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·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 ter-molecular 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$_2$S, 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$_2$S reacts instantaneously with all amines) and CO$_2$/H$_2$S absorption capacity. Thus, the choice of the alkanolamine among primary, secondary, and tertiary sterically or nonstereically hindered amine depends on the process requirements. For the bulk removal of CO$_2$ or removal of H$_2$S from a gas stream containing both H$_2$S 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$_2$S from a gas stream containing CO$_2$ and H$_2$S. 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-
Lutions of amino acid salts alone have also been used in the past for the (selective) removal of H₂S or CO₂ 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 (H₂S, CO₂) 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 CO₂ 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 CO₂ using aqueous amino acid salt solutions requires information, among others, on the kinetics of the reaction between CO₂ and amino acid salts. Unlike aqueous alkanolamines, there is limited information in the literature in general on the absorption of CO₂ in aqueous amino acid salt solutions, and in particular on the mechanism and kinetics of the reaction between CO₂ 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 CO₂ 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·m⁻³) and temperatures (285–305 K).

Literature Review

During the absorption of CO₂ in aqueous amino acid salt solutions, the following reactions can occur

\[ \text{CO}_2 + \text{Amino Acid} \rightleftharpoons \text{AmA} \text{COO}^- + \text{AmAH}^+ \]  \hspace{1cm} (1)

\[ \text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \]  \hspace{1cm} (2)

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^- \]  \hspace{1cm} (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; Pinse 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 CO₂ 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 CO₂ for 2 min. The initial partial pressure of CO₂ 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 CO₂ 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.

\[
\frac{\% \text{ Carbamate}}{\% \text{ Carbonate}} = \frac{k_{\text{AmA}}[\text{AmA}]}{k_{\text{OH}^-}[\text{OH}^-]}.
\]  \hspace{1cm} (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 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 \( k_{\text{OH}^-} \) used to predict \( k_{\text{AmA}} \) as per Eq. 4 was inaccurate compared to present-day values. The reported experimental values of \( k_{\text{AmA}} \) were recalculated using a more accurate value of \( k_{\text{OH}^-} \) (Pohorecki and Moniuk, 1988), and the resulting values are given in Table 1. The acidic

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>( T ) (K)</th>
<th>pKa</th>
<th>( k_{\text{AmA}} ) (m³·mol⁻¹·s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Alanine</td>
<td>291</td>
<td>10.01</td>
<td>3.49</td>
<td>Jensen and Faurholt (1952)</td>
</tr>
<tr>
<td>β-Alanine</td>
<td>291</td>
<td>10.41</td>
<td>5.81</td>
<td>Jensen and Faurholt (1952)</td>
</tr>
<tr>
<td>Glycine</td>
<td>291</td>
<td>9.97</td>
<td>5.93</td>
<td>Jensen et al. (1952)</td>
</tr>
<tr>
<td>Glycine</td>
<td>283</td>
<td>10.17</td>
<td>1.65</td>
<td>Caplow (1968)</td>
</tr>
<tr>
<td>Glycine</td>
<td>278–280</td>
<td>9.80*</td>
<td>( k_2 = 8.51 \times 10^4 \exp(-5.508/T) )</td>
<td>Penny and Ritter (1983)</td>
</tr>
</tbody>
</table>

* 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 $k_{\text{AmA}}$ as given in Table 1 have been recalculated because of the inaccuracy in the value of $k_{\text{OH}^-}$ 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 $k_{\text{AmA}}$ (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:

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

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 $k_{\text{AmA}}$ as reported by Caplow has been corrected using a more accurate value of $k_{\text{OH}^-}$, 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·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 ($k_z$) and acidic dissociation constant (pKa) of the amine used:

$$\log_{10} k_z = 0.34 \text{ pKa} + 0.45 \tag{6}$$

**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 $B$:

$$\text{CO}_2 + \text{RR'NH} \rightleftharpoons_{k_{-1}} \text{RR'}\text{N}^+\text{HCOO}^- \tag{7}$$

$$\text{RR'}\text{N}^+\text{HCOO}^- + B \rightleftharpoons_{k_3} \text{RR'}\text{NCOO}^- + \text{BH}^+ \tag{8}$$

