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Kinetics of the Reaction of CO_2 with Aqueous Potassium Salt of Taurine and Glycine

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The kinetics of the reaction between CO_2 and aqueous potassium salts of taurine and glycine was measured at 295 K in a stirred-cell reactor with a flat gas−liquid interface. For aqueous potassium taurate solutions, the temperature effect on the reaction kinetics was measured at 285 and 305 K. Unlike aqueous primary alkanolamines, the partial reaction order in amino acid salt changes from one at low salt concentration to approximately 1.5 at salt concentrations as high as 3,000 $mol \cdot m^{-3}$. At low salt concentrations, the measured apparent rate constant (k_{app}) for potassium glycinate is comparable to the values in literature. In the absence of reliable information in the literature on the kinetics and mechanism of the reaction, the applicability of the zwitterion and termolecular mechanism (proposed originally for alkanolamines) was explored. For the zwitterion mechanism, the forward second-order reaction rate constant (k_2) of the CO_2 reaction with amino acid salt seems to be much higher than for alkanolamines of similar basicity, indicating that the Bronsted plot for amino acid salts might differ from that of alkanolamines. The contribution of water to the deprotonation of zwitterion seems to be more significant than reported values for aqueous secondary alkanolamines.

Introduction

The removal of acid gases (like CO_2, H_2S, COS) from industrial and natural gas streams is an important operation in the process industry, and reactive absorption has been the most widely used method for their removal. Aqueous alkanolamine solutions are the commonly used reactive solvents in the gas-treating industry and numerous alkanolamines are available with widely varying reactivity toward CO_2 (while H_2S reacts instantaneously with all amines) and CO_2/H_2S absorption capacity. Thus, the choice of the alkanolamine among primary, secondary, and tertiary sterically or nonsterically hindered amine depends on the process requirements. For the bulk removal of CO_2 or removal of H_2S from a gas stream containing both H_2S and CO_2, information on the mechanism and kinetics of the reaction between CO_2 and the reactive component in the solvent are necessary for the design of the gas−liquid contactor. This information can also be used to improve the overall selectivity toward absorption of H_2S from a gas stream containing CO_2 and H_2S. In the case of alkanolamines, considerable information is available in the literature and has been recently summarized by Versteeg et al. (1996). Besides alkanolamines, carbonate−bicarbonate buffers are used in the bulk removal of CO_2 owing to the low steam requirement for their regeneration (hot carbonate process; Astarita et al., 1983). In actual modern industrial practice, additives (which act as rate promoters) to the carbonate solution are nearly always used. Kohl and Nielsen (1997) have summarized the list of chemicals found to enhance the rate of CO_2 absorption.

Amino acids are a class of chemical species used commercially (Giammarco−Vetrocoke Process) as promoters in carbonate solutions (Kohl and Nielsen, 1997). Also, aqueous so-

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lutions of amino acid salts alone have also been used in the past for the (selective) removal of H_2S or CO_2 from a variety of gas streams. The industrially tested Alkacid process uses three absorption liquids, namely Alkacid M, Alkacid dik, and Alkacid S, depending on the acid gas component (H_2S, CO_2) to be removed and the composition of the gas stream (Kohl and Nielsen, 1997). Of the three just mentioned, the M and dik processes use amino acid salts. The most commonly encountered amino acids used in the gas treating solvents are glycine (Giammarco−Vetrocoke), alanine (Alkacid, BASF), dimethyl glycine (Alkacid, BASF), diethyl glycine (Alkacid, BASF), and a number of sterically hindered amino acids (Exxon). Although amino acids are more expensive than alkanolamines, they have certain unique advantages due to their physical and chemical properties. The amino acid salt solutions were found to have better resistance to degradation, especially in the removal of acid gases from oxygen-rich gas streams like flue gas (Hook, 1997). Due to the ionic nature of the solutions, they also have negligible volatility and higher surface tension. Their reactivity and CO_2 absorption capacity are comparable to aqueous alkanolamines of related classes (Hook, 1997; Penny and Ritter, 1983).

Design of gas−liquid contactors for the removal of CO_2 using aqueous amino acid salt solutions requires information, among others, on the kinetics of the reaction between CO_2 and amino acid salts. Unlike aqueous alkanolamines, there is limited information in the literature in general on the absorption of CO_2 in aqueous amino acid salt solutions, and in particular on the mechanism and kinetics of the reaction between CO_2 and aqueous amino acid salt solutions. The available information is briefly summarized in the following section. In the present study, the kinetics of the reaction between CO_2 and aqueous potassium salt of taurine (2-aminoethansulfonic acid) and glycine (aminoacetic acid) were investigated over a wide range of concentrations (100−4,000 $mol \cdot m^{-3}$) and temperatures (285−305 K).

Literature Review

During the absorption of CO_2 in aqueous amino acid salt solutions, the following reactions can occur

$$CO_2 + AmA \rightleftharpoons AmACOO^- + AmAH^+ \quad (1)$$

$$CO_2 + OH^- \rightleftharpoons HCO_{3^-} \quad (2)$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3. \quad (3)$$

The forward rate constants as well as the equilibrium constants of the reaction (Eqs. 2 and 3) are available in the literature (Pohorecki and Moniuk, 1988; Pinsent et al., 1956; Edwards et al., 1978). However, the relative contribution of the reaction (Eqs. 2 and 3) to the overall absorption rate for most of the amino acid salts that possibly can be used in gas treating is not significant, and hence the forward rate constant of the reaction (Eq. 1) needs to be determined accurately. Most of the experimental techniques used in the past to measure the kinetics of the reaction between CO_2 and amino acid salts were relatively inaccurate (with respect to the experimental procedure and the interpretation of the results) in comparison to the present-day methods. Also, the amino acid salt concentration range over which the experiments were conducted was very low, as they were used mainly as promoters. It may be highly inaccurate to extrapolate the data to higher concentrations, which is of more use in the gas-treating process.

