CO_2 capture from flue gas using amino acid salt solutions

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Abstract
An initial kinetic study was performed on the reaction of CO_2 with various potassium amino acid salt solutions at 298 K. Kinetics were measured at 0.5 kmol/m^3, reason for which only apparent kinetic constants are presented. The results were compared with the work of Kumar et al. [1] and Penny and Ritter [2].

Keywords: CO_2, flue gas treatment, kinetics, potassium amino acid salt solutions

Introduction

One of the most alarming global environmental problems of today is the increase of the natural greenhouse effect. This problem is mainly caused by the increasing atmospheric carbon dioxide concentration due to the burning of fossil fuels for power generation. To reduce these problems, the carbon dioxide emissions from flue and fuel gases produced in combustion and gasification processes in power plants have to be decreased by efficiency improvements and carbon dioxide capture.

The removal of acid gases such as carbon dioxide, H_2S or COS by absorption in aqueous alkanolamine solutions is widely used in the chemical industry. Carbon dioxide reacts with primary and secondary amines, reaching an equilibrium of carbamate, bicarbonate, and carbonate species. The initial absorption reaction is the formation of the carbamate, which can then undergo hydrolysis to the bicarbonate and, if conditions such as pH are suitable, the carbonate species. The degree of hydrolysis of the carbamate is determined by parameters such as amine concentration, solution pH, and the chemical stability of the carbamate [3]. In aqueous solutions, carbon dioxide reacts with alkanolamines to the corresponding carbamate according to the following overall reaction [4]:

$$CO_{2(g)} + 2RNH_{2(l)} \rightleftharpoons RNH^{+}_{3(aq)} + RNHCOO^{-}_{(aq)} \quad (1)$$

The zwitterion reaction mechanism [3] is generally accepted as the reaction mechanism [5, 6]:

$$CO_{2(aq)} + RNH_{2(l)} \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} RN^{+}H_2COO^{-}_{(aq)} \quad (2)$$

$$RN^{+}H_2COO^{-}_{(aq)} + B \xrightarrow{k_B} RNHCOO^{-}_{(aq)} + HB^{+}_{(aq)} \quad (3)$$

Reaction (3) is the base-catalyzed deprotonation of the zwitterion by any base existing in the solution. According to this reaction mechanism the base can be either the amine, water, or a hydroxyl ion. Assuming a quasi-steady state condition for the zwitterion concentration, the reaction rate between CO_2 and the amine can be expressed as:

$$r_{CO_2} = k_{app}[CO_2] \quad (4)$$

$$k_{app} = \frac{[RNH_2]}{\frac{1}{k_2} + \frac{1}{\sum k_B[B]}} \quad (5)$$

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where:

$$k_B = \frac{k_2 k_{base}}{k_{-1}} \tag{6}$$

Because the hydroxyl concentration is low in the reaction of CO_2 with the amines, its contribution is assumed to be negligible [4, 7, 8]. On the other hand, when working with aqueous solutions of amines it is necessary to take the hydration of CO_2 into account. The hydration reaction of CO_2 with OH^- is fast and can enhance mass transfer:

$$CO_{2(aq)} + OH^-_{(aq)} \underset{}{\overset{k_{OH^-}}{\rightleftharpoons}} HCO^-_{3(aq)} \tag{7}$$

The overall pseudo-first-order reaction rate constant can then be expressed as:

$$k_{ov} = k_{app} + k_{OH^-}\left[OH^-\right] \tag{8}$$

Alkanolamines degrade as a result of long exposure or repeated use, because of side reactions with CO_2, oxygen, and other contaminants. Because the desire to separate CO_2 from flue gas streams is gaining momentum as a result of environmental concerns, there is an urgent need to develop new solvent systems that are stable in the presence of oxygen. Amino acids (AmA's) have the same functional groups as alkanolamines, and can be expected to behave similar towards carbon dioxide, but do not deteriorate in the presence of oxygen. Kumar et al. [1] have proven this assumption to be valid. Examples of AmA's are glycine and taurine.

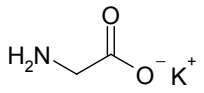

Figure 1. Potassium salt of glycine

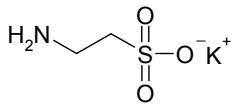

Figure 2. Potassium salt of taurine

An additional advantage of AmA's is the possibility of adding a salt function. The carboxylate group can be neutralized with potassium hydroxide, in order to produce the potassium salt of glycine. This salt function ensures the non volatility of the substance, which is helpful when working at stripper conditions (lowered pressure and elevated temperature). A third advantage is that they can be used in cooperation with simple polyolefin membranes, like polypropene. As opposed to MEA, which can only be used in combination with expensive membranes due to wetting problems.

