Use of metal-organics based solvents for CO₂ capture

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Abstract

There are a number of metal-organic compounds that can loosely be considered CA mimics and which are known to absorb CO₂ directly from the atmosphere. The metal-organic complex, \( \{\text{Zn}[\text{N}(\text{CH}_2(2-\text{py}))_3]\{\mu-\text{OH}\}\}_2(\text{NO}_3)_2 \) (I), is one such complex. In the present study, the sorption of CO₂ by water solutions of complex I have been studied by NMR (using D₂O as solvent and absorbing 99.9% \(^{13}\text{C}\) enriched CO₂) and vapor-liquid equilibria measurements to understand the mechanisms of sorption when using such complexes. The potential of I/water solvents for use in CO₂ capture has been evaluated by comparison with mono-ethanolamine (MEA)/water solvents. The metal-organic solvent shows higher sorption capacity than MEA on a molar basis; also, three cycle tests indicate that I/water solvents can be regenerated efficiently at low temperatures giving a potential significant reduction in regeneration energy requirements as compared to MEA/water solvents. On the other hand, due to its more than 14 times lower molar mass, MEA solvents have higher CO₂ sorption capacities on a kg solvent basis. The two solvents show similar sorption kinetics.

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1. Introduction

Carbon dioxide capture and storage of (CCS) is one way to reduce the CO₂ emissions to the atmosphere while making it possible to continue utilizing hydrocarbon-based fuels for power generation in a transition period before

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renewable energy technologies can provide most of the energy needed [1]. The use of alkanolamine-based solvents for post-combustion CO₂ capture is the technology that is closest to full scale realization. However, such solvents have two major drawbacks: The first is its relatively high energy requirement for alkanolamine regeneration [2]; the second is its low thermochemical stability under operative conditions, leading both to accumulation of high molecular weight waste compounds in the solvent phase [3] as well as release of potentially toxic components to the atmosphere [4]. The search for alternatives to alkanolamines is therefore urgent. Solvents based on water-soluble metal-organic complexes that are able to sorb CO₂ reversibly might be attractive alternatives. Carbon dioxide fixation and catalytic transformation into bicarbonate in relation to carbonic anhydrase (CA) and anhydrase mimicking Zn-complexes have been reviewed by a number of authors [5], and also CO₂ fixation in metal-organic complexes involving other metals have been described in several papers [6]. However, to our knowledge, examples of the use of metal organic complexes of this kind in cyclic sorption processes have still not been reported.

One such zinc complex, that forms stable complexes with CO₂ that we have studied in more detail, is shown in Figure 1 below. Our main aim has been to understand the mechanisms taking place upon CO₂ sorption and desorption in the I/water solvents based on in situ NMR experiments carried out at different conditions. Secondly, equilibrium and kinetic measurements of the absorption of CO₂ into the I/water solution has been estimated which then have been used to make a fair comparison of the potential of such metal-organic complex solutions as compared to state-of-the-art MEA solvents used for post-combustion CO₂ capture. Finally, the stability and limitations in using the metal-organic based solvents have been investigated, in particular limitations in metal-complex concentration and possible precipitation.

![Figure 1: Reaction of {Zn[N(CH2(2-py))3](μ-OH)}2(NO3)2 (I) with CO₂ to yield a tri-nuclear carbonate complex shown to the right. Taken from Murthy et al. [7]](image)

