Kinetics of absorption of carbon dioxide in aqueous amine and carbonate solutions with carbonic anhydrase

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ABSTRACT

In the present work the absorption of carbon dioxide in aqueous N-methyldiethanolamine (MDEA) and aqueous sodium carbonate with and without carbonic anhydrase (CA) was studied in a stirred cell contactor in the temperature range 298–333 K. The CA was present as free enzyme and is compared to the opportunity to immobilise CA on particles and on fixed packing. Based on the results with MDEA and sodium carbonate, the observed kinetics as a function of the free enzyme concentration are described. These results were incorporated into the Procede Process Simulator (Arendsen et al., 2012) to determine the impacts of the kinetic benefit of CA on commercial absorber sizing for carbon dioxide capture from flue gases. Based on simulations performed, CA in the absorption solution can provide substantial benefits for reducing absorber sizing with these normally kinetically limited, but energy efficient solvents. It was also shown that CA immobilised to fixed packing material is not a viable option for using CA in a carbon dioxide capture process.

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1. Introduction

Carbon dioxide from the flue gases of power plants and other industrial sources is commonly seen as one of the major contributors to climate change (Forster et al., 2007). The conventional method to capture this CO_2 is to apply an absorber–desorber process, in which the acid gas is separated using fast aqueous amine solutions such as monoethanolamine (MEA) or N-methyldiethanolamine (MDEA) promoted by piperazine (Kohl and Nielsen, 1997).

Although amine solutions are relatively well known, their potential application in flue gas processes encounters several drawbacks, most notably the unfavourable desorption energy requirements and the emission of various degradation products (Fostås et al., 2011; Jackson and Attalla, 2011).

Alternatively, solvents such as unpromoted MDEA or alkali-carbonate solutions seem very attractive as the solutions are more stable and less expensive. Moreover, compared to primary or secondary amines, they have relatively low heats of reaction with carbon dioxide, leading to the potential for lower regeneration energy costs in the desorber. However, application of these solvents in post-combustion capture of carbon dioxide is compromised by their low reactivity with CO_2 at typical flue gas conditions, which would result in unrealistically large absorber columns.

It is, however, possible to enhance the absorption rate to such an extent that these alternative solvents would be technically and economically viable with the introduction of the enzyme carbonic anhydrase (CA) applied as a catalyst. CA is a powerful catalyst that accelerates the transformation of carbon dioxide to the bicarbonate ion. CA is found in the blood of humans and other mammals and facilitates the efficient transfer of CO_2 during respiration (Dodgson, 1991; Chegwidden and Carter, 2000; Geers and Gros, 2000). Successful genetic modification of this enzyme makes it possible to use it in combination with aqueous tertiary amines and alkali-carbonate solutions within an industrial environment for flue gas treatment.

In this work, the absorption of carbon dioxide in aqueous MDEA solutions and aqueous sodium (bi)carbonate solutions has been studied in a stirred cell contactor over a wide range

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a_{GL}	gas–liquid contact area ($m^2 m^{-3}$)
a_{LS}	liquid–solid contact area ($m^2 m^{-3}$)
C	concentration ($mol\ m^{-3}$)
D	diffusion coefficient ($m^2 s^{-1}$)
J	absorption flux ($mol\ m^{-2} s^{-1}$)
k_A	(second order) reaction rate constant for component A ($m^3 mol^{-1} s^{-1}$)
k'	reaction rate constant (s^{-1})
k^*	enzyme enhanced reaction rate constant ($m^3 mol^{-1} s^{-1}$)
k_G	gas phase mass transfer coefficient ($m\ s^{-1}$)
k_L	liquid side G–L phase mass transfer coefficient ($m\ s^{-1}$)
k_{LS}	liquid side L–S phase mass transfer coefficient ($m\ s^{-1}$)
k_{OV}	overall rate constant (s^{-1})
k''_r	surface kinetic rate constant ($m\ s^{-1}$)
m	physical solubility ($C_{L,CO_2}/C_{G,CO_2}$)
P	pressure (Pa)
R	gas constant = 8.314 ($J\ mol^{-1} K^{-1}$)
T	temperature (K)
ToF	turnover factor
V	volume (m^3)

Greek

β	liquid hold-up in the column (m^3 liquid m^{-3} reactor)
δ	liquid height on the packing material (m)
η	viscosity (Pa s)

Super/subscripts

0	initial
Am	alkanolamine
CO_2	carbon dioxide
Enz	enzyme
eq	equilibrium
G	gas phase
H_2O	water
L	liquid phase
vap	vapour

Fig. 1. The mechanism of CO_2 hydration in presence of the enzyme carbonic anhydrase.

of temperatures and CA concentrations. Furthermore, the use of immobilised CA on particles and fixed packing are evaluated.

