A carbonic anhydrase inspired temperature responsive polymer based catalyst for accelerating carbon capture

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GRAPHICAL ABSTRACT

ABSTRACT

A temperature responsive carbonic anhydrase mimicking compound (PNiPAm-co-CyclenZn) was synthesised and characterized to assess its potential as a rate promoter for carbon dioxide (CO_2) capture using solvent absorption. Development of novel rate promoters, such as the catalytic polymer discussed in this study, can improve reaction kinetics and reduce the cost of CO_2 capture. Results showed that the lower critical solution temperature (LCST) of PNiPAm-co-CyclenZn is 33.7 °C which is close to the physiological temperature. Above the LCST, PNiPAm-*co*-CyclenZn undergoes a phase transition from a swollen hydrated state to a shrunken dehydrated state. This property can potentially enable easy separation of PNiPAm-co-CyclenZn from the CO_2 loaded solution exiting the absorber column so that it does not enter the high temperature stripping column. In the reaction between CO_2 and H_2O, the catalysis coefficient at 298 K of PNiPAm-co-CyclenZn was determined to be $380 \pm 20\,M^{-1}\,s^{-1}$ at a pH of 7.36 and $2330 \pm 40\,M^{-1}\,s^{-1}$ at a pH of 9.06. Arrhenius fitting of the catalysis coefficients showed an activation energy of 60 ± 2 kJ/mol at pH 7.36. This study presents the first example of a temperature responsive polymeric catalyst for carbon dioxide absorption. The catalyst was developed with the aim of increasing the absorption rates of carbon dioxide in bicarbonate forming amine solutions and carbonate solvents that have slow absorption kinetics.

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1. Introduction

It has been widely recognised that greenhouse gases emissions to the atmosphere, especially large amounts of carbon dioxide (CO_2), are major contributors to climate change [1,2]. Carbon capture and storage (CCS) is accepted as an efficient way to reduce the rise of CO_2 emissions in the atmosphere [3,4]. However, the high costs of carbon capture technologies are still a barrier for industrializing the CCS process [5]. Many carbon capture technologies including solvent absorption [6–9], solid adsorption [10], membrane technologies [11,12] and mineralization processes [13] have been investigated in the last decades for reducing the overall cost of CO_2 capture in order to encourage industrial implementation of CCS. Fast CO_2 uptake kinetics are essential for reducing the capture cost of these technologies.

Carbonic anhydrase (CA) is one of the fastest enzymes known [14]. It controls the conversion of CO_2 and water to bicarbonate and protons and is essential for all organisms, creatures and human beings [15]. Carbonic anhydrase has been widely used for promoting carbon capture processes in solvents [16–18], mineralization [19,20] and membrane contactors [21,22]. However, most studies have shown that the enzyme is unstable under harsh industrial conditions especially at high temperatures, such as those typically encountered in solvent desorption (393 K) [16,23]. Developing more industrially stable carbonic anhydrase enzymes or replacing natural carbonic anhydrase with mimicking compounds is recognized as a solution to this problem.

The catalysis mechanism of CA is outlined in Fig. 1 [24]. The co-ordinated hydroxide ion is stabilized by hydrogen-bonding with a neighbouring threonine residue (Thr199), which is activated by a closely related glutamic acid residue. The catalytic centre is encased within a 17 Å-deep cavity, the walls of which are lined with hydrophobic residues, which are particularly prevalent in the region of the 'deep' water. In the first step, the CO_2 displaces the 'deep' water, thus positioning itself close to the zinc bound hydroxide ion. In the second step, the CO_2 reacts with the hydroxide ion and this hydration reaction is facilitated by the proximate orientation of the zinc bound hydroxide ion to the enzyme-substrate complex. In the third step, the bicarbonate (HCO_3^-) ion is produced which diffuses from the pocket, and the zinc coordinating site is replaced by a molecule of water. The zinc ion binds a further molecule of water, which is deprotonated in the final, rate-limiting, step of the catalytic cycle. The zinc ion facilitates the deprotonation process due to its strong ability to accept electrons, allowing it to stabilise negative charge.

Despite the complicated protein structure and catalysis mechanism of natural carbonic anhydrase [24] (Fig. 1), the catalytic site is relatively simple [25]. Researchers have been studying mimicking compounds of carbonic anhydrase to understand its structure-reactivity relationship of the active site for decades. Metals centres including Zn (II) [26–28], Co (II) [26,27], Cu (II) [27,28], Ni (II) [29], Hg (II) [26] and Cd (II) [30] have been studied, among which Zn (II) is the most promising metal [26–28]. For Zn compounds, a range of ligands [27,31–36] have been investigated. However, research shows that the catalysis efficiency of these carbonic anhydrase mimicking compounds is still comparatively low compared with natural carbonic anhydrase and the ligands continue to face degradation or decomposition problems as operating temperatures increase. Despite understanding the structure of this enzyme, development of an effective polymer based carbonic anhydrase mimicking catalyst has not yet been realized.

