2 from bicarbonate is substantially easier than an equivalent carbamate, whilst acceptable rates of reaction are maintained to keep absorber sizes reasonable.[43]

The reason for the differing behaviour of these particular solutions may be understood with recourse to the thermodynamic basis of CO_2 capture, as the driving force for CO_2 absorption into solution is far greater than the penalty for converting carbamate into the less stable bicarbonate.[9,40] This gives rise to the speciation behaviour seen when loading 5M MEA and similar systems. When the amount of CO_2 in solution is small, carbamate predominates at equilibrium, as this is the most thermodynamically favourable product of CO_2 absorption. However, as the concentration of CO_2 rises, the stoichiometry of carbamate formation becomes a limiting factor. Bicarbonate then becomes a significant CO_2-derived product, as the driving force for CO_2 absorption *per se* (acid-base neutralisation) outweighs the inferior stability of bicarbonate compared to carbamate. Finally, a maximum CO_2 concentration is reached when either there is no base remaining (as seen in dilute solutions), or other thermodynamic penalties, including entropic considerations, outweigh the driving force for further absorption (as seen in the more concentrated solutions studied in this work).

The effect of substituting KOPh for a proportion of the MEA, following the above analysis, is to lower the stoichiometric limit upon carbamate formation, since one mole of amine (plus another mole of base) is required for this, while one mole of any base will suffice in order to absorb CO_2 as bicarbonate. By reducing the proportion of base that is amine, the carbamate limit is approached much more quickly and formation of bicarbonate is favoured. It must be noted that this requires an *excess* of KOPh over MEA, as in lesser proportions the limit upon carbamate formation would be unaffected, and indeed similar behaviour to that of MEA alone (see Figure 8(b) and (c)) is observed in these solutions.

While use of an excess of KOPh over MEA in theory produces greatly improved speciation and maximum CO_2 loading, this approach is not without its drawbacks. As earlier noted, precipitation of $KHCO_3$ occurred when high concentrations were formed, and excessive precipitation is usually best avoided in the engineering of a viable capture system. This may be avoided by the use of lower concentrations of base in solution (although this also lowers the rate and capacity for CO_2 absorption) or alleviated by increasing the operating temperature above 25 °C in order to increase $KHCO_3$ solubility. As noted above, capture of CO_2 into these phenoxide-containing solutions produced a biphasic system due to the low aqueous solubility of phenol, and this might reasonably be expected to affect the capture performance of the solution. Biphasic behaviour has been exploited previously, reducing regeneration heat required, usually by separation of bulk water from the regeneration step.[44-46] It is however unlikely that such biphasic behaviour can be exploited in this case for solvent regeneration, e.g. by separation and regeneration of CO_2 from the aqueous phase, because components of both phases are necessary for the desorption chemistry, with the phenol phase being required as the acid in the regeneration process, and the bulk of the CO_2 being in the aqueous phase.

No dramatic shift in speciation was observed in response to phase separation, as shown by comparison between Figure 8(a), where the solution remained monophasic, and Figure 8(e), which formed a biphasic mixture at absorbed CO_2 concentrations above 1.8 M. It is possible, however, that removal of phenol from the aqueous phase may drive the absorption equilibrium further towards bicarbonate formation and therefore produce a higher maximum CO_2 capacity.

3.3. Speciation of related amine blends.

In order to determine the magnitude of this effect a comparison with single-phase solutions was deemed necessary. This also provided the opportunity to obtain a direct comparison of more conventional amine blends with the new phenolate-amine blends. Hence, a range of typical amine blends, each containing 1 mol L^{-1} of a carbamate-forming amine (amine A) and 3 mol L^{-1} of a non-carbamate-forming amine (amine B), was prepared and their CO_2 capture behaviour studied using the same methods already described (Table 2). The amines employed were MEA (1), piperazine (PZ, 2), N-methyldiethanolamine (MDEA, 3), and 2-amino-2-methyl-1-propanol (AMP, 4), all of which are widely used in previously reported CO_2 capture studies, although it should be appreciated we are not necessarily studying them at optimally performing ratios.[10,16,47–50]

Table 2. Summary of the rate and capacity for CO_2 absorption into aqueous solutions containing 1 mol L^{-1} of A and 3 mol L^{-1} of B.

