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Use of metal-organics based solvents for CO$_2$ 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 CO$_2$ directly from the atmosphere. The metal-organic complex, $\{Zn[N[CH_2(2\text{-py})]_3](\mu\text{-OH})\}_2(NO_3)_2$ (**I**), is one such complex. In the present study, the sorption of CO$_2$ by water solutions of complex **I** have been studied by NMR (using D$_2$O as solvent and absorbing 99.9% ^{13}C enriched CO$_2$) and vapor-liquid equilibria measurements to understand the mechanisms of sorption when using such complexes. The potential of **I**/water solvents for use in CO$_2$ 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 CO$_2$ sorption capacities on a kg solvent basis. The two solvents show similar sorption kinetics.

1. Introduction

Carbon dioxide capture and storage of (CCS) is one way to reduce the CO$_2$ 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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.
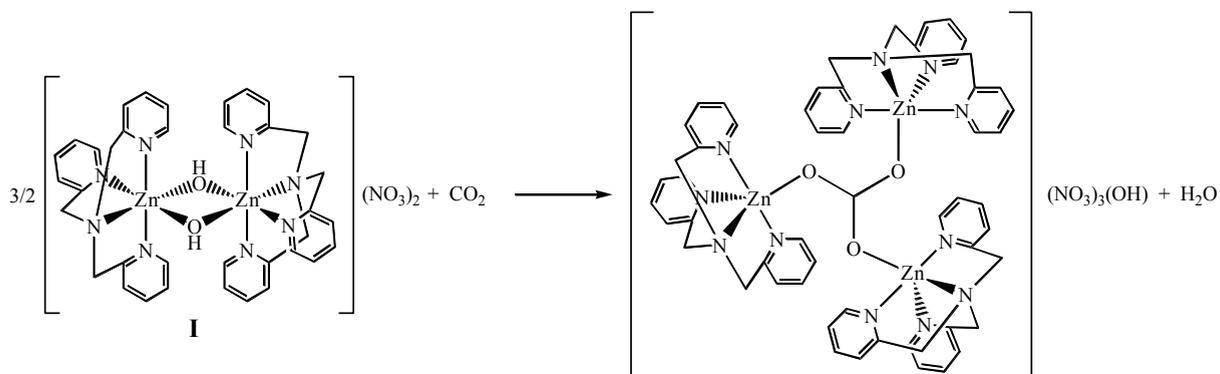
Figure 1: Reaction of $\{Zn[N[CH_2(2-py)]_3](\mu\text{-}OH)\}_2(NO_3)_2$ (**I**) with CO_2 to yield a tri-nuclear carbonate complex shown to the right. Taken from Murthy *et al.*[7]

2. Experimental

Large scale (150 g) synthesis of $\{Zn[N[CH_2(2\text{-}py)]_3](\mu\text{-}OH)\}_2(NO_3)_2$ *(I):* Due to the potential hazards [8] connected to the use of perchlorate (ClO_4^-) 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]: $Zn(NO_3)_2 \cdot 6H_2O$ 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 $Zn(NO_3)_2 \cdot 6H_2O$ (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 $N[CH_2(2\text{-}py)]_3$ (NN_3) (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 NN_3 solution was poured into the colorless Zn salt solution. Similarly, the colorless KOH solution was poured into the now pale red Zn/NN_3 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_2O.

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_2O. 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_2O 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_2O (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

Figure 2: Top: CO_2 bubbled through D_2O for 3 minutes. The peak around 127 ppm is dissolved CO_2(aq). Middle: CO_2 through ligand dissolved in D_2O for 3 minutes at room temperature. The left most peak is the common signal from CO_3^{2-}/HCO_3^-. Bottom: CO_2 through D_2O and Zn-complex **I** for 3 minutes at 40 °C. There are no significant differences in these spectra compared to those after absorption at 25 °C

amount of NN_3 in solution. Using a **I**/D_2O 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

volumetric capacities of the solvents that are relevant when estimating the size of the capture process.