Poly(N-isopropyl acrylamide) (PNiPAm) is a temperature responsive polymer that has found applications in macroscopic gels, microgels, membranes, sensors, biosensors, thin films, tissue engineering, and in drug delivery [37–40]. It changes hydrophilicity and hydrophobicity abruptly at the lower critical solution temperature (LCST). At temperatures lower than the LCST, PNiPAm orders itself in aqueous solution and the amide group is hydrogen bonded with the water molecules. While at higher temperatures, PNiPAm releases water, becomes hydrophobic and precipitates out from aqueous solution. Here, we have developed a carbonic anhydrase mimicking material using PNiPAm as the polymer support. The choice of PNiPAm is threefold; firstly, the interaction of water with the polymer provides the water necessary for the CA mechanism; secondly, the polyamide in the polymer structure mimics the amides of the protein backbone which is also crucial in the catalytic mechanism; and thirdly, the temperature responsiveness of PNiPAm enables further understanding of structure function relationships in regard to hydrophobicity of the nanoenvironment.

1,4,7,10-Tetraazacyclododecane (cyclen) is one of most efficient carbonic anhydrase mimicking compounds reported to date [31]. In this study, we synthesized a cyclen functionalized PNiPAm as a temperature responsive polymer mimicking carbonic anhydrase which will precipitate as temperature increases (> 308 K). This will allow the mimicking compound to be readily separated from the loaded solution of a traditional CO_2 solvent absorption process, and thus avoid carry-over into the higher temperature desorption process (typically of the order of 393 K) where it would be destabilised.

2. Martials and methods

2.1. Materials

Chemicals were used as received unless otherwise stated. Cyclen (1,4,7,10-Tetraazacyclododecane > 97.0%) 4-vinylbenzyl chloride, potassium carbonate (K_2CO_3), azobisisobutyronitrile (AIBN), and zinc perchlorate hexahydrate ($Zn(ClO_4)_2 \cdot 6H_2O$) were purchased from Sigma-Aldrich. Indicator 4-nitrophenol ($\geq 99.5\%$) was purchased from Fluka Analytical. Buffer MOPS (3-(N-Morpholino)propanesulfonic acid, > 99.5%) was purchased from Sigma-Aldrich. AIBN was recrystallized in methanol prior to use. N-isopropylacrylamide (NiPAm) (98%, stabilized with MEHQ) was supplied by Tokyo Chemical Industry Co., Ltd and was recrystallized from a mixture of toluene/hexane (v/v 2:3) prior to use. Tetrahydrofuran (THF) GPR Reactapur (stabilized with BHT) and toluene (Analar Normapur) were purchased from VWR Chemicals. Diethyl ether of RCI premium grade was obtained from ACI Labscan. Dichloromethane (DCM) and methanol of reagent grade from ChemSupply. Dialysis tubing (regenerated cellulose, SnakeSkin™, 3500 MWCO) was used to dialyze functionalized polymers. Carbon dioxide (CO_2) and its mixtures with nitrogen were purchased from Coregas
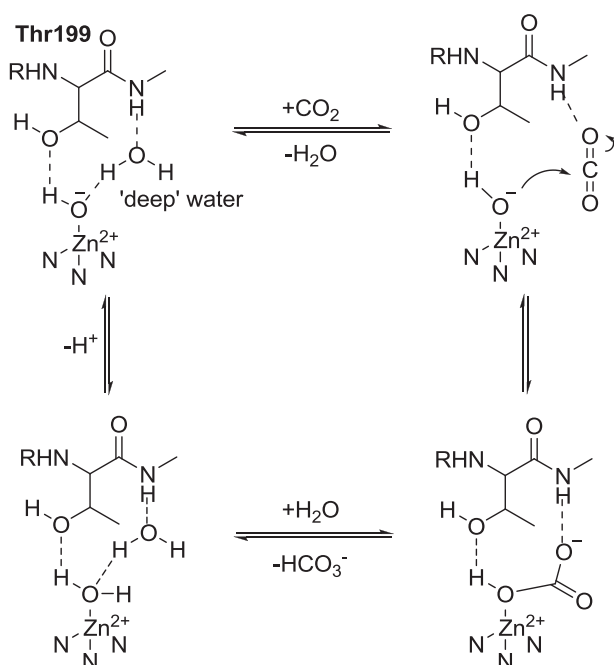

Fig. 1. Proposed mechanism for the hydration of CO_2 by carbonic anhydrase.