Entry	A (1 mol L^{-1})	B (3 mol L^{-1})	Abs. %[a]	Initial rate[b]	Absorbed CO_2 (mol L^{-1})
1	MEA	MDEA	72	0.13	2.90
2	MEA	AMP	75	0.20	2.52
3	MEA	KOPh	88	0.17	3.50
4	PZ	AMP	70	0.13	3.51

[a] Maximum mol% CO_2 absorbed relative to capture agent used.

[b] mol L^{-1} min^{-1}. Calculated from a linear extrapolation of initial slope of a plot of absorbed CO_2 against CO_2-liquid contact time.

[c] Maximum CO_2 concentration measured via carbonate bomb method. CO_2 loading conditions: 25 °C, 30 mL sample volume, CO_2 flow 0.3 L min^{-1} for 90 min.

In comparison with the equivalent phenoxide-containing solution (Table 1, entry 5), two of these solutions (the MEA/MDEA and PZ/AMP blends) produced a noticeably slower initial rate of absorption, whereas that for the MEA/AMP blend (Table 2, entry 2) was more comparable to the phenoxide blend.

The CO_2 capture performance of the phenoxide solution was, however, significantly better than the amine solutions at higher CO_2 concentrations, resulting in a very high maximum absorption of CO_2 (88% of total base concentration, compared to a maximum of 75% among the other amines). However, unlike the phenoxide solution, no precipitation of bicarbonate was observed in the amine blend solutions.

The MEA/MDEA and MEA/AMP solutions (Figure 9) showed significantly more bicarbonate formation at a lower CO_2 absorption threshold than in the solution of MEA alone, with a latter phase (>1 mol L^{-1} CO_2 absorbed) wherein bicarbonate predominates. However, the proportion of bicarbonate formed was somewhat lower than that observed in the comparable MEA/KOPh solution. Hence it appears that phenoxide particularly favours bicarbonate formation when compared with tertiary amines.