Jensen and Faurholt (1952). The reaction rates were determined by the "competitive" method. In this method, a given volume of an aqueous solution of alanine containing a known molar excess of sodium hydroxide was "shaken vigorously" with a gas phase containing CO_2 for 2 min. The initial partial pressure of CO_2 in the gas phase was 50 kPa. At the end of the reaction time, the carbamate content as well as the sum of carbamate and carbonate content in the reaction mixture were determined immediately. The ratio of carbamate to carbonate in the reaction mixture was used to determine the relative rates of the reaction of CO_2 with OH^- and amino acid. The rate of formation of carbamate was assumed to be first order with respect to amino acid, as given in Eq. 4.

$$\frac{\%\ \text{Carbamate}}{\%\ \text{Carbonate}} = \frac{k_{AmA}[AmA]}{k_{OH^-}[OH^-]}. \quad (4)$$

Here $[OH^-]$ and [AmA] are the averaged values of the initial and final concentration of OH^- and AmA measured during the experiment. The maximum concentrations of amino acid and NaOH used in the measurements were 150 and 90 mol m^{-3}, respectively, for α-alanine and 200 and 200 $mol \cdot m^{-3}$, respectively, for β-alanine. Because the gas−liquid mass-transfer coefficient cannot be estimated from their description of the experimental conditions, it is not possible to determine the suitability of the process conditions for kinetic measurements (i.e., the absorption regime cannot be determined). Also the value of k_{OH^-} used to predict k_{AmA} as per Eq. 4 was inaccurate compared to present-day values. The reported experimental values of k_{AmA} were recalculated using a more accurate value of k_{OH^-} (Pohorecki and Moniuk, 1988), and the resulting values are given in Table 1. The acidic

Table 1. Kinetic Data Available in the Literature on the Reaction Between CO_2 and Amino Acid Salt

Amino acid	T (K)	pKa —	k_{AmA} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Reference
α-Alanine	291	10.01	3.49	Jensen and Faurholt (1952)
β-Alanine	291	10.41	5.81	Jensen and Faurholt (1952)
Glycine	291	9.97	5.93	Jensen et al. (1952)
Glycine	283	10.17	1.65	Caplow (1968)
Glycine	278−303	9.80*	$k_2 = 8.51 \times 10^8 \exp(-5{,}508/T)$	Penny and Ritter (1983)

* At 293 K.

dissociation constants of the amino acids as reported by Jensen and Faurholt (1952) are also given in Table 1.

Jensen et al. (1952). Using a similar experimental technique to the one mentioned earlier, the authors reported the rate constant for the carbamate formation reaction. The values of k_{AmA} as given in Table 1 have been recalculated because of the inaccuracy in the value of k_{OH^-} as used by the authors.

Caplow (1968). The author studied the rates of reaction of CO_2 with glycine and a number of other amines at varying pH, using a sophisticated [but apparently not very accurate (Danckwerts, 1978)] version of the "competitive" method. As the calculated values of k_{AmA} (based on Eq. 4) increased with increasing solution pH for some amines, the author considered the carbamate formation reaction to be catalyzed by OH^- and modified Eq. 4 as follows

$$\frac{\%\ \text{Carbamate}}{\%\ \text{Carbonate}} = \frac{k_{AmA}[AmA] + k'_{AmA}[AmA][OH^-]}{k_{OH^-}[OH^-]} \quad (5)$$

However, for glycine it was found that the contribution of the second term in the numerator of Eq. 5 was not significant in comparison to the first term. The k_{AmA} as reported by Caplow has been corrected using a more accurate value of k_{OH^-}, and is given in Table 1.

Penny and Ritter (1983). The kinetics of the reaction between CO_2 and aqueous primary amines (including amino acid salts) was measured using a relatively more accurate stopped-flow technique, over the temperature range of 278–298 K. Due to limitations of the experimental technique, the maximum amine concentration that could be studied was 60 $mol \cdot m^{-3}$. Within this concentration range, the overall order of the reaction was found to be two. The authors used the zwitterion mechanism (Caplow, 1968; Danckwerts, 1979; see also next section) to explain the reaction kinetics. The following Brønsted relationship was proposed between the rate constant (k_2) and acidic dissociation constant (pKa) of the amine used:

$$\log_{10} k_2 = 0.34\ \text{pKa} + 0.45 \quad (6)$$

Reaction Mechanism

Zwitterion mechanism

It can be expected that the aqueous alkaline salts of glycine, alanine, and taurine exhibit a similar reactivity toward CO_2 as primary alkanolamines [say monoethanolamine, (MEA)] due to the similarity in the functional group ($-NH_2$) reacting with CO_2. In the case of primary and secondary alkanolamines, the reaction kinetics can be well described using the zwitterion mechanism proposed originally by Caplow (1968) and later reintroduced by Danckwerts (1979). As per the mechanism, CO_2 reacts with alkanolamines via the formation of a zwitterion, followed by the removal of a proton by a base B:

$$CO_2 + RR'NH \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} RR'N^+HCOO^- \quad (7)$$

$$RR'N^+HCOO^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} RR'NCOO^- + BH^+ \quad (8)$$

This second proton transfer step can be considered to be irreversible. With the assumption of a quasi-steady-state condition for the zwitterion concentration, the overall forward rate of the reaction is given by

$$R_{CO_2} = \frac{k_2[CO_2][Am]}{1 + \frac{k_{-1}}{\Sigma k_b[B]}} = \frac{[CO_2][Am]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2}\frac{1}{\Sigma k_b[B]}} \quad (9)$$

where Σk_b [B] is the contribution of all the bases present in the solution for the removal of protons. In lean aqueous solutions, the species amine, water, and OH^- can act as bases, as shown by Blauwhoff et al. (1984). For a few asymptotic situations, Eq. 9 can be simplified.

(I) $k_{-1}/(\Sigma k_b[B]) \ll 1$. This results in simple second-order kinetics, as experimentally found for aqueous MEA and implies that the zwitterion is deprotonated relatively fast in comparison to the reversion rate to CO_2 and amine:

$$R_{CO_2} = k_2[CO_2][Am] \quad (10)$$

(II) $k_{-1}/(\Sigma k_b[B]) \gg 1$. This results in a somewhat more complex kinetic-rate expression.

$$R_{CO_2} = k_2[CO_2][Am]\left(\frac{\Sigma k_b[B]}{k_{-1}}\right) \quad (11)$$

Depending on the relative contribution of various bases present in the aqueous solution to the deprotonation of the zwitterion, the preceding expression can explain any reaction order. If the deprotonation is mainly due to the amine, then the overall order of the reaction is three. It can also describe the shift in reaction order with a change in amine concentration, as has been experimentally observed for various secondary alkanolamines (Danckwerts, 1979; Versteeg and Oyevaar, 1989).

(III) In the absorption of CO_2 in alkanolamines dissolved in nonaqueous solvents (e.g., alcohols), the deprotonation of the zwitterion is solely due to amine. For this case, Eq. 9 reduces to

$$R_{CO_2} = \frac{k_2[CO_2][Am]}{1 + \frac{k_{-1}}{k_{Am}[Am]}} \quad (12)$$

Only at low concentrations of amine, the second term in the denominator becomes significant and the partial order in amine is higher than one (two being the limiting case when $k_{-1}/(k_{Am}[Am]) \gg 1$), and this reduces to one at very high amine concentrations.