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

$$R_{\text{CO}_2} = \frac{k_z[\text{CO}_2][\text{Am}]}{1 + \frac{[\text{CO}_2][\text{Am}]}{\Sigma k_b[B]}} \tag{9}$$

where $\Sigma k_b[B]$ 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) $k_{-1}/(\Sigma k_b[B]) \approx 1$. 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:

$$R_{\text{CO}_2} = k_z[\text{CO}_2][\text{Am}] \tag{10}$$

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

$$R_{\text{CO}_2} = k_z[\text{CO}_2][\text{Am}] \left(\frac{\Sigma k_b[B]}{k_{-1}}\right) \tag{11}$$

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 Oye-vaar, 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

$$R_{\text{CO}_2} = \frac{k_z[\text{CO}_2][\text{Am}]}{1 + \frac{[\text{CO}_2][\text{Am}]}{k_{\text{Am}}[\text{Am}]}} \tag{12}$$

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 $k_{-1}/(k_{\text{Am}}[\text{Am}]) \gg 1$), and this reduces to one at very high amine concentrations.

In general, a plot of the apparent rate constant ($k'[\text{Am}]^{n'}$) against the amine concentration ([Am]) gives the partial reaction order ($n$) in amine. The trend line for Eq. 9 of the zwi-
The numerical value of $k$ in the preceding discussion is one. However, the second-order rate constant, $k_2$ (based on the zwitterion mechanism), obtained directly from the experimental kinetic data ($k'\langle Am\rangle^2/\langle Am\rangle$) 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) amine concentrations.

Applying the zwitterion mechanism to the reaction of CO$_2$ with aqueous amino (sulfonic or carboxylic) acid salts results in:

$$CO_2 + K^-O_3S - R - NH_2^+ + K^-O_3S$$

$$- R - NH_2^+COO^-$$

(16)

$$+ K^-O_3S - R - NH_2^+COO^- + B^+ + K^-O_3S$$

$$- R - NHCOO^- + BH^+.$$  

(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.

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

(18)
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 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:

\[
\begin{align*}
\text{HO}_2C - R - \text{NH}_3^+ & \xrightleftharpoons{\text{H}^+} \text{O}_2C - R - \text{NH}_3^+ \\
& \xrightleftharpoons{\text{H}^+} \text{O}_2C - R - \text{NH}_2
\end{align*}
\]  

(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 (\(P_{\text{vap}}\)) was noted down and pure CO was introduced into the reactor. The initial CO partial pressure of the reactor was adjusted for different amino acid salt concentrations to maintain a constant amine conversion or average CO loading for all the experiments. In the present experiments, the initial CO partial pressure was adjusted to have a final CO 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 (\(P_{\text{vap}}\)) decrease due to the absorption of CO\(_2\) was recorded. The reaction kinetics can be determined if the following conditions are satisfied.

\[
2 < \text{Ha} \ll E_{\text{CO}_2,=} 
\]  

(20)

where

\[
\text{Ha} = \frac{\sqrt{k_m D_{\text{CO}_2}}}{k_L} 
\]  

(21)

\[
E_{\text{CO}_2,=} = \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{AmA}}}} + \sqrt{\frac{D_{\text{AmA}}}{D_{\text{CO}_2}}} \frac{[\text{AmA}]RT}{v_{\text{AmA}}P_{\text{CO}_2,m_{\text{CO}_2}}} 
\]  

(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,

\[
J_{\text{CO}_2}A = \sqrt{k_m D_{\text{CO}_2} m_{\text{CO}_2} P_{\text{CO}_2}} \left( \frac{A}{RT} \right) \text{mol} \cdot \text{s}^{-1} 
\]  

(23)
The information on the solubility and diffusivity of CO₂ in aqueous amino acid salt solutions is given in the Appendix. The actual partial pressure of CO₂ at any instant \( P_{CO_2,t} \) was calculated according to the following relation:

\[
P_{CO_2,t} = P_{tot,t} - P_{vap}
\]

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

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

The value of \( k_{OH^-} \) was obtained from Pohorecki and Momiuk (1988), and the reaction between CO₂ 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 CO₂ 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.

