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Kinetics of the reversible reaction of CO_{2(aq)} with taurate in aqueous solution

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Abstract:

Taurate has potential as an absorbent for CO₂ capture and is also an effective rate promoter in aqueous NH₃-based absorbents. However, the detailed reaction mechanism involved in the reaction of $CO_{2(aq)}$ with taurate in aqueous solution is not available and the reaction rate and equilibrium constants for some reactions in the mechanism are not yet determined. This limits our understanding of the role of taurate in the capture process using NH₃/taurate mixture and hinders the rigorous rate-based process simulation. In this work, we studied the reaction of taurate with CO₂ in aqueous solution with added acid-base indicators at 288.0, 298.0, 308.0 and 318.0 K. Stopped-flow spectrophotometry was applied to record absorbance of the solutions which reflects pH changes via coloured acid-base indicators as a function of time and over the wavelength range from 400.0 - 700.0 nm. Through global analysis of the kinetic data from the stopped flow reactor, we determined the temperature dependence of the rate and equilibrium constants using a detailed reaction scheme including all reactions in the taurate-CO₂-H₂O system. We then used stopped-flow spectrophotometry to investigate the effect of taurate on the reaction of CO₂ in the mixed taurate-NH₃-CO₂-H₂O system at 298.0 K. The reaction mechanism for the reaction of the taurate and NH₃ mixture with CO_{2(aq)} is found to be a simple combination of two individual systems. Taurate in the mixture can significantly

enhance CO₂ absorption rate and NH₃ can work as a proton sink allowing more taurate available for CO₂ and potential reduction of ammonia loss.

Keywords: Taurate, ammonia, CO2 capture, reaction mechanism, amino acid

1. Introduction

Post combustion capture (PCC) is viewed as the most promising technology in a near term for significant reduction of CO₂ emissions from the existing coal or natural gas based power plants¹⁻³. Commercial deployment of amine based PCC, currently the leading technologies is hindered by high material and capital costs, high energy consumption, and solvent degradation ⁴⁻⁸.

Aqueous ammonia (NH₃) has received considerable interest as an alternative absorbent for CO₂ capture due to its low cost, high chemical stability and CO₂ loading capacity, and low absorption heat and regeneration energy requirements ⁹⁻¹⁵. It also has the added potential to remove multiple flue gas components to produce valuable ammonium salts for use as fertilisers ¹⁶⁻¹⁸. However, NH₃-based capture faces two major challenges that limit its economic feasibility: low CO₂ absorption rates resulting in oversized absorbers and thus high capital costs; high NH₃ loss rates due to the relatively high volatility of NH₃ compared to other traditional amine based absorbents ^{19, 20}. A number of approaches have been explored to address these two issues, including process optimization ^{15, 21, 22}, new process configuration ²³⁻²⁷ and introduction of additives as rate promoters ^{28, 29} or NH₃ evaporation suppressants ^{4, 30, 31}. The new approaches typically improve one aspect but comprise on other aspects. For example, addition of PZ to aqueous NH₃ can significantly increase CO₂ absorption rate, but at the expenses of an increase in NH₃ loss ^{29, 32}. Further advancement of NH₃ based CO₂ capture needs to explore more effective approaches to promote CO₂ absorption and reduce ammonia emission simultaneously.

Our recent work using amino acid as rate prompters show that, comparing to ammonia alone solutions, the mixtures of taurine and NH_3 can increase CO_2 absorption rate and lower NH_3 loss ³³. These positive results have motivated us for further study to address knowledge gap on the taurate and mixture of ammonia and taurine/taurate based CO_2 capture.

Taurate has received considerable attention as a potential absorbent for CO₂ capture ³⁴⁻³⁷. Sanchez-Fernandez et al. investigated CO₂ capture by precipitating amino acid salt solvents and selected potassium taurate as the baseline amine acid salt solvent ³⁵. The equilibrium based process simulation showed that the reboiler duty for the solvent regeneration can be reduced by 45% compared to the conventional monoethanolamine based process. To fully evaluate the potential of using taurate for CO₂ capture, the reaction kinetics between CO₂ and taurate need to be well understood and determined.