Here, the reaction kinetics of carbon dioxide with several potassium AmA salt solutions will be studied with a stirred cell setup at 298 K. To ascertain the validity of the setup used, the reaction kinetics of diethanolamine was also studied at 298 K. The AmA salts that were investigated are: 6-aminohexanoic acid (6-ahx), β-alanine (b-ala), L-arginine (arg), L-glutamic acid (glu), DL-methionine (met), L-proline (pro), sarcosine (sar). All chemicals come from Sigma-Aldrich and have purities of at least 98 %.

Methodology and results

Experiments were performed in a closed stirred cell reactor (see Figure 3). Carbon dioxide could be fed to the reactor from two supply vessels that respectively had volumes of ~325 and ~85 ml, or directly from the gas cylinder. The pressure in the reactor, which has a volume of ~720 ml, could be kept constant by a Brooks Smart Series pressure controller model 5850S. The maximum front pressure is 5 bar with a control range of 0 to 1.5 bar. The stirred cell, a double walled glass reactor, was closed by two stainless steel flanges. The reactor is thermostatted with a Julabo MC-4 thermostat. Two separate operating stirrers were used to stir the gas and liquid phase separately. A pressure transducer was connected to the reactor for monitoring the pressure in the reactor, and a second one was connected to the gas supply vessels for determining the pressure in the vessels.

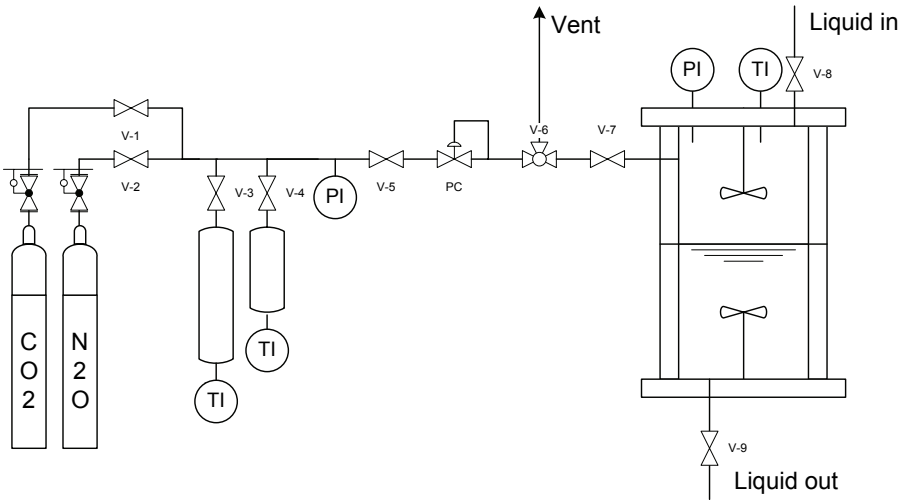

Figure 3. Schematic of the stirred cell setup

The reaction kinetics can be determined when measuring in the pseudo first order reaction regime, which is the case when the following conditions are satisfied:

$$2 < Ha \ll E_A^{\infty} \tag{9}$$

with

$$Ha = \sqrt{\frac{k_{ov} D_{CO_2}}{k_l^2}} \tag{10}$$

and

$$E_A^{\infty} = \sqrt{\frac{D_{CO_2}}{D_{AmA}}} + \sqrt{\frac{D_{AmA}}{D_{CO_2}}} \frac{[AmA]RT}{\nu_{CO_2} m_{CO_2} P_{CO_2}} \tag{11}$$

The Hatta-number should at least be five times smaller than the infinite enhancement factor. The carbon dioxide absorption rate can then be described by:

$$J_{CO_2} = \sqrt{k_{ov} D_{CO_2}} \frac{m_{CO_2} P_{CO_2}}{RT} \tag{12}$$

There were two operating modes that could be applied. Either the pressure in the reactor was kept constant, and the pressure drop was measured in the supply vessel, or the reactor was closed off, and the pressure drop in the reactor was measured. The first operating mode was necessary when the reaction rate of CO_2 with the AmA salt was too high, resulting in very high Hatta numbers. A very high Hatta number has the consequence that the starting pressure in the reactor must be very low (close to the water vapor pressure), to meet condition (9). The pressure drop in the reactor would be too fast to accurately measure the kinetics, and therefore the first operating mode had to be used. The relation between the pressure and time in the supply vessel can be obtained from an in stationary mass balance:

$$P_{CO_2}\Big|_t = P_{CO_2}\Big|_{t=0} - \sqrt{k_{ov} D_{CO_2}} \frac{m_{CO_2} P_R A_{GL}}{V_{SV}} t \tag{13}$$

