

**GHGT-9****Development of catalysts for fast, energy efficient post combustion capture of CO₂ into water; an alternative to monoethanolamine (MEA) solvents.**

Raymond Davy *

RMIT University, School of Applied Sciences, (Applied Chemistry), Melbourne, Victoria, 3001. Australia.

Abstract

The aim is to develop fast catalytic absorption/ desorption of CO₂ at low temperatures using water as solvent. The naturally occurring zinc metallo-enzyme carbonic anhydrase (CA) can concentrate CO₂ using a reversible hydration/dehydration cycle at neutral pH and at ambient temperatures. A number of macrocyclic and tripodal complexes of zinc (II), and other metals that mimic the CA catalytic process, proceed by hydration of CO₂ to bicarbonate followed by the reverse dehydration of the bicarbonate to regenerate CO₂. This initial study is of the fast catalysis of the reverse reaction (the dehydration of the bicarbonate ion back to CO₂) at temperatures in the range 20–55 °C. The turnover rate constants for the catalytic desorption have been measured for zinc-1,4,7,10-tetraazacyclo-dodecane, (zinc-cyclen), the zinc tripodal complexes: zinc-nitrilo-tris(2-benzimidazolyl-methyl-6-sulfonic acid), (zinc-L1S), and zinc-tris(2-benzimidazolylmethyl)-amine, (zinc-LI). CA or the zinc complexes are proposed for utilization in a water based capture process, hence avoiding the energy intensive steam stripping steps necessary with amine solvents.

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1. Introduction

The flue gases from conventional industrial plants using carbon based fuels typically contain 4 - 14% carbon dioxide, with the balance consisting mainly of nitrogen, small quantities of unconsumed oxygen and also combustion process impurities that are formed from the fuel. The carbon dioxide level in these combustion gases is insufficient for direct compression of the flue gases (to extract the carbon dioxide) to be a cost effective option. To separate CO₂ from the flue gases, chemical or physical absorption is required; however the partial pressure of CO₂ is not high enough to favour physical absorption. Most plants that implement post combustion carbon dioxide capture do so with a chemical absorption–stripping cycle using an amine solvent. The solvent of choice is monoethanolamine (MEA) for this mature technology. Disadvantages associated with the use of MEA include its corrosive properties, a relatively high vapour pressure with consequent requirements to make up evaporative losses,

* Corresponding author. Tel.: +61 -3-9925-1015 ; fax: +61 -3-9925-3747 .

E-mail address: ray.davy@rmit.edu.au

chemical and thermal degradation occurring in the absorption-stripping cycle, (particularly as a result of impurities - SO_x , NO_x and unburnt oxygen). A further major disadvantage of MEA is the energy cost in the stripping procedure. To regenerate the MEA and strip the carbon dioxide requires considerable energy to heat the solvent to temperatures over 100°C . If an alternative solvent system or a less energy intensive absorption-stripping methodology could be developed, this would make the retrofit of existing post carbon combustion plants with a carbon capture facility an economically more attractive option. The first objective is to study some metal complexes - particularly of zinc(II) - that mimic the active site of the enzyme CA and show catalyzed absorption-desorption of CO_2 at high catalytic rates approaching those found for carbonic anhydrase.

2 Theory:

2.1 Amine solvents

Davison [1] and Rochelle [2] have reviewed the alkanolamine solvents, (amine solvents). CO_2 is a weak acidic gas that is absorbed into a solvent containing the amine, (a weak base), where RNHCOO^- is carbamate ion which is formed with both primary and secondary amines, but tertiary amines (and hindered amines) form the bicarbonate ion in a reaction with water as shown below from Rochelle et.al. [3], and Davidson [1]. (Equations 1 and 2).



The absorption capacity of tertiary amines is twice that of primary or secondary amines, (from equations 1 and 2 above), however the rate of absorption is lower Davidson [1], Trachtenberg and Bao [4].