Kumar et al. studied kinetics of the reaction of CO_2 with aqueous potassium salts of taurine over a wide range of salt concentrations (100 – 4000 mol/m³) and temperatures (285-305 K) in a stirred–cell reactor ³⁶. Both zwitterion mechanism and termolecular mechanism were used to describe the reactions involved between CO_2 and taurate in aqueous solution and determine kinetic data for reactions from the experimentally obtained kinetic data. When the zwitterion mechanism was used, the forward second–order reaction rate constant (k, m³mol⁻¹s⁻¹) for the reaction of CO_2 with taurate as a function of temperature (T, K) can be described by the following equation:

$$k = 3.23 \times 10^9 * \exp\left(\frac{-5700}{T}\right)$$
 (E1)

Penny and Ritter ³⁸ showed that a single Brønsted plot can be used to link the rate constants with the basicity of the amine and amino acid. In case of taurate, the calculated rate constant at 295 K from the plot is $3.6 \text{ m}^3 \text{mol}^{-1}\text{s}^{-1}$, while the value obtained from equation 1 is $12.6 \text{ m}^3 \text{mol}^{-1}\text{s}^{-1}$ at the same temperature and is significant higher. The big difference suggested that more kinetic study is needed to understand the mechanistic aspect of the reaction

kinetics and determine the kinetic parameters for the reactions involved. Sodiq et al. used the stopped-flow technique to study the reaction kinetics of $CO_{2(aq)}$ in sodium taurate solutions at taurate concentrations of 5–50 mol/m³ (mM) and temperatures of 298–313 K ³⁴. Their study provided the Arrhenius expression for the forward rate constant of the reaction between $CO_{2(aq)}$ and taurate, as shown by equation 2.

$$k = 5.44 \times 10^8 * \exp\left(\frac{-5780}{T}\right) \tag{E2}$$

The values obtained are significantly lower than those reported by Kumar et al. Wei et al. proposed taurate to be a promising absorbent for CO_2 capture at flue gas temperature and used a wetted wall column to measure the absorption rate of CO_2 into taurate solutions with and without CO_2 at taurate concentrations of 2-6 kmol/m³ (M) and in a temperature range of 293-353 K ³⁷. The forward reaction rate constants for the reaction of CO_2 with taurate were derived from the CO_2 absorption results and shown as follows:

$$k = 3.7 \times 10^9 * \exp\left(\frac{-6074}{T}\right)$$
(E3)

The values from equation 3 fall between those from equations 1 and 2.

As aforementioned, a number of studies have been carried out to determine the kinetics of the reaction of taurate with CO_2 in aqueous solution. However, few have focused on developing a detailed reaction scheme including all possible chemical pathways and reactions. This knowledge gap hinders the development of a rate-based CO_2 capture process involving use of taurate and limits our understanding of the role of taurate in CO_2 absorption in taurate– NH_3 mixtures. Previous work using wetted-wall column often relied on assumptions to simplify the absorption process and the link between the liquid phase reactions with the measured CO_2 absorption rate. As a result, the reaction kinetic parameters obtained does not represent a complete comprehensive reaction model for the chemical reactions. We consider homogeneous techniques using stopped-flow measurements as the most suitable method for investigation of fast reaction kinetics in a chemical reaction system in the absorpe of influential mass transfer

effects. Traditional stopped-flow measurements that rely on conductivity detection have several shortcomings given that the overall conductivity is measured and is produced from the combined effects of all ions in solution (indistinguishable signal for individual species). In this work, we employ advanced stopped-flow spectrophotometry utilising changes in absorbance induced from the presence of coloured acid-base indicators, and thus pH, in the solutions. The resulting data can be used to elucidate the reaction mechanism of CO₂ in taurate solutions alone and in NH₃-taurate mixtures.