**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 CO₂ 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·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·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·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·m⁻³) to 2 at high amine concentrations (Blauwhoff et al., 1984; Versteeg and Oyenavar, 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 \( k_{CH_2OH/k_{-1}} \) 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 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>
<thead>
<tr>
<th>Amine</th>
<th>( T ) (K)</th>
<th>pKa</th>
<th>( k_2 ) (m⁴·mol⁻³·s⁻¹)</th>
<th>( k_{amA/k_{-1}} ) (m²·mol⁻¹)</th>
<th>( k_{H_2O/k_{-1}} ) (m²·mol⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium taurate</td>
<td>295</td>
<td>9.14</td>
<td>12.60</td>
<td>1.30×10⁻⁴</td>
<td>4.23×10⁻⁶</td>
<td>Present study</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>295</td>
<td>8.96</td>
<td>2.42</td>
<td>3.86×10⁻⁴</td>
<td>5.31×10⁻⁷</td>
<td>Litt et al. (1992)</td>
</tr>
</tbody>
</table>

Figure 4. Experimental results for aqueous potassium taurate at different temperatures.
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 $k_3$ 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 (pK$a$) 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 ($k_{app}^2 = k_2[H_2O]/[\cdot]$), as explained earlier using Eq. 13. Even in the present case, the apparent second-order rate constant ($k_3^*$) at 295 K is 2.96 m$^{-1}$·mol$^{-1}$·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·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 ($\approx 0.02$ 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 ($2 < Ha \leq E_{CO_2}$) 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·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 ($k_{app}^2/B$) 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 down to reactant molecules or form final reaction products (carbamate)

\[
\text{CO}_2 + K^- \cdot O_3S - R - \text{NH}_2 + B \\
\frac{k_s}{k_{-1}} [\text{Encounter Complex}] \\
\downarrow k_e \\
+ K^- \cdot O_3S - R - \text{NHCOO}^- + BH^+ 
\]

(26)

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

\[
R_{CO_2,B} = \frac{k_{3,B}k_e}{k'_{-1} + k_e} \left[ \text{RNH}_2 \right] [B] [\text{CO}_2] \\
\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} 
\]

(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:

\[
R_{CO_2} = R_{CO_2,\text{AmA}} + R_{CO_2,\text{H}_2\text{O}} \\
\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1} 
\]

(28)

\[
R_{CO_2} = \frac{k'_e}{k'_{-1} + k_e} \left[ k_{3,\text{AmA}} [\text{RNH}_2] [\text{RNH}_2] [\text{CO}_2] \\
+ k_{3,\text{H}_2\text{O}} [\text{RNH}_2] [\text{H}_2\text{O}] [\text{CO}_2] \right] 
\]

(29)

\[
R_{CO_2} = k'_{\text{AmA}} [\text{RNH}_2] [\text{RNH}_2] [\text{CO}_2] \\
+ k'_{\text{H}_2\text{O}} [\text{RNH}_2] [\text{H}_2\text{O}] [\text{CO}_2], 
\]

(30)

where

\[
k'_{\text{AmA}} = \frac{k_e}{k'_{-1} + k_e} k_{3,\text{AmA}}; \\
k'_{\text{H}_2\text{O}} = \frac{k_e}{k'_{-1} + k_e} k_{3,\text{H}_2\text{O}} \\
\text{mol}^{-2} \cdot \text{m}^6 \cdot \text{s}^{-1}. 
\]

(31)

Surprisingly, Eq. 30 is similar to Eq. 11 (though there are no assumptions like \(k_{-1}/\Sigma k_{3,B}B \approx 1\), 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 \(k_{\text{app}}\) 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:

\[
k_2 = 3.23 \times 10^9 \exp \left( - \frac{5.700}{T} \right) \text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1} 
\]

(32)

\[
\frac{k_{\text{H}_2\text{O}}}{k_{-1}} = 2.29 \times 10^{-8} \exp \left( \frac{1.483}{T} \right) \text{m}^3 \cdot \text{mol}^{-1} 
\]