2. Experimental

Large scale (150 g) synthesis of {Zn[N(CH2(2-py))3](μ-OH)}2(NO3)2 (I): Due to the potential hazards [8] connected to the use of perchlorate (ClO₄⁻) anions contained in the originally described complex [7], we have chosen to use the analogous nitrate complex that is expected to have similar reactivity in aqueous solution. A 150 g batch of I was prepared following a similar procedure as described for the perchlorate complex [7]: Zn(NO₃)₂•6H₂O and KOH were used as received from commercial sources. Methanol was used directly from the bottle without any other purification, drying, or degassing. A 1 L Schlenk flask was charged with Zn(NO₃)₂•6H₂O (114.5 g, 0.385 mol) and placed under Ar. Similarly, a 500 ml Schlenk flask and a 250 ml Schlenk flask were charged with N(CH2(2-py))3 (NN₃) (111.9 g, 0.385 mol) and KOH (26.0 g, 0.463 mol), respectively, and placed under Ar. Methanol solutions of the three compounds were made by adding 250, 150, and 100 ml MeOH, respectively, under an Ar flow. Under an Ar flow, the blood-red NN₃ solution was poured into the colorless Zn salt solution. Similarly, a 500 ml Schlenk flask and a 250 ml Schlenk flask were charged with N(CH2(2-py))₃ (NN₃) (111.9 g, 0.385 mol) and KOH (26.0 g, 0.463 mol), respectively, and placed under Ar. Methanol solutions of the three compounds were made by adding 250, 150, and 100 ml MeOH, respectively, under an Ar flow. Under an Ar flow, the blood-red NN₃ solution was poured into the colorless Zn salt solution. Similarly, the colorless KOH solution was poured into the now pale red Zn/NN₃ solution. Precipitation immediately occurred, and stirring slowed. Another 100 ml MeOH was added to the reaction to increase stirring speed. The heterogeneous reaction was stirred under Ar for 90 min, and then approximately 360 ml of the volatiles was removed in vacuo. The resulting mixture was then filtered in the air with a Büchner funnel. The flask and filter cake was washed with 75
ml MeOH. Nearly all the solvent from the combined, dark red filtrate and wash was removed on a Roto-vap. 250 ml diethyl ether was added to the red-orange slurry and the mixture was stirred for 45 min. The insolubles were then filtered off and dried, to give an off-white solid (155.6 g, 0.179 mol, 93 % yield). $^1$H NMR showed the expected signals for the product, plus residual signals consistent with unreacted NN$_3$ (less than 2 mol %) and traces of MeOH and Et$_2$O.

Characterization by NMR: NMR experiments were performed at 9.4 T on a Bruker Avance III 400 MHz spectrometer using a BBFO Plus double resonance probe head at 298 K or 313 K; the spectra were processed using MestreNova software. 1D $^1$H, $^{13}$C, with and without decoupling protons, COSY, HSQC, and HMBC experiments were carried out to assign peaks to the C-atoms in the Zn complexes. Temperature calibrations were done using methanol chemical shift variations. Most samples have been prepared by dissolving about 50 mg complex I or ligand in D$_2$O. 99.9 % $^{13}$C CO$_2$ enriched gas was bubbled through the solution in the NMR tube for three minutes. Experiments using 9 and 15 minutes bubbling time showed no significant increase in CO$_2$ derived signals, hence the solutions with ligand or Zn complex I were saturated after 3 minutes bubbling.

Measurements of CO$_2$ sorption: Sorption kinetics was studied in a simple screening setup as described by Ma'mun et al. [9]. Solvent CO$_2$ sorption capacities were estimated from Vapor-liquid equilibria measurements using a LABMAX setup [10]. Measurements were carried out on pure water, 3.0 wt% I/water and 3.0 wt% MEA/water using 10% CO$_2$/N$_2$ as. Absorption was performed at 40ºC, and desorption at 80ºC. Three cycles were measured for each solvent.

3. Results and discussion

Both quantitative NMR and sorption measurements have been conducted to gain insight on the mechanisms of sorption by I/water solvents. Initial NMR experiments (shown in Figure 2) using 99.9 % $^{13}$CO$_2$ enriched gas show that pure D$_2$O only dissolves CO$_2$ (single peak at 127 ppm), no bicarbonate or carbonate species are observed within the time of the measurements (Typically 1-2 hr). A similar experiment carried out with the ligand, NN$_3$, dissolved in D$_2$O (Figure 2, middle) shows, beside the dissolved $^{13}$CO$_2$ peak, the presence of a peak corresponding to HCO$_3$-/CO$_3^{2-}$ at around 163 ppm, typical for free carbonate species at the relevant pH. The amount of bicarbonate/carbonate corresponds to around 7% of the amount of NN$_3$ in solution. Using a I/D$_2$O solution (Figure 2, bottom) a broad HCO$_3$-/CO$_3^{2-}$ peak at around 165 ppm is observed, the estimated amount of carbonate corresponds to around 67% of the NN$_3$ present. These simple experiments clearly show that the Zn-complex (I) significantly enhances bicarbonate/carbonate formation. While NN$_3$/water solutions only work as poor physical absorbents giving only small amounts of bicarbonate/carbonate, complex I/water solutions clearly give a different kind of carbonate product. The fact that the peak positions of the various carbon atoms in the NN$_3$ ligands also change positions when CO$_2$ is introduced strongly indicates that a new Zn-containing complex is formed upon sorption, most probably corresponding to complex 2 in Figure 1. Attempts to isolate the CO$_2$ containing product formed, to prove its structure, has so far not been successful.