2.2 Carbonic anhydrase.

Carbonic anhydrase (CA) is an enzyme found in virtually every animal and plant with catalytic function (equation 3) of converting CO_2 to bicarbonate (hydration) and the reverse (bicarbonate dehydration). The protein has a

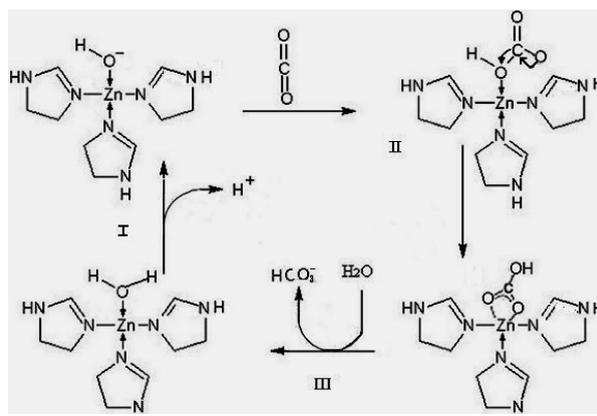


molecular weight around 30,000g/mol; zinc(II) is the metallic ion at the active site of CA, coordinated through three histidine amino acid residues and a water/hydroxide ligand (water ligand pKa around 7) to complete the tetrahedral coordination geometry. Carbonic anhydrase is one of the fastest enzymes known with one molecule able to turnover a million molecules of bicarbonate per second, Lindskog and Liljas [5], and according to Trachtenberg et.al. [20], the CA turnover rate is more than 4,000 times faster than MEA. The mechanism of the catalysis by CA (Figure 1) has been summarized concisely by Nakata et. al. [6] and by B auer et. al. [7], as follows:

- I. Deprotonation of the liganded water $(\text{His})_3\text{-Zn}^{2+} \cdot \text{H}_2\text{O} \rightleftharpoons (\text{His})_3\text{-Zn}^{2+} \cdot \text{OH}^- + \text{H}^+$
 - II. Nucleophilic attack of $(\text{His})_3\text{-Zn}^{2+} \cdot \text{OH}^-$ on CO_2 to form $(\text{His})_3\text{-Zn}^{2+} \cdot \text{HCO}_3^-$
 - III. Ligand exchange – the zinc bound HCO_3^- ligand is replaced by H_2O and the $(\text{His})_3\text{-Zn}^{2+} \cdot \text{OH}_2$ is reformed.
- $$(\text{His})_3\text{-Zn}^{2+} \cdot \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons (\text{His})_3\text{-Zn}^{2+} \cdot \text{H}_2\text{O} + \text{HCO}_3^-$$

Figure 1. Mechanism of catalysis of CA.

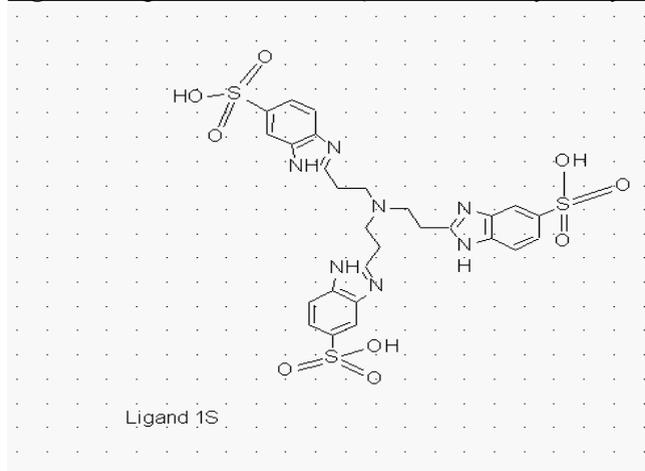
Zinc is the metallic ion at the active site of CA; several model compounds of zinc, (Table 1), also show activity for hydration of carbon dioxide and the reverse dehydration reaction. Again the zinc atom is the active catalytic centre of the reactions. Christianson and Fierke [13] in their review, have suggested that CA uses a proton shuttle of amino acids to achieve the fast deprotonation of the liganded water to the active