The relation between the pressure and time in the reactor, when closed off, is given by:

$$\ln P_{CO_2}\Big|_t = \ln P_{CO_2}\Big|_{t=0} - \sqrt{k_{ov} D_{CO_2}} \frac{m_{CO_2} A_{GL}}{V_G} t \tag{14}$$

For all AmA salt solutions the second operating mode was used to determine the k_{ov}. The determination of k_{ov} from the pressure time curve is also described in Blauwhof et al. [4]. The reactor was validated with CO_2 absorption experiments in diethanolamine (DEA) solutions with concentrations of 0.6, 1.0 and 2.0 kmol/m^3. The results were compared with Versteeg and Oyevaar [8] and Blauwhof et al. [4], and were in good agreement with each other.

The potassium salts of the selected AmA's were made by dissolving the AmA in demineralized water and adding an equimolar amount of potassium hydroxide (Riedel-de-Haën). This neutralization step is necessary because the amino acid is present as it zwitterionic form when dissolved in water. And in its zwitterionic form, the amine group is completely protonated and therefore incapable of reacting with the carbon dioxide.

The densities and viscosities of the different AmA salt solutions with concentrations ranging from 0.25 up to 3.5 kmol/m^3 (depending on the solubility of the AmA) were measured with an AP Paar DMA 58 density meter and an ubbelohde viscometer. Solubility and diffusivity were determined using the CO_2-N_2O analogy [9] and a modified Stokes-Einstein relation, given by [10]:

$$\left(D_{N_2O} \cdot \eta^{0.74}\right)_w = \left(D_{N_2O} \cdot \eta^{0.74}\right)_{AmA} \qquad (15)$$

The k_{ov} was determined at 298 K and concentrations of 0.5 kmol/m^3. The concentrations of the solutions were determined by potentiometric titration with a 1.000 N HCl solution (Merck). The pH of the absorbent solution was measured after each experiment with a Metrohm 3 M KCl pH-electrode. The hydroxyl ion concentration was calculated from this pH. The determined k_{ov} values are presented in Table 1, together with the pKa values of the amine groups.

Table 1. k_{ov} values for potassium AmA salts

Amino Acid Salt	pKa	[AmA] (kmol·m^{-3})	k_{ov} (s^{-1})
Taurine	9.06*	0.486	1240
Methionine	9.2†	0.498	809
Glutamic Acid	9.98†	0.492	1419
Sarcosine	10.21*	0.501	2979
β-Alanine	10.33*	0.499	1496
Proline	10.64†	0.495	7146
6-Aminohexanoic Acid	10.95*	0.502	1271
Arginine	12.48†	0.444	3732

*Hamborg et al. [11], †Perrin [12]

Discussion and Conclusions

To calculate the k_{app} from the k_{ov} values it is essential to know the kinetic constant of reaction (7). Pochorecki and Moniuk [13] give three correlations for k_{OH^-}, depending on the ionic strength of the solution and the alkali metal present (Na^+, K^+, or Li^+). The non-ideal behaviour of the liquid phase is lumped into the kinetic constant, making the reaction rate "constant" dependent on the concentration. Considering the high pKa values (12-13) of some AmA salt solutions, and thus high ionic strength of the solution, it can be concluded that the values for k_{OH^-} given by the Pohorecki and Moniuk relation will be very inaccurate. A recent study from Haubrock et al. [14] has shown it to be better to account for liquid phase non-idealities by applying activity coefficients in the kinetic expression. The writers have shown that this approach gives much better results at higher ionic strengths. The only drawback is the need for a thermodynamic model to calculate the kinetics, which is presently not at hand. Therefore, for now we assume that $k_{app} \approx k_{ov}$.