Figure 3 shows kinetic and sorption capacity data for water, 3.0 wt% I/water and 3.0 wt% MEA/water solvents derived at 40 ºC under 10 kPa CO$_2$. Data shown on a molar basis give information on stoichiometry of the eventual chemical reactions taking place during sorption, while the data given on a ’kg solvent’ basis give information on the
For the MEA/water solvent the normal trend is observed: an initial rapid sorption until a molar CO$_2$/MEA ratio of around 0.5 is achieved followed by a rapid decrease in sorption rate. CO$_2$ reacts with two MEA molecules forming a monoethanolcarbamate/monoethanolammonium ion pair [11]. When stoichiometric amounts of CO$_2$ have reacted, there is no more MEA available for sorption, and the slower physical sorption by the water will take over leading to a limiting sorption capacity of around 0.5 mol CO$_2$/mol MEA in the first cycle. The 3$^{rd}$ cycle with MEA/water given in the top left plot of Figure 3 shows a lower total capacity, which is expected since solvent regeneration is carried out at relatively low temperature, 80ºC, a temperature where only a small fraction of the carbamate formed during absorption is decomposed back into MEA and CO$_2$. The 3$^{rd}$ cycle therefore mostly show the physisorption part of the sorption.

For the 3.0 wt% I$_2$/water solution the trend is similar; the sorption is very rapid initially, until a molar CO$_2$/I$_2$ ratio above 1.0 is achieved, after which the rate of sorption declines until a molar ratio of around 2.0 is reached. The initial sorption rate occurs faster than the measurements, indicated by the first data point at about 1.3. Noting that a carbonate/I$_2$ molar ratio of 1.33 was obtained from NMR analyses at similar conditions, it is natural to assume that the first rapid part can be assigned to the reaction between complex I and CO$_2$ shown in Figure 1. The sharp change in the curve at around 2.0 indicates that a completely different sorption mechanism takes over, probably a lower energy physisorption. Since the shape of the curves in the ‘kg solvent’ based curves are similar for the metal-organic and MEA cases (lower plots of Figure 3) this further supports that physisorption of CO$_2$ in the water takes place at the end of each plot, however, both MEA and the metal-organic complex I seems to enhance the physisorption of

![Figure 3: Rate/capacity plots of water (green), 3.0 wt% I$_2$/water (red) and 3.0 wt% MEA/water (blue) derived at 40 °C. The upper two plots show results from the 1$^{st}$ (left) and 3$^{rd}$ (right) absorption cycle on a molar basis, while the lower two plots show the same data on a kg solvent basis.](image)
CO₂ since less physisorption is observed in the pure water case.

Comparing the results for the 3.0 wt% I/water solution in the 3rd cycle with those for the 1st cycle, there is only a modest reduction in sorption capacity, indicating that most of the sorbed CO₂ is released already at the mild regeneration conditions used (80°C). The possibility to regenerate at lower temperatures than typically 120°C for MEA would significantly reduce the energy requirement of the solvent stripping unit where solvent regeneration takes place. The required regeneration energy is the sum of three contributions; the first is the heating of the solvent itself from the temperature where sorption takes place to the regeneration temperature, the second being the energy of sorption and the third the heat needed to evaporate a part of the solvent in order to sweep gas itself from the temperature where sorption takes place. The required regeneration energy is the sum of three contributions; the first is the heating of the solvent based solvents: Due to the high molecular weight of typical metal-organic complexes like complex I (M= 869.5 g/mol), more than 14 times higher than for MEA (M= 61 g/mol), the volumetric sorption of the I/water is significantly lower than that of MEA/water. For MEA based solvents, typically 30 wt% solutions are used (4.92 mol/kg solvent). A similar concentration level of complex I is not achievable due to the high molecular weight. In addition, reaching really high concentrations of metal-organic complexes is more likely limited by the solubility of such complexes in water. This will be further examined in the ongoing project.

1. Conclusions

We have, based on NMR and VLE experiments, shown that water solutions of the metal-organic complex, \{Zn[N(CH₂(2-py)]₃[μ-OH]}₂(NO₃)₂ (I), can sorb CO₂ reaching CO₂/I molar ratios of around 2.0. From three cycle experiments it has also been shown that close to complete regeneration can be achieved already at 80°C with I/water solvents, a temperature where only a small fraction of the monoethanolcarbamate formed when CO₂ is sorbed by MEA/water solvents is decomposed. If I/water solvents can be regenerated below the solvent boiling temperature, significant reduction in regeneration energy requirements could be obtained, leading to a significant reduction in energy penalty for the total capture process.

However, since the molecular weight of complex I is more than 8 times higher than that of MEA, the sorption capacity both on a volume basis and on a ‘kg solvent’ basis is significantly lower than that of MEA/water. The use of less concentrated I/water solvents would then require much larger volumes of both sorption and regeneration columns, or alternatively, the development of a rapid temperature swing process with cycle times much shorter than the normal cycle times used for MEA/water based solvents.

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