liganded hydroxide form for the next hydration cycle, and that the process is also enhanced by a hydrophobic pocket which is an integral part of the CA metallo-protein. Nakata et. al. [6] have determined that the mechanistic step facilitated by the zinc is the same in both the enzyme and the mimicking complexes which lack the proton shuttle enhancement, therefore CA is a considerably faster catalyst than these smaller zinc (II) complexes. Further, diffraction studies by these authors have shown that the hydrophobic pocket of CA is not relevant in the zinc-cyclen complex - (Figure 3) - and similar but smaller in the zinc-L1S complex. According to Vahrenkamp [12], the zinc metal ion is apparently ideal for catalytic purposes due to redox inertness, high kinetic lability and low thermodynamic stability. For an acid, the pKa is the pH at which the acid is 50% deprotonated. The pH of the chemical environment together with the pKa of the water/ hydroxide ligand attached to the zinc metal entity in the CA enzyme catalyst (or the metal complex catalyst) is the determinant of the form of the catalyst and hence the direction of the catalysis. Since the liganded water in CA has its pKa around 6.8, Kimura [15], the predominant form of CA above pH 6.8 will be the L_3Zn-OH^- form. This OH^- form catalyses the hydration of carbon dioxide to bicarbonate ion, while below pH 6.8 the L_3Zn-OH_2 is the predominant form which catalyses the reverse reaction, the dehydration of the bicarbonate ion. Zinc (II) has a high affinity for bicarbonate ion as a monodentate ligand, and Koike and Kimura [8] postulate that if the zinc were more acidic, the bicarbonate may become deprotonated to carbonate ion and act as a bidentate ligand. The pKa of unbound water is around 15.5 so as discussed by Vahrenkamp [12], the zinc metal has reduced the pKa of the bound water by around 7-8 pKa units in CA (and also in the mimetic zinc complexes) making hydroxide available to react with CO_2 at near neutral pH.

2.3. Inorganic zinc catalysts modeled on the active site of CA:

Figure 2. Ligand 1S: Nitrilo-tris(2-benzimidazolymethyl-6-sulfonic acid)



A number of zinc(II) complexes and several examples of complexes of divalent cobalt, copper and nickel ions have been prepared as models for carbonic anhydrase II, Ge et.al. [9], Koike and Kimura [8], Nakata et.al. [6], Zhang et.al. [10], and [11], Vahrenkamp [12]. Nakata et.al. [6] and Koike and Kimura [8] have published studies of a water-soluble macro cyclic zinc(II) complex, the Tripod Zn-L1S – Zn-Nitrilo-tris(2-benzimidazolymethyl-6-sulfonic acid), see Figure 2; in addition, a sparingly water soluble tripod without sulfonate groups – Zn-L1, Zn-Tris-(2-benzimidazolymethyl)-amine. Both of these complexes mimic the catalytic effect of carbonic anhydrase and have high activity for carbon dioxide absorption. Zinc (II) complexed with ligand L1S, was able to catalyse the

capture of CO_2 at a rate extrapolated almost to within an order of magnitude of that of carbonic anhydrase. A number of other simple zinc complexes prepared by researchers previously, modelled on carbonic anhydrase, have been shown to activate the bound ligand water molecule for nucleophilic attack towards CO_2 . Both the CA enzyme and the zinc complex catalysts employ a similar mechanism of catalysis, but the CA enzyme is faster due to some additional catalytic enhancing features not present in the smaller simplified inorganic complexes including the proton shuttle mechanism within the protein of CA Christianson and Fierke [14].