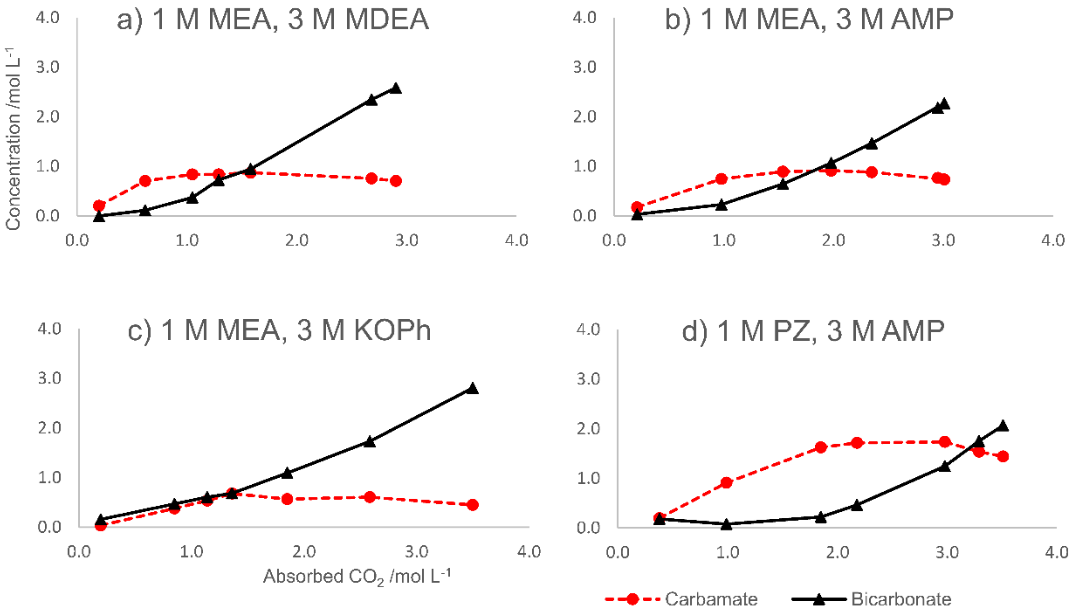

Figure 9. CO$_2$-derived species formed by absorption of CO$_2$ into solutions containing 1 mol L^{-1} of A and 3 mol L^{-1} of B, where A and B are, respectively: a) MEA and MDEA; b) MEA and AMP; c) MEA and KOPh; d) PZ and AMP. All solutions studied at 25 °C and also contained 5 mmol L^{-1} DSS as an internal ^{1}H NMR standard. Note that in the case of the piperazine solution, the concentration of the piperazine (bis)carbamate is counted double, in accordance with the number of moles of CO$_2$ absorbed in this molecule.

The most obvious chemical difference between the two groups of species is the phase separation caused by formation of partially immiscible phenol. This may contribute to the driving force in favour of CO$_2$ absorption by removing phenol from the reaction equilibrium. It is unlikely that the observed difference is pK$_a$-related, since while the pK$_a$ of phenol (9.95) is somewhat higher than those of MDEA (8.57),[51] that of AMP is similar (9.82) and so a pK$_a$-related effect would be expected to mainly affect the MEA/MDEA blend due to the lower pK$_a$ of the tertiary amine.

It is evident from Figure 9 that the behaviour of the piperazine solution is particularly divergent. This is due to the fact that, as a diamine, a variety of structures are possible when reacting with CO$_2$, and the molecule has twice as many potential carbamate-forming moieties, as previously described.[8] Therefore, the observed speciation is much more similar to that of some of the mixtures in Figure 8 (see, for example, 8(e)), wherein there is not a sufficient excess of non-carbamate-forming amine in order to produce a large amount of bicarbonate.

4. Conclusions

This work has shown that potassium phenoxide is indeed fully capable of acting as CO_2 capture solvent component particularly when used in conjunction with amines capable of carbamate formation. Testing of a variety of blends shows that inclusion of KOPh in MEA blends leads to absorption of higher concentrations of CO_2 without notably harming the rate of absorption. In particular, the use of an excess of phenoxide over MEA resulted in a capture solvent that produced significant amounts of bicarbonate as the CO_2 derived product. Since bicarbonate is less thermally stable than carbamate, this could provide a capture solvent that requires significantly less energy in order to regenerate and thus is less costly to use for post-combustion CO_2 capture. Further more detailed studies would be required to verify this as the actual picture is a complex balance of a range of factors. The maximum concentration of phenoxide-based solvents is limited by the solubility of the $KHCO_3$ capture product as excessively high concentrations lead to precipitation that may prove prohibitive. Additional factors such as solvent viscosity, specific heat capacity, cost, degradation rates and corrosivity can also impact on solvent viability, and alternative tertiary amines, which may provide superior performance compared to MDEA are also feasible.

Comparison of phenoxide with the amine blends investigated (which admittedly may not be optimal for each individual blend) showed that while species formation is comparable, the capture performance of phenoxide is significantly superior at high concentrations of CO_2. This can be possibly attributed to the complex phase behaviour of the phenoxide-based solvent owing to the limited aqueous solubility of phenol. How this might affect performance in an industrial-scale capture system is uncertain and will be the subject of future studies. Nevertheless, this work clearly demonstrates the viability of potassium phenoxide and, by implication, related compounds as CO_2 capture agents, and therefore broadens the options available to chemists and engineers seeking to develop improved industrially viable and economic CO_2 capture and storage process.

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Declaration of interest.

DB, CS and GJ are all employees of C-Capture Ltd. CMR is an employee of the University of Leeds, and is also a Director of C-Capture, and holds shares in the company.