In general, a plot of the apparent rate constant ($k'[Am]^n$) against the amine concentration ([Am]) gives the partial reaction order (n) in amine. The trend line for Eq. 9 of the zwit-

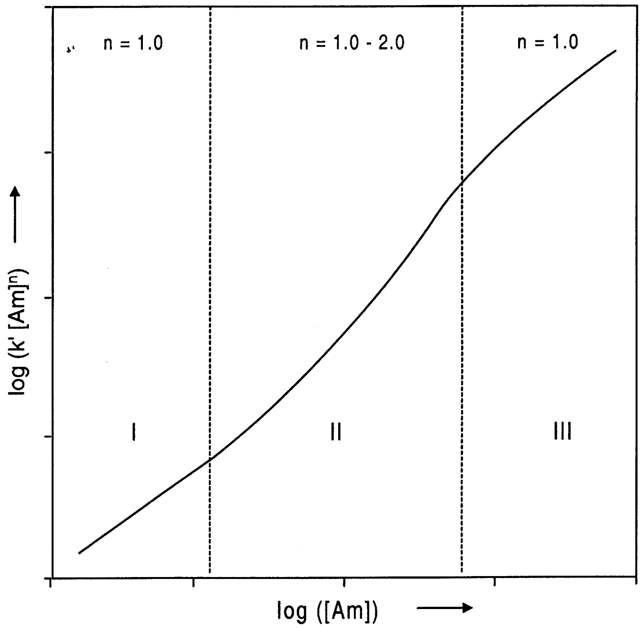

Figure 1. Kinetic behavior of the reaction of CO_2 with alkanolamines and amino acid salts.

Trendline based on Eq. 9 of the zwitterion mechanism.

terion mechanism is shown in Figure 1, which gives a qualitative indication of the concentration range over which the individual mechanistic rate constants can possibly be explicitly measured or estimated. For very low amine concentration, Eq. 9 will reduce to the following form and the partial reaction order in amine is one

$$R_{CO_2} = k_2[CO_2][Am]\left(\frac{k_{H_2O}[H_2O]}{k_{-1}}\right) \tag{13}$$

At moderately high amine concentrations, the contribution of amine and water to the zwitterion deprotonation are equally significant, and hence Eq. 9 must be used in its complete form to describe the experimental kinetic data. For very high amine concentrations at which the contribution of water to the overall deprotonation rate becomes negligible, and also the numerical value of $k_{-1}/(k_{Am}[Am])$ is far less than 1, Eq. 9 reduces to

$$R_{CO_2} = k_2[CO_2][Am] \tag{14}$$

In the preceding discussion, the contribution of the OH^- ions to the deprotonation step has been assumed to be negligible [which is the case for the most commonly used weakly basic amines (DEA, DIPA, MEA) and amino acids (glycine, taurine)]. From Eq. 14 it is clear that k_2 can be explicitly measured independent of other constants at very high amine concentrations, provided the following condition is satisfied:

$$\frac{k_{H_2O}[H_2O]}{k_{-1}} \ll \frac{k_{Am}[Am]}{k_{-1}} \gg 1 \tag{15}$$

For secondary alkanolamines in aqueous solutions (say DEA, DIPA), the value of k_{Am}/k_{-1} is approximately 1×10^{-4} $m^3\cdot mol^{-1}$ (Versteeg et al., 1996). This indicates that the k_2 can only be measured explicitly at amine concentrations far higher than 10^4 $mol\cdot m^{-3}$, which is a practically unrealistic amine concentration range. So the rate constants in Eq. 9 need to be measured in the concentration range falling under Zones II and I. It should be noted that some of the experimental techniques used in the kinetic measurements, like the stopped-flow technique, can be mostly used for very low amine concentrations only, that is, Zone I (Penny and Ritter, 1983). Under these situations, one can expect the partial order in amine to be one. However, the second-order rate constant, k_2 (based on the zwitterion mechanism), obtained directly from the experimental kinetic data ($k'[Am]^n/[Am]$) may be underestimated if the contribution of k_{H_2O} to the deprotonation as shown in Eq. 13 is assumed to be negligible. For a good estimation of the zwitterionic rate constants, experimental measurements need to be done from very low (at which k_{H_2O}/k_{-1} can be estimated accurately) to high (at which k_{Am}/k_{-1} can be obtained) concentrations of amine.

Applying the zwitterion mechanism to the reaction of CO_2 with aqueous amino (sulfonic or carboxylic) acid salts results in

$$CO_2 + {}^+K^-O_3S-R-NH_2 \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} {}^+K^-O_3S-R-NH_2{}^+COO^- \tag{16}$$

$${}^+K^-O_3S-R-NH_2{}^+COO^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} {}^+K^-O_3S-R-NHCOO^- + BH^+. \tag{17}$$

It can be observed that the principal difference in applying the zwitterion mechanism to aqueous primary alkanolamines and amino acid salts seems to be the ionic charge associated with the reactant product as well as the intermediate species. This difference may significantly influence the stability and deprotonation rate of the zwitterion, and hence the overall order of the reaction in aqueous amino acid salt solutions may differ from aqueous primary alkanolamines.

Termolecular mechanism

Crooks and Donnellan (1989) questioned the validity of the zwitterion mechanism based on the argument that the number of fitting parameters required to describe the experimental data is too high (four) and the numerical values of the parameters (especially the deprotonation rate constants) in some cases seems to be physically unrealistic. The authors proposed a single-step, termolecular mechanism (see Figure 2) and the reaction rate equation (Eq. 18) to describe their experimental kinetic data, which is, in fact, similar to one of the limiting cases ($k_{-1}/(\Sigma k_b[B]) \gg 1$) of the zwitterion mechanism.

$$R_{CO_2} = k'[RNH_2][RNH_2][CO_2] + k''[RNH_2][H_2O][CO_2]. \tag{18}$$

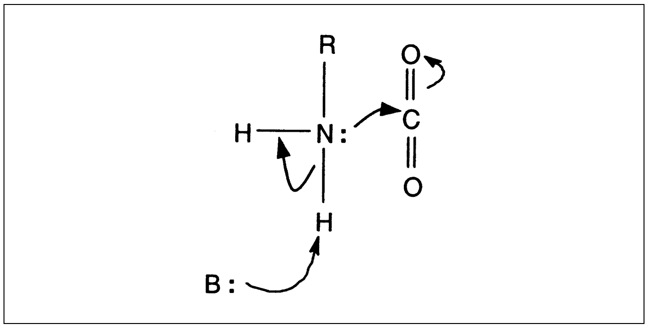

Figure 2. Single-step, termolecular reaction mechanism (Crooks and Donnellan, 1989).

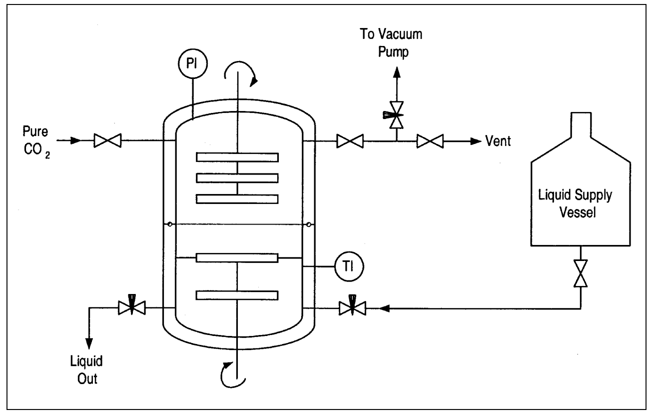

Figure 3. Experimental setup.