2.4. In this study water is proposed as a solvent for CO_2 capture, using CA mimetic complexes as catalysts. The aim of this research is to develop processes for CO_2 capture that have reduced energy requirements, and are less susceptible to degradation as experienced with the amine absorbents. Several authors, - Trachtenberg and Bao [4], Bond et.al. [14], Rochelle [2], Rochelle et. al. [3], [16] have proposed the use of water with promoters as the solvent for CO_2 capture. The enzyme carbonic anhydrase, (CA), is a protein - one of the fastest biological catalysts known - that has been studied because of its fast hydration and dehydration of CO_2 in water. Both Trachtenberg and Bao [4], and Bond et. al. [14] have proposed the use of carbonic anhydrase as the catalyst for an energy efficient capture procedure; however a carbonic anhydrase catalyst system is subject to the limiting factors associated with all

proteins (temperatures below 60° - 70° centigrade are required, there is a considerable cost of production by over-expression, a limited pH stability range, and solubility versus ionic strength etc. being some of the disadvantages).

Figure 3. Zinc cyclen (zinc 1,4,7,10-tetracyclododecane [11]).



Zinc-1,5,9-triazacyclododecane, (zinc-N3ane), and the more catalytically active zinc 1,4,7,10-tetracyclododecane, zinc-cyclen, (Figure 3), are discussed by Zhang et.al [10] and Zhang and van Eldik [11]. Such complexes could be used to capture CO₂ into water. If the stability and catalytic efficiency of the catalysts can be proven, - the laboratory studies could then be scaled up for pilot plant studies. The inorganic complexes would be expected to be much more stable to extremes of heat, pH, impurities and ionic strength than CA, they have low molecular weights (compared to CA with molecular weight around 30,000g/mol), hence the use of the inorganic catalysts in a capture system should be more cost effective than CA or the amine system. In the initial studies described here, the dehydration rate constants by the zinc(II)cyclen and zinc(II) tripod complexes have been measured.

3 Experimental:

3.1 Ligands.

3.1.1 Cyclen was purchased from Macrocyclics Pty Ltd and used without further purification.

3.1.2 Tripod L1 Tris-(2-benzimidazolymethyl)-amine was synthesized from *o*-phenylene diamine and nitrilotriacetic acid by the method described by Thompson et.al. [17]. Nitrilotriacetic acid (15.3 g, 0.08 mol) and *o*-phenylene diamine (27 g, 0.25 mol) were finely ground and heated together at 200 °C in an oven. The reaction mixture was cooled, crushed then dissolved in methanol, decolorized by boiling with charcoal, filtered hot and then the volume was reduced with the product crystallizing out in 50% yield.

3.1.3 Tripod L1S, Nitrilo-tris(2-benzimidazolymethyl-6-sulfonic acid), was prepared by the method as described by Nakata et.al. [6].

3.2 Complexes.

3.2.1 Bovine Carbonic anhydrase from erythrocytes was purchased from the Sigma Company and used without further purification.

3.2.2 Zinc-Cyclen: Zinc-1,4,7,10-tetraazacyclododecane (zinc-Cyclen) was prepared by the method of Zhang et. al. [11]. The ligand 1,4,7,10-tetraazacyclododecane, (Cyclen - 150 mg, 0.87 mmol), and zinc perchlorate Zn(ClO₄),6H₂O, (325 mg, 0.87 mmol), were dissolved separately in 5 mL of ethanol and the zinc perchlorate solution was added over an hour and a half to the ligand solution with the temperature maintained at 50 -60 °C, a white precipitate was formed, washed in ethanol and dried over silica gel. Yield 100 mg, 25%.

3.2.3 Copper Cyclen: Cyclen (150 mg, 0.87 mmol), and copper acetate (162 mg, 0.87 mmol) were dissolved separately in 5 mL of ethanol and added together over 1.5 h. The light blue colour of the copper acetate became a royal blue colour as the complex was formed. The deep blue solution was evaporated to dryness. The copper-cyclen complex was extremely soluble in ethanol and in water, and the solid was deliquescent. Yield 145 mg, 69%.

3.2.4 Zinc-L1 tripod: Zinc-tris-(2-benzimidazolymethyl)-amine was prepared by the method of Thompson et.al. [17]. Stoichiometric amounts of Zn(ClO₄),6H₂O and L1 were dissolved separately in hot ethanol and the hot solutions mixed with stirring. Reduction of volume and cooling produced a solid product. Yield 35%.