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Supporting Information. ^1H NMR data and tables of speciation for all capture agents compositions discussed.

References

1 M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, H.J. Herzog, G. Jackson, J. Kemper, S. Krevor, G.C. Maitland, M. Matuszewski, I.S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D.M. Reiner, E.S. Rubin, S.A. Scott, N.

Shah, B. Smit, J.P.M. Trussler, P. Webley, J. Wilcox and N. Mac Dowell, Energy Environ. Sci., 2018, **11**, 1062.

2 M. Caplow, J. Am. Chem. Soc., 1968, **90**, 6795–6803.

3 N. McCann, D. Phan, X. Wang, W. Conway, R. Burns, M. Attalla, G. Puxty and M. Maeder, J. Phys. Chem. A, 2009, **113**, 5022–5029.

4 P. V. Danckwerts, Chem. Eng. Sci., 1979, **34**, 443–446.

5 D. Fernandes, W. Conway, X. Wang, R. Burns, G. Lawrance, M. Maeder and G. Puxty, J. Chem. Thermodyn., 2012, **51**, 97–102.

6 C. Perinu, B. Arstad and K.-J. Jens, Int. J. Greenh. Gas Control, 2014, **20**, 230–243.

7 S. A. Freeman, R. Dugas, D. Van Wagener, T. Nguyen and G. T. Rochelle, Energy Procedia, 2009, **1**, 1489–1496.

8 G. Rochelle, E. Chen, S. Freeman, D. Van Wagener, Q. Xu and A. Voice, Chem. Eng. J., 2011, **171**, 725–733.

9 W. Conway, X. Wang, D. Fernandes, R. Burns, G. Lawrance, G. Puxty and M. Maeder, J. Phys. Chem. A, 2011, **115**, 14340–14349.

10 R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas and D. Gelowitz, Ind. Eng. Chem. Res., 2006, **45**, 2414–2420.

11 A. Adeosun and M. R. M. Abu-Zahra, Energy Procedia, 2013, **37**, 211–218.

12 D. P. Hagewiesche, S. S. Ashour, H. A. Al-Ghawas and O. C. Sandall, Chem. Eng. Sci., 1995, **50**, 1071–1079.

13 A. L. Soli and R. H. Byrne, Mar. Chem., 2002, **78**, 65–73.

14 A. H. England, A. M. Duffin, C. P. Schwartz, J. S. Uejio, D. Prendergast and R. J. Saykally, Chem. Phys. Lett., 2011, **514**, 187–195.

15 Y. Du, Y. Yuan and G. T. Rochelle, Chem. Eng. Sci., 2016, **155**, 397–404.

16 W. Conway, S. Bruggink, Y. Beyad, W. Luo, I. Melián-Cabrera, G. Puxty and P. Feron, Chem. Eng. Sci., 2015, **126**, 446–454.

17 W.-J. Choi, K.-C. Cho, S.-S. Lee, J.-G. Shim, H.-R. Hwang, S.-W. Park and K.-J. Oh, Green Chem., 2007, **9**, 594–598.

18 G. Fytianos, S. Ucar, A. Grimstvedt, A. Hyldbakk, H. F. Svendsen and H. K. Knuutila, Int. J. Greenh. Gas Control, 2016, **46**, 48–56.

19 L. Onel, M. A. Blitz, J. Breen, A. R. Rickard and P. W. Seakins, Phys. Chem. Chem. Phys., 2015, **17**, 25342–25353.

20 L. Onel, M. A. Blitz and P. W. Seakins, J. Phys. Chem. Lett., 2012, **3**, 853–856.

21 N. Dai and W. A. Mitch, Environ. Sci. Technol., 2013, **47**, 13175–13183.

22 A. J. Reynolds, T. V. Verheyen, S. B. Adeloju, E. Meuleman and P. Feron, Environ. Sci. Technol., 2012, **46**, 3643–3654.