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 3rd 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 3rd cycle therefore mostly show the physisorption part of the sorption.
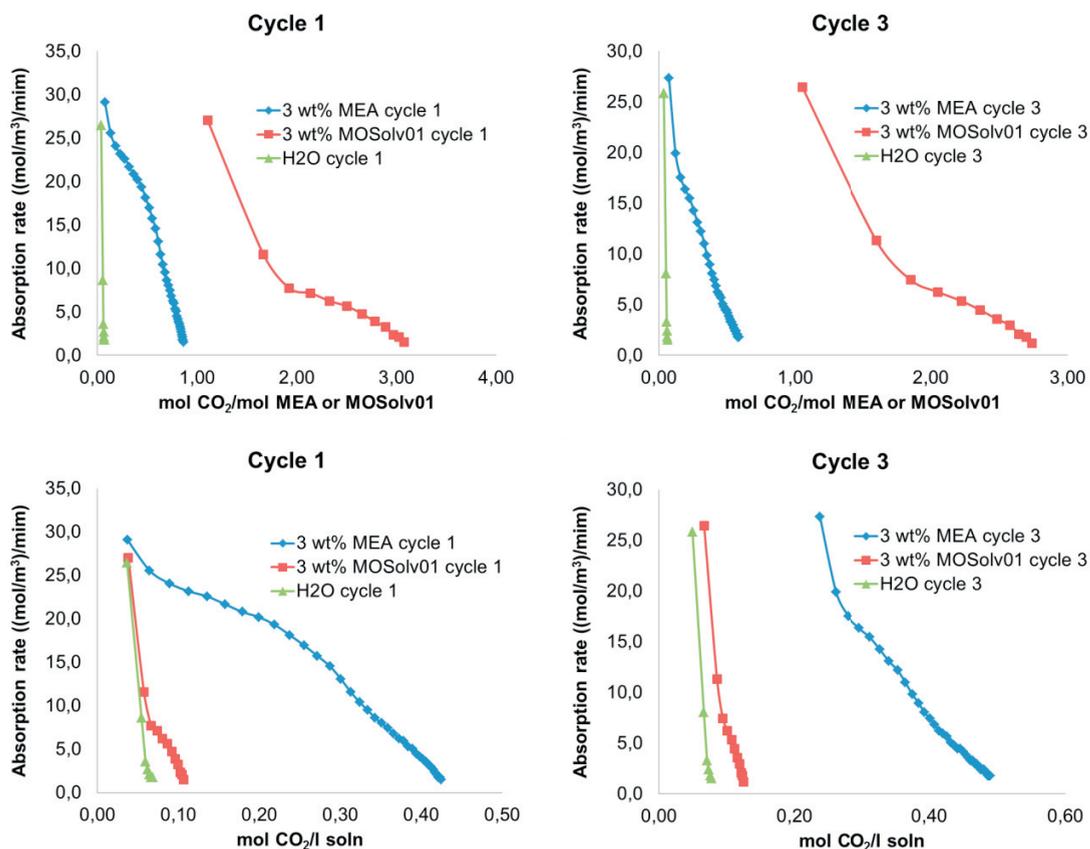
Figure 3: Rate/capacity plots of water (green), 3.0 wt% **I**/water (red) and 3.0 wt% MEA/water (blue) derived at 40 °C. The upper two plots show results from the 1st (left) and 3rd (right) absorption cycle on a molar basis, while the lower two plots show the same data on a kg solvent basis.

For the 3.0 wt% **I**/water solution the trend is similar; the sorption is very rapid initially, until a molar CO_2/**I** 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** 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

CO_2 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 is sorption capacity, indicating that most of the sorbed CO_2 is released already at the mild regeneration conditions used (80ºC). The possibility to regenerate at lower temperatures than typically 120ºC 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 is the heat needed to evaporate a part of the solvent in order to sweep gas [12]. If we manage to keep the temperature of regeneration lower than the boiling point of the solvent, the first and third contributions will be strongly reduced. In addition, there might be additional reduction in the energy requirements for regeneration if the sorption energy of eq. 1 is lower than that of MEA.

However, looking at the curves in the lower part of Figure 3, the situation is not so promising for metal-organics 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[CH$_2$(2-py)]$_3$](µ-OH)}$_2$(NO$_3$)$_2$ (**I**), can sorb CO_2 reaching CO_2/**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 80ºC with **I**/water solvents, a temperature where only a small fraction of the monoethanolcarbamate formed when CO_2 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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