3.2.5 Zinc-L1S tripod: The zinc-L1S tripod, (Zn-Nitrilo-tris(2-benzimidazolymethyl-6-sulfonic acid) was prepared by the method of Nakata et. al. [6]. An aqueous solution of L1S and Zn(ClO₄),6H₂O was adjusted to pH 7 with NaOH solution. Addition of ethanol produced a blue-white solid compound. Yield 25%.

3.3 Kinetic measurements were performed by following the loss in weight using a loosely stoppered conical flask on an analytical balance with 2-5 mL of 1M sodium bicarbonate solutions added to buffer and enzyme. Blank measurements were also performed to take account of evaporative losses and spontaneous dehydration of the bicarbonate solutions at the acidic pH 6. A typical experiment was performed as follows: Into a conical flask with a stopper was measured 25 mL of a 0.1M acetate buffer pH 6, one drop of Dow Corning antifoam, and 0.5 mL of catalyst at a concentration of 3-10 mg/mL. In a separate flask was mixed 2.5 mL of 1.0M NaHCO₃ solution and 42 mL of water. At zero time the solutions were mixed and the weight recorded on an analytical balance accurate to 0.0005 g. The weight was recorded every 30 seconds to obtain an estimate of the initial rate of reaction (loss of CO₂).

4. Results and Discussion.

The second order rate constants $k_{cat}^h (M^{-1} s^{-1})$ and $k_{cat}^d (M^{-1} s^{-1})$ for the hydration or dehydration reactions respectively as reported in the literature and / or measured in this study are summarized in Table 1.

Table 1. The kinetic data for carbonic anhydrase and some model metal (zinc) complexes that show reversible hydration of CO₂ to bicarbonate ion and the dehydration of bicarbonate back to CO₂.

Complex/ Enzyme	pKa of H ₂ O ligand	Temperature °C	pH	k_{cat}^h M ⁻¹ S ⁻¹	k_{cat}^d M ⁻¹ S ⁻¹	Reference
HCAI	ca. 7	25	7	200,000	-	[11]
HCAII	ca. 7	25	7	1,100,000	220,000	[11]
Co(II)HCA	ca. 6.58	25	7	305,000	-	[11]
Bovine CA	ca. 7	25	6		35,000	This study
Bovine CA	ca. 7	55	6		95,000	This study
Zn-N3ane-OH ⁻	7.3	25	8-10	581	-	[10]
Zn-N3ane-H ₂ O	7.3	25	ca. 6	-	4.8	[8], [7]
Zn-cyclen -OH ⁻	8.1	25	>9	3,300		[11]
Zn-cyclen -H ₂ O	8.1	25	ca. 6		51	[11]
Zn-cyclen -H ₂ O	8.1	25	6		55	This study
Zn-cyclen -H ₂ O	8.1	55	6		168	This study
Cu-cyclen -H ₂ O	8.1	25	6		63	This study
Cu-cyclen -H ₂ O	8.1	55	6		121	This study
Tripod ZnL1S	8.3	15	9.5	3,300		[6]
Tripod ZnL1S	8.3	25	9.5	10,000* (*extrapolated)		[6]
Tripod ZnL1S	8.3	25	6		363	This study
Tripod ZnL1S	ca 8.3	55	6		797	This study
Tripod ZnL1	ca 8.3	25	6		235	This study
Tripod ZnL1	ca 8.3	55	6		684	This study

The catalysts studied in this work, (Table 1), carbonic anhydrase (CA) which is a zinc(II) metallo-enzyme, model zinc(II) and copper(II) complexes with cyclen, tripodal complexes with L1 and L1S, are suggested as suitable catalysts to be used in the CO₂ absorption/desorption process, using water as solvent in place of high concentrations of amine solvents. The zinc (II) complexes have been reported to mimic the activity and the mechanism as shown by

CA for the $\text{CO}_2/\text{HCO}_3^-$ reaction cycle. In this study, the second order rate constants $k_{\text{cat}}^{\text{d}}$, for the dehydration reaction at 25 °C and 55 °C have been calculated for comparison with the fast CA enzyme.