Assuming that the backward reaction in the zwitterion mechanism is negligible compared to the deprotonation of the zwitterion, meaning that (k_{-1} / ($k_2 \cdot \Sigma\, k_{base}[B]$) << 1), the reaction kinetics will simplify into second-order kinetics, given by:

$$r_{CO_2} = k_2 [AmA][CO_2] \tag{16}$$

The reaction rate constant k_2 is then equal to k_{app} / [AmA]. However, Versteeg and Oyevaar [8] have shown for aqueous DEA solutions that there is a shift in reaction order with a change in the amine concentration. For very low DEA concentrations the reaction rate expression will ultimately change into [8]:

$$r_{CO_2} \approx \frac{k_2}{k_{-1}} k_{H_2O} [H_2O][AmA][CO_2] \tag{17}$$

The k_{app} of DEA at a concentration of 0.5 kmol/m^3 (k_{app} = 215 s^{-1}) is therefore much lower than $k_2 \cdot$[DEA] = 1620 s^{-1}. Kumar et al. [1] have shown this behaviour is also exhibited by AmA salt solutions. When the k_{ov} values are compared to the Brønsted relation given by Penny and Ritter [2] (see Figure 4, where k_{ov} are the experimentally determined values of Table 1), the value of MEA is corresponding with this relation, but the one of DEA is not. This follows from the deviating reaction order at lower DEA concentrations. The intrinsic reaction rate constant k_2 of DEA does correspond with the Brønsted relation of primary and secondary alkanolamines [15]. This can be an explanation for the apparently too low k_{ov} values of the measured AmA salt solutions, resulting in an underestimation of the intrinsic reaction rate constant k_2. It is therefore necessary to do kinetic measurements at different AmA salt concentrations, in order to determine the individual mechanistic reaction rate constants (k_2, k_{-1}, k_{H2O}, k_{AmA}, and k_{OH}-) and the correct reaction order.

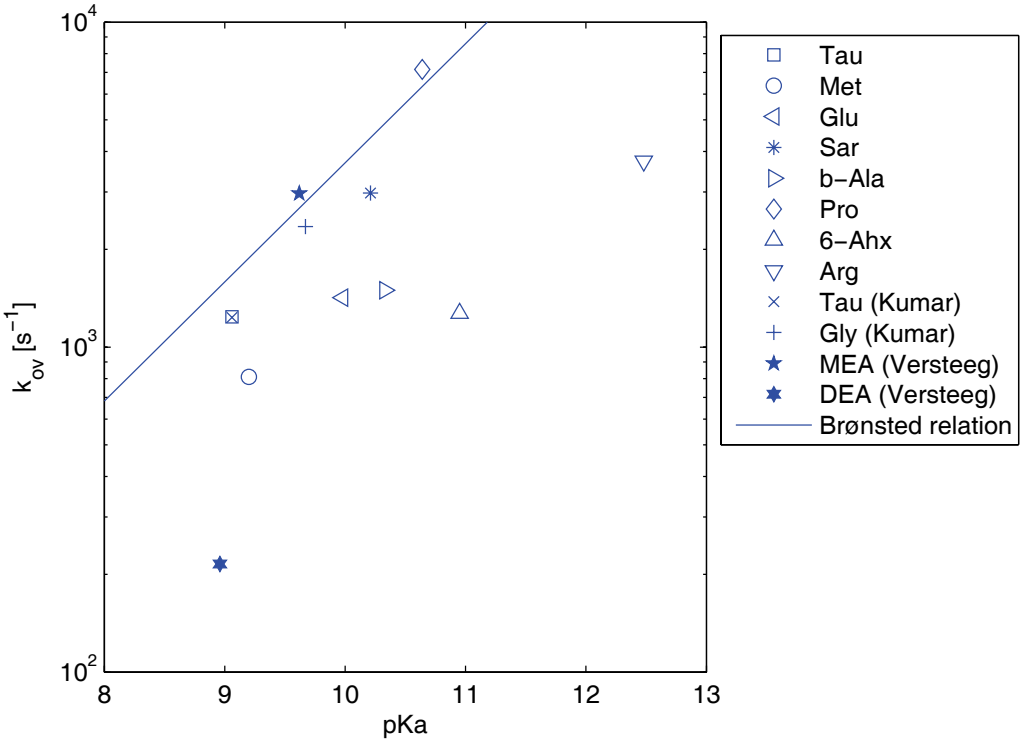

Figure 4. k_{ov} vs pKa; Tau (Kumar) and Gly (Kumar) [1]; MEA (Versteeg) and DEA (Versteeg) [15]; Brønsted relation taken from Penny and Ritter [2] with k_{ov} = exp(0.844·pKa – 6.44)·[AmA]

In the present work the kinetics between CO_2 and 0.5 kmol/m^3 aqueous AmA salt solutions have been studied at 298 K. The overall reaction rate constants are presented and compared with the Brønsted relation of Penny and Ritter [2]. More experimental kinetic data for different AmA salt concentrations will be presented in the future to determine the intrinsic reaction rate constants.

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