Although the termolecular mechanism can describe the fractional reaction orders for aqueous alkanolamine solutions, it fails to explain the occurrence of changing reaction orders with concentration of amine observed for nonaqueous alkanolamine solutions, as was experimentally observed by many investigators (Versteeg and Van Swaaij, 1988a; Sada et al., 1985). For most purposes, Eq. 9 and its various limiting cases serve as a good engineering model to describe all type of experimental kinetic behavior of amines. In the absence of sufficient kinetic data with regard to the reaction of CO_2 with aqueous amino acid salt solutions, both the reaction mechanisms are considered in the present study.

Experimental Studies

Chemicals

The potassium salt of a selected amino acid was prepared by neutralizing (by titration) the amino acid (Merck) dissolved in deionized, distilled water, with an equimolar quantity of potassium hydroxide (Merck) in a standard flask. The neutralization reaction was carried out with constant cooling. The amino acid dissolved in water exists as a zwitterion (Form II in Eq. 19), with the amino group completely protonated. The ionic equilibria of the amino acids in water exists as follows:

$$\begin{array}{ccc} \underset{\mathrm{I}}{HO_2C-R-NH_3{}^+} & \underset{}{\overset{-H^+}{\rightleftharpoons}} & \underset{\mathrm{II}}{{}^-O_2C-R-NH_3{}^+} \\ & \overset{-H^+}{\rightleftharpoons} & \underset{\mathrm{III}}{{}^-O_2C-R-NH_2} \end{array} \tag{19}$$

Addition of KOH results in deprotonation of the amino group, resulting in chemical species III. Only this deprotonated amine species (III) can react with acid gases. The concentration of the deprotonated amine (amino acid salt) was estimated potentiometrically by titrating with standard HCl solutions. The experimentally determined amine concentrations were accurate to within 0.5%.

Experimental setup and procedure

The experiments were carried in a stirred vessel with a smooth gas–liquid interface, and the reactor was operated batchwise with respect to the gas and liquid phases (Figure 3). The reactor was all glass, thermostatted, and consisted of upper and lower parts, sealed gas tight using an O-ring and screwed flanges. The reactor had magnetic stirrers in the gas (upper) and liquid (lower) phases, and the stirring speed could be controlled independently of one or the other. The pressure in the gas phase was measured using a digital pressure transducer (Drück) and was recorded in the computer.

The experimental procedure is similar to the one described in detail by Blauwhoff et al. (1984) and will be only briefly summarized here. A freshly prepared amino acid salt solution was charged into the reactor from the liquid supply vessel and degassed under vacuum to remove dissolved gases. After degassing, the vapor–liquid equilibrium was established. The gas-phase pressure (P_{vap}) was noted down and pure CO_2 was introduced into the reactor. The initial CO_2 partial pressure of the reactor was adjusted for different amino acid salt concentrations to maintain a constant amine conversion or average CO_2 loading for all the experiments. In the present experiments, the initial CO_2 partial pressure was adjusted to have a final CO_2 loading of 0.03 ± 0.005 (mol CO_2/mol amine) for all the experiments. For these low CO_2 loading and using amines with a relatively high value of the equilibrium constant for Eq. 1, the influence of reversibility is negligible (Blauwhoff et al., 1984). The stirrer in both phases was turned on and the pressure ($P_{tot,t}$) decrease due to the absorption of CO_2 was recorded. The reaction kinetics can the determined if the following conditions are satisfied.

$$2 < \mathrm{Ha} \ll E_{CO_2,\infty}, \tag{20}$$

where

$$\mathrm{Ha} = \frac{\sqrt{k_{ov} D_{CO_2}}}{k_L} \tag{21}$$

$$E_{CO_2,\infty} = \sqrt{\frac{D_{CO_2}}{D_{\mathrm{AmA}}}} + \sqrt{\frac{D_{CO_2}}{D_{\mathrm{AmA}}}}\,\frac{[\mathrm{AmA}]\mathrm{RT}}{\upsilon_{\mathrm{AmA}} P_{CO_2,t} m_{CO_2}}. \tag{22}$$

If this condition (Eq. 20) is fulfilled, the reaction can be considered to be pseudo-first-order and the CO_2 absorption rate is given by,

$$J_{CO_2} A = \sqrt{k_{\mathrm{ov}} D_{CO_2}}\, m_{CO_2} P_{CO_2,t} \left(\frac{\mathrm{A}}{\mathrm{RT}}\right)\ \mathrm{mol \cdot s^{-1}} \tag{23}$$

The information on the solubility and diffusivity of CO_2 in aqueous amino acid salt solutions is given in the Appendix. The actual partial pressure of CO_2 at any instant ($P_{CO_2,t}$) was calculated according to the following relation:

$$P_{CO_2,t} = P_{tot,t} - P_{vap} \tag{24}$$

In aqueous amino acid salt solutions, the overall rate constant, k_{ov}, comprises mainly the contributions of the reactions in Eqs. 1 and 2:

$$k_{ov} = k_{OH^-}[OH^-] + k_{app} \quad s^{-1} \tag{25}$$

The value of k_{OH^-} was obtained from Pohorecki and Moniuk (1988), and the reaction between CO_2 and water (Eq. 3) was neglected due to its negligible contribution to the overall reaction rate.

Results and Discussion

The kinetics of the reaction between CO_2 and aqueous potassium taurate solution was measured at 285, 295, and 305 K. For comparison, the kinetic measurements were also carried out for aqueous potassium glycinate solutions at 295 K.

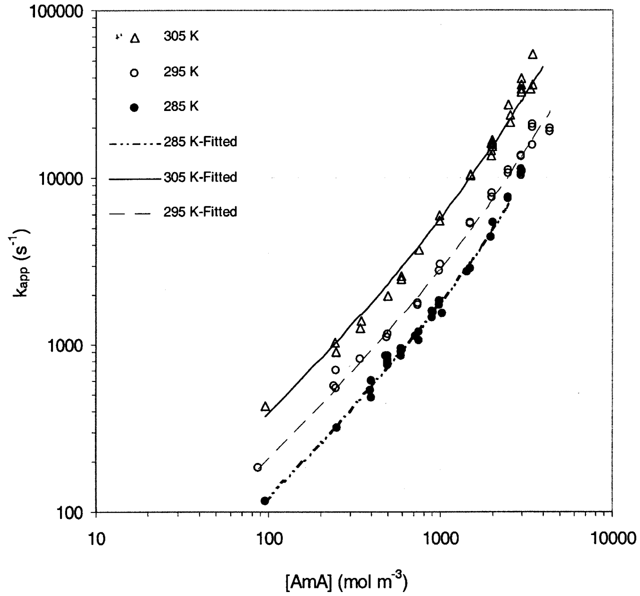

Figure 4. Experimental results for aqueous potassium taurate at different temperatures.