The basis of the catalysis is the lowering of the pKa of the liganded water molecule attached to the zinc metal from the pKa of around 15.5 for the free water molecule, to around pKa = 7 in CA and in the range of pKa = 6 – 9 in the mimetic complexes. Catalysis of the forward reaction (hydration of CO_2 to HCO_3^-) proceeds at the high end of the pH range (around pH 9) with the concurrent release of a proton, when the active catalyst is in the $[\text{L}-\text{Zn}-\text{OH}]$ form. The reverse reaction (dehydration of HCO_3^-) proceeds at the lower pH (around pH 6), with the active form of the catalyst as $[\text{L}-\text{Zn}-\text{OH}_2]$.

Simsek and Bond [14], and Bond et. al. [21], have investigated the use of the enzyme CA to catalyze CO_2 hydration, (the absorption step), and proposed that the subsequent sequestration should be done by precipitation using sources of cations, (particularly calcium ions); the sources proposed included seawater, waste brines from desalination operations, or from saline aquifers. In this proposal, Simsek and Bond [14] note that the amounts of solids produced and the amounts of brines required would be very large – a 300 MW plant would produce around 290 tonne of CO_2 per hour and require around 750,000 tonne of seawater per hour and produce 666 tonne of calcium carbonate per hour. Trachtenberg and Bao [4] suggested the use of CA in a contained liquid membrane (CLM) utilizing CA as catalyst with a pressure differential between the feed (hydration) side and the sweep (dehydration/ stripping) side of the membrane. This approach is a novel means of reducing the stripping penalty, and is fast enough to be feasible for further development. (The pressure differential aspect may also enhance a catalytic process of the type that is proposed in this study).

Both of these proposed methodologies could be used as an alternative to MEA absorption and stripping, particularly if the enzyme could be made more robust by stabilization. Simsek and Bond [18] have suggested the CA enzyme may be immobilized in chitosan/alginate beads, and Bao and Trachtenberg [4] have reported a lifetime of up to six months without immobilization would apply to CA in the contained liquid membrane. In practical terms, Bao and Trachtenberg [4] have defined CA as a family of enzymes, each with a different temperature range, and catalysis of the reaction rate is only modestly temperature sensitive, and have suggested that for a thermophilic form of the enzyme CA the upper temperature limit is around 85 °C.

The approach suggested in this study is the use of bulk liquid and catalyst to capture CO_2 from flue gases (at up to 15% of CO_2) as bicarbonate at high pH, around 9, and then strip the CO_2 using the same catalyst with lowered pH around 6. The zinc mimetic catalyst is to be used for both the forward and the back reaction, as it is switched from the liganded (OH^- /dehydrogenated) active hydration catalytic form to the water liganded (dehydration active form) by passive and active (perhaps electrochemical) control of the pH. The optimum pH for the absorption (hydration) process is at least one pH unit above the pKa of the liganded $\text{H}_2\text{O}/\text{OH}^-$ in the catalyst where 90% of the catalyst is in the deprotonated (OH^-) active form. For the stripping (dehydration reaction) the pH needs to be at least one pH unit below the pKa of the water ligand in the protonated (H_2O) form. Lindsog and A. Liljas [5] give the pKa values that apply; for CA the pKa of the liganded water is around 6.9 and for the zinc complexes the pKa's have values between 7 – 8.5, so at pH 9 or above the hydration catalyst function of CA is favoured, while at pH 6 or below the dehydration function of the CA catalyst is the active reaction.