(33)

\[
\frac{k_{\text{AmA}}}{k_{-1}} = 2.36 \times 10^{-6} \exp \left( \frac{1.225}{T} \right) \text{m}^3 \cdot \text{mol}^{-1}. 
\]

(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>
<thead>
<tr>
<th>Amino Acid Salt</th>
<th>(T) (K)</th>
<th>(pK_a^\text{e})</th>
<th>(k_{3,\text{AmA}}^{\text{e}}) (m(^3) \cdot mol(^{-1}) \cdot s(^{-1}))</th>
<th>(k_{3,\text{H}_2\text{O}}^{\text{e}}) (m(^3) \cdot mol(^{-1}) \cdot s(^{-1}))</th>
<th>(k_2^{\text{e}}) (m(^3) \cdot mol(^{-1}) \cdot s(^{-1}))</th>
<th>(k_2^{\text{e}}) (m(^3) \cdot mol(^{-1}) \cdot s(^{-1}))</th>
<th>(k_2^{\text{e}}) (m(^3) \cdot mol(^{-1}) \cdot s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium taurate</td>
<td>285</td>
<td>9.38</td>
<td>6.78</td>
<td>1.86 \times 10^{-4}</td>
<td>4.23 \times 10^{-6}</td>
<td>7.20 \times 10^{-4}</td>
<td>2.02 \times 10^{-5}</td>
</tr>
<tr>
<td>Potassium taurate</td>
<td>295</td>
<td>9.14</td>
<td>12.60</td>
<td>1.30 \times 10^{-4}</td>
<td>3.39 \times 10^{-6}</td>
<td>9.71 \times 10^{-4}</td>
<td>3.69 \times 10^{-5}</td>
</tr>
<tr>
<td>Potassium taurate</td>
<td>305</td>
<td>8.91</td>
<td>25.20</td>
<td>1.41 \times 10^{-4}</td>
<td>3.01 \times 10^{-6}</td>
<td>2.24 \times 10^{-3}</td>
<td>6.60 \times 10^{-5}</td>
</tr>
<tr>
<td>Potassium glycinate</td>
<td>295</td>
<td>8.67</td>
<td>49.68</td>
<td>6.04 \times 10^{-5}</td>
<td>2.69 \times 10^{-6}</td>
<td>2.09 \times 10^{-3}</td>
<td>1.18 \times 10^{-4}</td>
</tr>
</tbody>
</table>

*Perrin (1965).
**Zwitterion mechanism constants.
†Termolecular mechanism constants.
solutions showed greater reactivity toward CO over potassium glycinate than that of taurine (9.14), the contribution of the reaction mechanism observed with this experimental system, it is possible to ascertain the termolecular mechanism can also be 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.

Acknowledgment

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Notation

- $A =$ gas–liquid interfacial area, m$^2$
- $B =$ base (H$_2$O, OH$^-$, AmA, or Am)
- $D_i =$ diffusion coefficient of component $i$, m$^2$s$^{-1}$
- $E =$ enhancement factor, dimensionless
- $E_{CO_2,\infty} =$ infinite enhancement factor for the mass transfer of CO$_2$,
  dimensionless

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·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·m$^{-3}$. This behavior was observed for both potassium taurate and potassium glycinate solutions. For potassium glycinate, the apparent second-order rate constant ($k_2^a = k_2k_{H_2O}[H_2O]/k_1$) obtained from the present study is in good agreement with the literature.
Ha = Hatta number, dimensionless

$J_{CO_2} = CO_2$ absorption mole flux, $mol \cdot m^{-2} \cdot s^{-1}$

$k'$, $k''$ = rate constants, $mol^{-1} \cdot m^{-3} \cdot s^{-1}$

$k'_{AmA}$ = termolecular mechanism rate constant for AmA, $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_{H_2O}$ = termolecular mechanism rate constant for $H_2O$, $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_{\text{w}}$ = zwitterion mechanism rate constant, $s^{-1}$