Aqueous potassium taurate

The measured values of the apparent rate constants (k_{app}) in relation to the potassium taurate concentrations at 295 K are shown in Figure 4. In the calculation of the apparent rate constant using Eq. 25, the contribution of the reaction between OH^- and CO_2 to the overall rate was found to be insignificant due to the low basic strength of taurine (pKa). At low taurate concentrations (less than 100 $mol \cdot m^{-3}$), it was practically difficult to measure the reaction kinetics in the "$E = Ha$" absorption regime (Eq. 20) due to the diffusion limitations of the reactant species in the liquid phase. From Figure 4, it can be observed that the partial reaction order (n) in amino acid salt increases with the molar salt concentration. For salt concentrations less than 1,000 $mol \cdot m^{-3}$, n approaches the value of 1 for the range of temperatures studied, and it increases to approximately 1.5 at salt concentrations as high as 4,000 $mol \cdot m^{-3}$. This seems similar to the behavior of aqueous diethanolamine (DEA) where the order with respect to the amine was found to change from 1 at very low amine concentration ($< 100\ mol \cdot m^{-3}$) to 2 at high amine concentrations (Blauwhoff et al., 1984; Versteeg and Oyevaar, 1988). However, DEA is a secondary alkanolamine in contrast to the currently used amino acid salt, which has a primary amino functional group.

The experimental k_{app} data were regressed to the reaction rate expression (Eq. 9) by means of a Levenberg–Marquardt fitting procedure. It was found that the contribution of the OH^- ions to deprotonation of the zwitterion was not significant and was left out from Eq. 9 in the fitting procedure. The fitted rate constants are summarized in Table 2, along with the zwitterionic constants of some selected primary and secondary alkanolamines, for which reasonably accurate information is available in the literature. For aqueous amino acid salt solutions, there seems to be a significant difference in the kinetic behavior as well as in the magnitude of the zwitterionic rate constants from the aqueous alkanolamines.

(1) Contrary to primary aqueous alkanolamines (such as MEA), the partial reaction order in amino acid salt (containing the primary amino group) changes with the molar salt concentration. This indicates that the deprotonation step in the zwitterion mechanism is not much faster than the zwitterion formation step, a behavior typically exhibited by the secondary aqueous alkanolamines. Also, it indicates that the zwitterion of the amino acid salt is less stable compared to primary alkanolamines.

(2) More significantly, the numerical value of k_{Am}/k_{-1} for amino acid salt is lower than that for aqueous alkanolamines (secondary alkanolamines) and that of k_{H_2O}/k_{-1} is higher by almost an order of magnitude. This qualitatively indicates that water contributes significantly to the deprotonation even at moderately high amine concentrations. It should be noted that for secondary alkanolamines, the steric hindrance of the additional alkanol group has a negative influence on the deprotonation of the zwitterion by an amine as compared to aqueous primary alkanolamine or amino acid salt. So, in contrast

Table 2. Zwitterion Mechanism Constants for CO_2 Absorption in Aqueous Potassium Taurate Solutions

Amine	T (K)	pKa —	k_2 ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	k_{AmA}/k_{-1} ($m^3 \cdot mol^{-1}$)	k_{H_2O}/k_{-1} ($m^3 \cdot mol^{-1}$)	Reference
Potassium taurate	295	9.14	12.60	1.30×10^{-4}	4.23×10^{-6}	Present study
Monoethanolamine	295	9.62	4.94	—	—	Versteeg et al. (1996)
Diethanolamine	295	8.96	2.42	3.86×10^{-4}	5.31×10^{-7}	Littel et al. (1992)

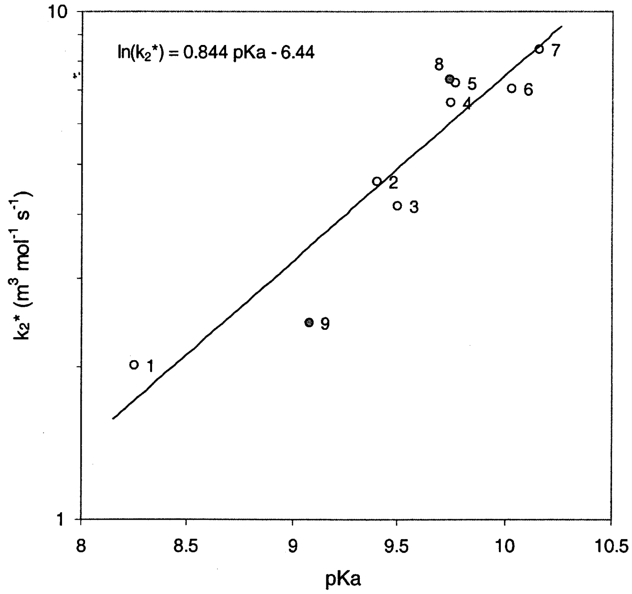

Figure 5. Brønsted plot for primary amines based on the experimental data of Penny and Ritter (1983) at 295 K and data from this work.

1. Glycylglycine salt; 2. benzylamine; 3. 2-aminoethanol (DEA); 4. glycine salt; 5. 2-phenethylamine; 6. 2-aminopropan-1-ol; 7. 3-phenyl-1-propylamine; 8. glycine salt (present work); 9. taurine salt (present work). Here k_2^* obtained from the work of Penny and Ritter (1983) is $k_{app}/[Am]$ and from the present study is $k_2 k_{H_2O}[H_2O]/k_{-1}$.

to the general expectation for the amino acid salt, the contribution of water to the deprotonation of the zwitterion is considerable.

(3) The value of k_2 is much higher than that expected from the Brønsted plot of Penny and Ritter (1983). These authors have shown that a single Brønsted plot can be used to relate k_2 with the basicity of the amine (pKa) for both alkanolamines as well as amino acid salts. It should be noted that the k_2 measured by the authors was instead an apparent rate constant ($k_2^* = k_2 k_{H_2O}[H_2O]/k_{-1}$), as explained earlier using Eq. 13. Even in the present case, the apparent second-order rate constant (k_2^*) at 295 K is 2.96 $m^3 \cdot mol^{-1} \cdot s^{-1}$. This value falls in line with the Brønsted plot of Penny and Ritter (1983) at 295 K (Figure 5). In Figure 5, the values of k_2 at 295 K used in the plot were recalculated from the experimental data of Penny and Ritter (1983). It can be concluded that the Brønsted plot for amino acid salts based on the intrinsic value of k_2 obtained over the complete range of concentrations may be different from that of alkanolamines. More experimental kinetic data for different amino acid salts are required to verify this hypothesis.