The dehydration (stripping) reaction is the energy intensive step so the initial studies have been made of the rates of dehydration, but all the catalysts considered have been shown to catalyze reversibly. It should be noted however that there is an apparent general trend for the dehydration rate to be one or two orders of magnitude smaller than for the hydration reaction. This is apparent from Table 1; for CAII, for the hydration $k_{\text{cat}}^{\text{h}}$ is $10^6 \text{ M}^{-1}\text{s}^{-1}$ – with the corresponding dehydration $k_{\text{cat}}^{\text{d}}$ around $10^5 \text{ M}^{-1}\text{s}^{-1}$, Zhang and van Eldik [11]. Similarly, for Zn-N3ane, $k_{\text{cat}}^{\text{h}}$ is around $600 \text{ M}^{-1}\text{s}^{-1}$ [10], while $k_{\text{cat}}^{\text{d}}$ for Zn-N3ane $\text{M}^{-1}\text{s}^{-1}$ is around $5 \text{ M}^{-1}\text{s}^{-1}$ for dehydration [8], [7]; for the cyclen-Zn the figures are $k_{\text{cat}}^{\text{h}}$ around $3300 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{cat}}^{\text{d}}$ around $51 \text{ M}^{-1}\text{s}^{-1}$ [11]. Finally for the tripod Zn-L1S, $k_{\text{cat}}^{\text{h}}$ is around $10000 \text{ M}^{-1}\text{s}^{-1}$ as extrapolated (to 25 °C) by Nakata et. al., and $k_{\text{cat}}^{\text{d}}$ (for dehydration) values of 363/ 797 $\text{M}^{-1}\text{s}^{-1}$ have been measured at 25 °C / 55 °C in this study (Table 1).

From Bao and Trachtenberg [4], the carbonic anhydrases are a family of enzymes that have an upper limit for the thermophilic forms of 85 °C, and the rate of catalysis of CA is not very responsive to temperature increases. In this study it has been determined that the zinc complexes examined can be expected to be more stable than CA at the

increased temperatures, and have a larger k value at higher temperatures. The utilization of waste heat alone from power generation may be sufficient to provide a high enough temperature for fast catalysis of the stripping step.

The pH in the experiments of this study have been controlled by buffer solutions and/ or adjusted by acid or base additions. The hydration reaction releases hydrogen ions automatically as the CO_2 is absorbed, and the dehydration reaction releases hydroxide ions in the reverse reaction. Thus the pH momentum is automatically adjusted in the correct direction ready for a new catalytic absorption or desorption cycle; to maintain optimum velocity in scaled up industrial systems however the pH may need to be further adjusted perhaps electrochemically, to ensure that the catalyst is optimally converted to the form required for the forward or reverse reaction required. The additional electrical power for electrochemical control could also allow production of hydrogen gas which could be offset against the additional energy requirement. Aines et.al. [22] have proposed that ion pumping of bicarbonate, that is reverse osmosis, could be used to effect an increase in the concentration of bicarbonate, and this process alone could be used to capture and then strip CO_2 . If ion pumping was included, the catalytic effect of the mimetic zinc complexes would assist in increasing the bicarbonate concentration at the higher pH.

A recent report from Mani et. al. [23], reported the absorption of CO_2 into potassium carbonate solutions at temperatures in the range of 10 – 60 °C followed by addition of zinc(II) salts resulting in a partial stripping of CO_2 (accompanied by the production of basic zinc carbonate precipitates). This process is of interest because of the fast rates of absorption and desorption of CO_2 - again associated with zinc at low (ambient) temperatures - although it is not the reversible capture/stripping catalysis using the zinc complexes (such as Zn-LIS) that has been proposed in this study.

5. Conclusion

These initial studies of several zinc complexes which mimic the catalytic function of carbonic anhydrase, demonstrate that a CO_2 capture system in water may be feasible to reduce the energy penalty and other disadvantages inherent in the current technology using amine solvents. The initial rates of dehydration that can be achieved by using the zinc catalysts are less than those of the fast CA enzyme, but can be achieved at moderate temperatures and around neutral pH, at a rate that is comparable with that of amine systems. Additional research is to be undertaken to examine further complexes and to develop the laboratory studies for an improved process and up-scaling. Future directions of investigations: the zinc catalysts may be able to be immobilized in polymeric matrices in a similar way to the immobilization as reported by Bond et al [21], or alternatively finely divided heterogeneous catalysts instead of the homogeneous systems discussed here may be viable.

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