23 J. R. Pliego Jr and J. M. Riveros, Phys. Chem. Chem. Phys., 2002, **4**, 1622–1627.

24 Vetrocoke S.p.A., Br. Pat., 786 669 A, 1967.

25 Z. Marković, S. Marković and N. Begović, J. Chem. Inf. Model., 2006, **46**, 1957–1964.

26 V. Barbarossa, F. Barzagli, F. Mani, S. Lai and G. Vanga, J. CO_2 Util., 2015, **10**, 50–59.

27 C. Wang, H. Luo, H. Li, X. Zhu, B. Yu and S. Dai, Chem. Eur. J., 2012, **18**, 2153–2160.

28 C. Wang, H. Luo, D. Jiang, H. Li and S. Dai, Angew. Chem. Int. Ed., 2010, **49**, 5978–5981.

29 G. Fan, A. G. H. Wee, R. Idem and P. Tontiwachwuthikul, Ind. Eng. Chem. Res., 2009, **48**, 2717–2720.

30 S. K. Bharti and R. Roy, Trends Anal. Chem., 2012, **35**, 5–26.

31 T. Suda, T. Iwaki and T. Mimura, Chem. Lett., 1996, **25**, 777–778.

32 F. Barzagli, F. Mani and M. Peruzzini, Energy Environ. Sci., 2009, **2**, 322–330.

33 A. F. Ciftja, A. Hartono and H. F. Svendsen, Int. J. Greenh. Gas Control, 2013, **16**, 224–232.

34 A. F. Ciftja, A. Hartono and H. F. Svendsen, Int. J. Greenh. Gas Control, 2014, **27**, 169–177.

35 J. P. Jakobsen, J. Krane and H. F. Svendsen, Ind. Eng. Chem. Res., 2005, **44**, 9894–9903.

36 A. Dreimanis, J. Sediment. Petrol., 1962, **32**, 520–529.

37 J. C. Schink, J. H. Stockwell and R. A. Ellis, J. Sediment. Res., 1979, **49**, 651–653.

38 P. D. Vaidya and E. Y. Kenig, Chem. Eng. Technol., 2007, **30**, 1467–1474.

39 N. McCann, D. Phan, D. Fernandes and M. Maeder, Int. J. Greenh. Gas Control, 2011, **5**, 396–400.

40 D. Fernandes, W. Conway, R. Burns, G. Lawrance, M. Maeder and G. Puxty, J. Chem. Thermodyn., 2012, **54**, 183–191.

41 W. Böttinger, M. Maiwald and H. Hasse, Fluid Phase Equilib., 2008, **263**, 131–143.

42 O. Söhnel and P. Novotny, Densities of Aqueous Solutions of Inorganic Substances, Elsevier, Amsterdam, 1985.

43 D. Aaron and C. Tsouris, Sep. Sci. Technol., 2005, **40**, 321–348.

44 S. Zhang, Y. Shen, P. Shao, J. Chen and L. Wang, Environ. Sci. Technol., 2018, **52**, 3660-3668.

45 L. Wang, Y. Zhang, R. Wang, Q. Li, S. Zhang, M. Li, J. Liu and B. Chen, Environ. Sci. Technol., 2018, **52**, 14556-14563.

46 S. Zhang, Y. Shen, L. Wang, J. Chen and Y. Lu, Applied Energy, 2019, **239**, 876-897.

47 D. Tong, G. C. Maitland, M. J. P. Trusler and P. S. Fennell, Chem. Eng. Sci., 2013, **101**, 851–864.

48 A. S. Lee, J. C. Eslick, D. C. Miller and J. R. Kitchin, Int. J. Greenh. Gas Control, 2013, **18**, 68–74.

49 T. Wang and K.-J. Jens, Int. J. Greenh. Gas Control, 2014, **24**, 98–105.

50 T. Wang and K.-J. Jens, Energy Procedia, 2013, **37**, 306–313.

51 A. Tagiuri, M. Mohamedali and A. Henni, J. Chem. Eng. Data, 2016, **61**, 247–254.

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