(4) There is an unique problem associated with the absorption of CO_2 in aqueous amino acid salt solutions that can influence the experimental kinetic measurements. During the absorption of CO_2 precipitation of certain reaction products occurs in some aqueous amino acid salt solutions. Hook (1997) has made a qualitative study of this phenomenon for different classes of amino acid salts. Independent of the present work, experiments on the vapor–liquid equilibria of CO_2–potassium taurate show that precipitation occurs in the liquid phase during CO_2 absorption in solutions having salt concentrations higher than 2,000 $mol \cdot m^{-3}$, depending upon the liquid temperature. Precipitation was observed at reasonably high partial pressures of CO_2 (hence, at higher CO_2 loading), and this critical loading or CO_2 partial pressure at which precipitation occurred decreased with an increase in the salt concentration in the liquid. In the kinetic experiments, the CO_2 loading has been kept low (~ 0.02 mol CO_2/mol salt), and so there is no precipitation in the liquid bulk. However, it cannot be excluded that microparticles can precipitate at the gas–liquid interface where the concentration of the reaction products is at its maximum. These miniscule particles might redissolve in the liquid bulk as they move away from the interface (due to stirring). The influence of precipitation (though not visually observed during the experiments) can result in an increase in the mass-transfer coefficient due to interfacial turbulence (Westerterp et al., 1983). However, it should be noted that the kinetic experiments have been measured in the $E = Ha$ regime ($2 < Ha \ll E_{CO_2,\infty}$) and any marginal change in the value of k_L should not affect the resulting kinetic data. In the range of partial pressures in which the measurements were made, any influence of this phenomenon can be expected only for amino acid salt concentrations greater than approximately 2,500 $mol \cdot m^{-3}$, for a liquid temperature of 295 K or above. Even if the precipitation at the interface would occur, the effect should be negligible in the $E = Ha$ regime, and hence the difference in the kinetic behavior seems to be due to the mechanistic aspects of the reaction. Nevertheless, in the regression of the experimental kinetic data to obtain zwitterion mechanism constants, the experimental data in the range of amine concentrations where local precipitation cannot be excluded have been neglected.

Mechanistically there can be a significant difference in the zwitterion mechanism applied to the primary or secondary alkanolamines and amino acid salts at the molecular or ionic level (see also the subsection on the zwitterion mechanism). This can have an influence on the relative rates of the reverse reaction of the zwitterion to CO_2 and amine and the deprotonation step ($k_{-1}/\Sigma k_b[B]$) and can possibly offer an explanation for the difference between the experimental results and the one expected for the primary amines.

(1) *Stability of the Zwitterion.* The zwitterion of the amino acid salt could be inherently less stable than that of MEA due to the multiple charges associated with the amino acid salt zwitterion (see the reaction in Eq. 16). Other charged species (reactant and products) may also have a negative influence on its stability.

(2) *Deprotonation of the Zwitterion.* The zwitterion can be deprotonated by the amine, water, and OH^- ions. As mentioned earlier, the contribution of the OH^- ions to the deprotonation is usually negligible. From the numerical value of the deprotonation constants (especially that of water) in comparison to alkanolamines, it seems to be relatively easy for the uncharged water molecules to form hydrogen bonding with the zwitterion (charged at both ends) as compared to the charged amino acid salt. The mechanism of the deprotonation step has been explained in detail by Caplow (1968).

As an alternative to the zwitterion mechanism, the single-step–termolecular reaction mechanism proposed by Crooks and Donnellan (1989) was considered and was assumed to occur in two steps (see Figure 2). In the first step, CO_2, amine, and the base (maybe amine) forms an intermediate product, which is a "loosely bound encounter complex." The complex can then break back down to reactant molecules or form final reaction products (carbamate)

$$CO_2 + {}^+K^-O_3S - R - NH_2 + B \underset{k'_{-1}}{\overset{k_3}{\rightleftharpoons}} [\text{Encounter Complex}] \xrightarrow{k_e} {}^+K^-O_3S - R - NHCOO^- + BH^+ \quad (26)$$

The overall forward reaction rate equation can be derived with the assumption of a quasi-steady-state condition for the encounter complex concentration:

$$R_{CO_2,B} = \frac{k_{3,B}k_e}{k'_{-1} + k_e}[RNH_2][B][CO_2] \quad \text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1} \quad (27)$$

In the present case, the principal bases contributing to the deprotonation are the amino acid salt and water. Depending upon the deprotonating base, B, the encounter complex will differ for each base and the net forward rate should be the sum of the individual reaction rates of the two reactions in which the amino acid salt and water act as base, B:

$$R_{CO_2} = R_{CO_2,AmA} + R_{CO_2,H_2O} \quad \text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1} \quad (28)$$

$$R_{CO_2} = \frac{k'_e}{k'_{-1} + k_e}\{k_{3,AmA}[RNH_2][RNH_2][CO_2] + k_{3,H_2O}[RNH_2][H_2O][CO_2]\} \quad (29)$$

$$R_{CO_2} = k'_{AmA}[RNH_2][RNH_2][CO_2] + k'_{H_2O}[RNH_2][H_2O][CO_2], \quad (30)$$

where

$$k'_{AmA} = \frac{k_e}{k'_{-1} + k_e}k_{3,AmA}; \quad k'_{H_2O} = \frac{k_e}{k'_{-1} + k_e}k_{3,H_2O} \quad \text{mol}^{-2}\cdot\text{m}^6\cdot\text{s}^{-1}. \quad (31)$$

Surprisingly, Eq. 30 is similar to Eq. 11 (though there are no assumptions like $k_{-1}/\Sigma k_b[B] \gg 1$, as in the case of the zwitterion mechanism). The experimental kinetic data were regressed for Eq. 30 using the previously mentioned numerical technique, and the optimal solutions are given in Table 3.

Temperature dependence of zwitterion and termolecular mechanism constants

To understand the influence of temperature on reaction kinetics, experiments were conducted at 285 and 305 K as well. The measured apparent rate constants (k_{app}) are shown in Figure 4, and the trend is identical to the measurements at 295 K, that is, an increase in the partial order in amino acid salt with an increase in salt concentration. The regressed value of the kinetic rate constants based on Eqs. 9 and 30 are given in Table 3:

$$k_2 = 3.23 \times 10^9 \exp\left(-\frac{5,700}{T}\right) \quad \text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1} \quad (32)$$

$$\frac{k_{H_2O}}{k_{-1}} = 2.29 \times 10^{-8} \exp\left(\frac{1,483}{T}\right) \quad \text{m}^3\cdot\text{mol}^{-1} \quad (33)$$

$$\frac{k_{AmA}}{k_{-1}} = 2.36 \times 10^{-6} \exp\left(\frac{1,225}{T}\right) \quad \text{m}^3\cdot\text{mol}^{-1}. \quad (34)$$

Of the zwitterion mechanism constants, only k_2 was found to be strongly temperature dependent, while the deprotonation constants were found to be less sensitive to temperature. Relatively accurate values of the taurate and water deprotonation constants can be obtained at very high and low taurate concentrations, respectively. For example, at very low salt concentrations, the deprotonation of the zwitterion is mostly due to water. However, in the present study, due to the limitations of the experimental technique at low taurate concentrations as well as scatter in the experimental data at very high taurate concentrations, it was practically difficult to do measurements in these salt concentration ranges.