$k_s$ = second-order rate constant, $mol^{-1} \cdot s^{-1}$

$k^*$ = apparent second-order rate constant ($k_{app}/[AmA]$, $mol^{-1} \cdot s^{-1}$

$k_{3,B}$ = termolecular mechanism rate constant for $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_{app}$ = apparent rate constant, $s^{-1}$

$k_B$ = zwitterion mechanism deprotonation rate constant for AmA, $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_1$ = termolecular mechanism rate constant, $s^{-1}$

$k_{H_2O}$ = zwitterion mechanism deprotonation rate constant for $H_2O$, $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_L$ = liquid-phase mass-transfer coefficient, $m \cdot s^{-1}$

$k_{OH}$ = zwitterion mechanism deprotonation rate constant for $OH^-$, $m^6 \cdot mol^{-2} \cdot s^{-1}$

$k_o$ = overall rate constant, $s^{-1}$

$m$ = physical solubility ([CO$_2$]$_{0}$/[CO$_2$]$_{eq}$), dimensionless

$n$ = partial order of the reaction in amine acid salt, dimensionless

$o$ = overall order of the reaction, dimensionless

$P_{CO_2}$ = instantaneous partial pressure of $CO_2$, Pa

$P_{Tot}$ = instantaneous total pressure of reactor, Pa

$P_{vap}$ = vapor pressure of the liquid, Pa

$R$ = universal gas constant (8.3145), $J \cdot mol^{-1} \cdot K^{-1}$

$R_{CO_2}$ = rate of reaction of $CO_2$, $mol \cdot m^{-3} \cdot s^{-1}$

$T$ = temperature, K

$v$ = stoichiometric coefficient, dimensionless

[ ] = concentration, $mol \cdot m^{-3}$

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\begin{align*}
\text{Sada, E., H. Kumuzawa, Z. Q. Han, and M. A. Butt,} & \text{ “Chemical Kinetics of the Reaction of Carbon Dioxide with Ethanolamines in Nonaqueous Solvents,” AIChE J., 31, 1297 (1985).}
\end{align*}

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\begin{align*}
\text{Appendix I: Physicochemical Parameters for Determining Kinetic Constants}
\end{align*}

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 $N_O$, 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 $N_O$ ($m$) in aqueous potassium tauroate solutions (Kumar et al., 2001)

\begin{align*}
\log(m/m_0) = KC_s, \tag{A1}
\end{align*}

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

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is given by the following relation,

\[ K = \sum (h_i + h_G) n_i \, \text{m}^3\cdot\text{kmol}^{-1} \]  \quad (A2)

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

\[ h_+ : \quad 0.0922 \, \text{m}^3\cdot\text{kmol}^{-1} \]  \quad (A3)

\[ h_- : \quad 0.0249 \, \text{m}^3\cdot\text{kmol}^{-1} \]  \quad (A4)

For the solubility of \(\text{N}_2\text{O}\) in aqueous potassium glycinate solutions, the anion-specific constant is given by

\[ h_- : \quad 0.0276 \, \text{m}^3\cdot\text{kmol}^{-1} \]  \quad (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 \(\text{N}_2\text{O}\) in water \((m_w)\) was obtained from the work of Versteeg and van Swaaij (1988b).

### Diffusion coefficient

The diffusion coefficient of \(\text{N}_2\text{O} (D_{\text{N}_2\text{O}})\) 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 \(\text{N}_2\text{O}\) in aqueous potassium taurate solutions

\[ D_{\text{N}_2\text{O}} \mu^{0.74} = \text{constant}. \]  \quad (A6)

The information on the dependence of viscosity \((\mu)\) 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)

\[ \left( \frac{D}{D_w} \right)_{\text{N}_2\text{O}} = \left( \frac{D}{D_w} \right)_{\text{CO}_2}. \]  \quad (A7)

The diffusion coefficients of CO\(_2\) \((D_{\text{CO}_2,w})\) and \(\text{N}_2\text{O} \((D_{\text{N}_2\text{O},w})\) 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. Manuscript received Dec. 18, 2001, and revision received June 12, 2002.