2. Theoretical background

2.1. Kinetics

In aqueous (sodium) carbonate systems, carbon dioxide can react with:

1 hydroxide ion (Pinsent et al., 1956; Pohorecki and Moniuk, 1988)

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

with the following overall forward reaction rate:

$$R_{CO_2} = k_{OH}C_{OH}C_{CO_2} = k'_{OH}C_{CO_2} \qquad (1)$$
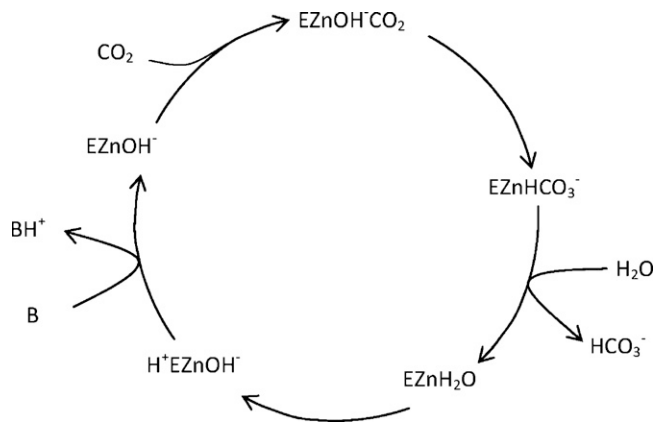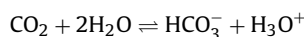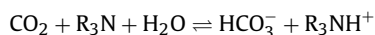
2 water (Pinsent et al., 1956; Kern, 1960)

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

with the following overall forward reaction rate:

$$R_{CO_2} = k_{H_2O}C_{CO_2} = k'_{H_2O}C_{CO_2} \qquad (2)$$

In the case of a tertiary alkanolamine system, CO_2 can also react with:

3 tertiary alkanolamine (Versteeg and van Swaaij, 1988a; Littel et al., 1990; Benamor and Aroua, 2007)

$$CO_2 + R_3N + H_2O \rightleftharpoons HCO_3^- + R_3NH^+$$

with following overall forward reaction rate:

$$R_{CO_2} = k_{Am}C_{Am}C_{CO_2} = k'_{Am}C_{CO_2} \qquad (3)$$

Since these reactions occur simultaneously and in parallel, the overall forward reaction rate constant of this system becomes:

$$k_{OV} = k'_{OH} + k'_{H_2O}(+k'_{Am}) \qquad (4)$$

In the presence of the enzyme carbonic anhydrase the reaction mechanism is extended with Fig. 1 presented"wheel of reactions" (Lindskog and Silverman, 2000; Larachi, 2010).

The base used during enzyme regeneration can either be the carbonate ion, hydroxide ion, alkanolamine or even the during reaction formed bicarbonate ion (Larachi, 2010). In the latter case, carbon dioxide and water are released as protonated base.

In the presence of the enzyme carbonic anhydrase, reaction 2 is the most important reaction during absorption of carbon dioxide into aqueous MDEA solutions. The forward reaction rate constant for the enzyme catalysed reaction is calculated from the overall forward reaction rate (Penders-van Elk et al., 2012):

$$k^*_{H_2O} = \frac{k_{OV,with\ enzyme} - k_{OV,without\ enzyme}}{C_{H_2O}} \qquad (5)$$

Eq. (5) is only valid if the experiments are in the pseudo first order regime for all reactions involved.

All above mentioned reactions are equilibrium reactions. When the absorption solution gets loaded with CO_2, the reverse reactions also become important; even stripping of CO_2 can occur. In that case the interpretation of the experimental results is not straight forward. Therefore, the Procede Process Simulator (PPS) is used for the interpretation of the experiments with a CO_2-loading larger than 0.5 mol CO_2/mol Na. PPS is a flow sheeting tool, specially designed for steady state simulation of acid gas treating processes, developed by Procede (van Elk et al., 2009; Procede, 2011; Arendsen et al., 2012).