Potassium glycinate

The kinetics of the reaction between CO_2 and aqueous potassium glycinate solutions was studied at 295 K to compare it to the reaction mechanism proposed for aqueous potassium taurate solutions. It should be noted that taurine is an amino sulfonic acid, whereas glycine is an amino carboxylic acid. However, during the reaction of CO_2 with amino acid salts, the acidic group probably has no direct influence

Table 3. Temperature Influence on the Zwitterion (Eq. 9) and Termolecular (Eq. 30) Reaction Mechanism Constants

Amino Acid Salt	T (K)	pKa*	k_2^{**} ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	$k_{AmA}k_{-1}^{**}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	$k_{H_2O}k_{-1}^{**}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	$k'^{\dagger}_{AmA}$ ($\text{m}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$)	$k'^{\dagger}_{H_2O}$ ($\text{m}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$)
Potassium taurate	285	9.38	6.78	1.86×10^{-4}	4.23×10^{-6}	7.20×10^{-4}	2.02×10^{-5}
Potassium taurate	295	9.14	12.60	1.30×10^{-4}	3.39×10^{-6}	9.71×10^{-4}	3.69×10^{-5}
Potassium taurate	305	8.91	25.20	1.41×10^{-4}	3.01×10^{-6}	2.24×10^{-3}	6.60×10^{-5}
Potassium glycinate	295	9.67	49.68	6.04×10^{-5}	2.69×10^{-6}	2.09×10^{-3}	1.18×10^{-4}

*Perrin (1965).
**Zwitterion mechanism constants.
†Termolecular mechanism constants.

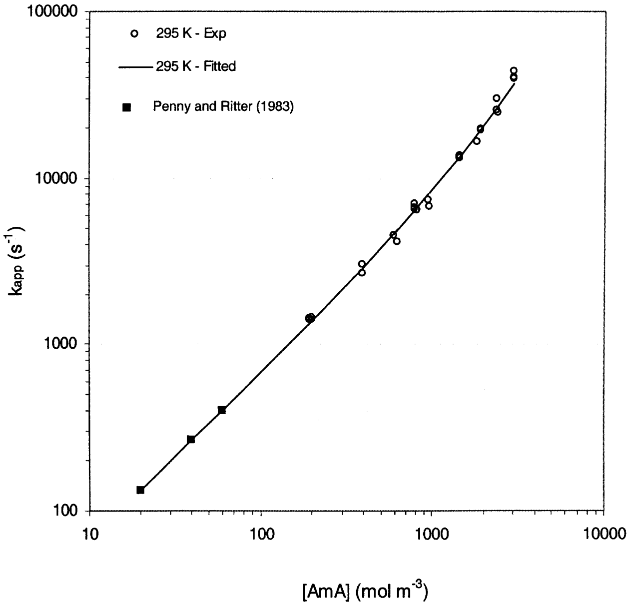

Figure 6. Experimental results for aqueous potassium glycinate at 295 K.

on the reaction rate. During the absorption of CO_2 in aqueous potassium glycinate solutions, precipitation does not occur even at very high CO_2 loading (Hook, 1997). Therefore, with this experimental system, it is possible to ascertain whether the difference in the reaction mechanism observed for amino acid salts (in comparison to alkanolamines) can be attributed to the precipitation phenomenon that can occur for taurate solutions at high salt concentrations. Figure 6 shows the measured values of k_{app} as a function of the amino acid salt concentration. Though the pKa of glycine (9.85) is higher than that of taurine (9.14), the contribution of the reaction between OH^- ions and CO_2 to the overall rate was still negligible (less than 1%). Aqueous potassium glycinate solutions showed greater reactivity toward CO_2 over potassium taurate due to the higher basic strength (pKa) of glycine.

Like potassium taurate solutions, aqueous solutions of potassium salt of glycine also exhibit a change in partial reaction order in amino acid salt with the molar concentration of the salt. Again due to the limitations of the experimental technique, reliable measurements could not be made using potassium glycinate solutions that had concentrations lower than 200 $mol \cdot m^{-3}$. The experimental k_{app} data was regressed to the rate equations of the two reaction mechanisms discussed earlier (Eqs. 9 and 30). Due to insufficient data at lower amine concentrations, it was difficult to get a good optimal solution, and hence the apparent rate constant (k_{app}) from the work of Penny and Ritter (1983) was used in the regression to supplement the k_{app} data from the present work. The resulting rate constants of the reaction mechanism are given in Table 3. As can be expected, the value of k_2 (49.68 $m^3 \cdot mol^{-1} \cdot s^{-1}$) is very high compared to the published data (Penny and Ritter, 1983; Jensen et al., 1952), and is also greater than that of taurine. However, the calculated apparent $k_2^*(k_2 k_{H_2O}[H_2O]/k_{-1} = 7.3$ $m^3 \cdot mol^{-1} \cdot s^{-1}$) is in good agreement with the reported value (6.61 $m^3 \cdot mol^{-1} \cdot s^{-1}$) of Penny and Ritter (1983) and is also shown in Figure 5 for comparison. It should be noted that even in the absence of the experimental data of Penny and Ritter, the calculated value of k_2^* obtained from the optimal value of the regressed zwitterionic constants were within ± 0.2 $m^3 \cdot mol^{-1} \cdot s^{-1}$. Among the zwitterionic deprotonation constants, the value of k_{AmA} for glycine is lower than for taurine at identical temperatures, whereas the deprotonation constant corresponding to that of water is comparable within accuracy of the estimation of the constants and in the range of the amino acid salt concentrations studied. The termolecular mechanism constants are also given in Table 3, and the values of the two constants are higher than for taurine.

Conclusion

The kinetics of the reaction of CO_2 with aqueous potassium salt of taurine was investigated over a wide range of salt concentrations (100–4,000 $mol \cdot m^{-3}$) and temperatures (285–305 K). Similarly, kinetic data for the reaction of CO_2 with aqueous potassium glycinate solutions were obtained at 295 K. Unlike primary aqueous alkanolamines, aqueous amino acid salts show an increase in the partial reaction order in amino acid salt from one at molar salt concentrations larger than approximately 1,000 $mol \cdot m^{-3}$. This behavior was observed for both potassium taurate and potassium glycinate solutions. For potassium glycinate, the apparent second-order rate constant ($k_2^* = k_2 k_{H_2O}[H_2O]/k_{-1}$) obtained from the present study is in good agreement with the literature.

The zwitterion mechanism can be conveniently used to describe the experimental kinetic data. However, the numerical value of the rate constants (especially k_2) is very different from that of aqueous alkanolamines. For both taurine and glycine salts, the value of k_2 is far higher than the values that can be expected, based on the Brønsted plot for aqueous amines reported in the literature (Versteeg et al., 1996; Penny and Ritter, 1983). This indicates that the Brønsted plot of amino acids might be different from that of aqueous alkanolamines. Based on the zwitterion mechanism, the role of water in the zwitterion deprotonation seems to be significantly larger than reported in the literature for aqueous alkanolamines. As with aqueous alkanolamines, the termolecular mechanism can also be used to describe the experimental kinetic data. However, more experimental kinetic data are required for different types of amino acid salts to conclude on the mechanistic aspects of the reaction kinetics.

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Notation

A = gas–liquid interfacial area, m^2
B = base (H_2O, OH^-, AmA, or Am)
D_i = diffusion coefficient of component i, $m^2 \cdot s^{-1}$
E = enhancement factor, dimensionless
$E_{CO_2,\infty}$ = infinite enhancement factor for the mass transfer of CO_2, dimensionless

Ha = Hatta number, dimensionless
J_{CO_2} = CO_2 absorption mole flux, $mol \cdot m^{-2} \cdot s^{-1}$
k', k'' = rate constants, $(mol \cdot m^{-3})^{1-O}\ s^{-1}$
k'_{AmA} = termolecular mechanism rate constant for AmA, $m^6 \cdot mol^{-2} \cdot s^{-1}$
k'_{H_2O} = termolecular mechanism rate constant for H_2O, $m^6 \cdot mol^{-2} \cdot s^{-1}$
k_{-1} = zwitterion mechanism rate constant, s^{-1}
k'_{-1} = termolecular mechanism rate constant, s^{-1}
k_2 = second-order rate constant, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_2^* = apparent second-order rate constant (k_{app}/[AmA]), $m^3 \cdot mol^{-1} \cdot s^{-1}$
$k_{3,B}$ = termolecular mechanism rate constant, $m^6 \cdot mol^{-2} \cdot s^{-1}$
k_{AmA} = zwitterion mechanism deprotonation rate constant for AmA, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_{app} = apparent rate constant, s^{-1}
k_b = zwitterion mechanism deprotonation rate constant by base B, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_e = termolecular mechanism rate constant, s^{-1}
k_{H_2O} = zwitterion mechanism deprotonation rate constant for H_2O, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_L = liquid-phase mass-transfer coefficient, $m \cdot s^{-1}$
k_{OH^-} = zwitterion mechanism deprotonation rate constant for OH^-, $m^3 \cdot mol^{-1} \cdot s^{-1}$
k_{ov} = overall rate constant, s^{-1}
m = physical solubility $([CO_2]_{liq}/[CO_2]_{gas})_{eq}$, dimensionless
n = partial order of the reaction in amine acid salt, dimensionless
o = overall order of the reaction, dimensionless
$P_{CO_2,t}$ = instantaneous partial pressure of CO_2, Pa
$P_{Tot,t}$ = instantaneous total pressure of reactor, Pa
P_{vap} = vapor pressure of the liquid, Pa
R = universal gas constant (8.3143), $J \cdot mol^{-1} \cdot K^{-1}$
R_{CO_2} = rate of reaction of CO_2, $mol \cdot m^{-3} \cdot s^{-1}$
T = temperature, K
v = stoichiometric coefficient, dimensionless
[ ] = concentration, $mol \cdot m^{-3}$

Abbreviations

Am = alkanolamine
AmA = amino acid salt
MEA = monoethanolamine
DEA = diethanolamine
DIPA = diisopropanolamine

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Appendix I: Physicochemical Parameters for Determining Kinetic Constants

The solubility and diffusivity of CO_2 in aqueous amino acid salt solutions are required for the estimation of the kinetic parameters from the basic experimental data (P_{CO_2} vs. t). Since there is no published information in the open literature, these parameters were experimentally determined independently of the present study (Kumar et al., 2001). As CO_2 reacts with the aqueous amino acid salt solutions, the physical solubility (m) and diffusivity (D_{CO_2}) of CO_2 were indirectly estimated from the solubility and diffusivity of N_2O, respectively, in aqueous salt solutions.

Physical solubility

A model similar to that of Schumpe (1993) was used to describe the experimental data on the solubility of N_2O (m) in aqueous potassium taurate solutions (Kumar et al., 2001)

$$\log(m_w/m) = KC_s, \tag{A1}$$

where C_s is the salt concentration in kmol m^{-3}. For a single salt, the Sechenov constant, K, based on the Schumpe model is given by the following relation,

$$K = \Sigma(h_i + h_G)n_i. \quad m^3 \cdot kmol^{-1} \tag{A2}$$

The temperature-independent anion (h_-) and cation-specific constants (h_+) for potassium taurate are

$$h_+: \; 0.0922 \quad m^3 \cdot kmol^{-1} \tag{A3}$$

$$h_-: \; 0.0249 \quad m^3 \cdot kmol^{-1}. \tag{A4}$$

For the solubility of N_2O in aqueous potassium glycinate solutions, the anion-specific constant is given by

$$h_-: \; 0.0276 \quad m^3 \cdot kmol^{-1}. \tag{A5}$$

The temperature-dependent gas (CO_2)-specific constant (h_G) was obtained from the database of Schumpe (1993), and the solubility of CO_2 in aqueous potassium taurate solution was estimated using Eq. A1. The solubility of CO_2 and N_2O in water (m_w) was obtained from the work of Versteeg and van Swaaij (1988b).

Diffusion coefficient

The diffusion coefficient of N_2O (D_{N_2O}) in an aqueous potassium taurate solution was obtained from Kumar et al. (2001). A modified Stokes–Einstein equation was used to estimate the diffusion coefficient of N_2O in aqueous potassium taurate solutions

$$D_{N_2O}\, \mu^{0.74} = \text{constant}. \tag{A6}$$

The information on the dependence of viscosity (μ) on the amino acid salt concentration is available in Kumar et al. (2001). The diffusion coefficient of CO_2 in aqueous potassium taurate solutions was estimated according to Gubbins et al. (1966)

$$\left(\frac{D}{D_W}\right)_{N_2O} = \left(\frac{D}{D_W}\right)_{CO_2}. \tag{A7}$$

The diffusion coefficients of CO_2 ($D_{CO_2,W}$) and N_2O ($D_{N_2O,W}$) in water were obtained from the published work of Versteeg and van Swaaij (1988b). The diffusion coefficient of CO_2 in aqueous potassium glycinate was estimated similarly.

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