In this work, firstly, we developed a detailed reaction scheme for taurate and $CO_{2(aq)}$ based on previously developed mechanisms for amino acids including sarcosinate ^{39, 40}. The fast reversible reaction between $CO_{2(aq)}$ and taurate was investigated using stopped-flow spectrophotometry at 288.0, 298.0, 308.0 and 318.0 K by following absorbance, and thus pH changes, coupled to coloured acid–base indicators over the wavelength range from 400– 700 nm. The rate and equilibrium constants for the reaction of $CO_{2(aq)}$ with taurate have been determined from global analysis of the kinetic data and the corresponding activation and thermodynamic values also determined. Based on the understanding of the taurate system we further explored the effect of taurate on the reaction kinetics of $CO_{2(aq)}$ in a mixed taurate-NH₃ system using stopped-flow spectrophotometry at 298.0 K. The availability of this detailed reaction scheme for the taurate and mixed taurate-NH₃ system will guide the understanding of PCC absorbent systems and facilitate ongoing simulation of taurate based absorbent systems.

2. Methdology

We have developed a stopped-flow spectrophotometric technique for the fast CO_2 -amine reaction system coupled to the spectral changes and protonation equilibria of coloured acidbase pH ^{41, 42}. The technique was applied to develop the detailed reaction mechanism involved in the reaction of $CO_{2(aq)}$ with monoethnaolamine, ammonia, sarcosinate (an aminoa acid salt), piperazine and many other amines and to determine the reaction rate and equilibrium constants for the corresponding reactions ^{40, 43-45}. This works builds on these previous research efforts and firstly developed a detailed reaction scheme including all the reactions in the taurate-CO₂-H₂O system. The reactions are shown by red dotted lines and purple solid lines in Figure 1. We determined all unknown reaction rates for the reaction of $CO_{2(aq)}$ with taurate (k_9 , k_{-9}) and equilibrium constants (K_{10} , K_{12}) in the system by global analysis of the series of measurement data. In terms of the reaction of $CO_{2(aq)}$ with the mixture of taurate and NH₃, we assumed there is no synergistic effect between taurate and NH₃. In other words, the reactions of $CO_{2(aq)}$ with the taurate/NH₃ mixture are simply a combination of all individual reactions in the two systems. Based on this assumption, we combined the NH₃-CO₂-H₂O reaction scheme developed by Wang et al. ⁴⁶ and that for the taurate-CO₂-H₂O together to develop a comprehensive reaction scheme for the taurate-NH₃-CO₂-H₂O system, as shown in Figure 1.



Figure 1. General reaction scheme including all reactions in the TAU⁻– NH_3 – CO_2 – H_2O system. TAU⁻ refers to taurate.

As shown in Figure 1, the taurate– CO_2 – H_2O reaction scheme includes $CO_{2(aq)}$ hydration, taurate/NH₃ carbamic acid formation, and all protonation equilibria reactions, which are

expressed by Equations (R1) to (R12). The kinetic parameters of the reactions of $CO_{2(aq)}$ with H_2O and OH^- as well as the reactions of $CO_{2(aq)}$ with NH_3 were redetermined in the previous works of Wang et al. ^{40, 42} and these values were used in the present work. We determined the protonation contant of taurate (K₁₁) in our previous work, so four unknown parameters (k₉, k. 9, K₁₀, K₁₂) were requried to be fitted in the global data fitting program.

The CO_{2(aq)} hydration reactions:

$$CO_2(aq) + H_2O \xrightarrow[k_1]{k_1} H_2CO_3$$
 (R1)

$$CO_2(aq) + OH^- \xrightarrow{k_2} HCO_3^-$$
 (R2)

$$\operatorname{CO}_3^{2-} + \operatorname{H}^+ \xrightarrow{\operatorname{K}_3} \operatorname{HCO}_3^-$$
 (R3)

$$HCO_{3}^{-} + H^{+} \xleftarrow{K_{4}} H_{2}CO_{3}$$
(R4)

$$OH^- + H^+ \xleftarrow{K_5} H_2O$$
 (R5)

The carbamate formation and protonation reactions of NH₃:

$$NH_3 + H^+ \xleftarrow{K_6} NH_4^+$$
 (R6)

$$NH_{3} + CO_{2}(aq) \xrightarrow{K_{7}, k_{7}} NH_{2}CO_{2}H$$
(R7)

$$NH_{2}CO_{2}^{-} + H^{+} \xleftarrow{K_{8}} NH_{2}CO_{2}H$$
(R8)

The carbamate formation and protonation reactions of taurate:

$$NH_2C_2H_4O_2SO^{-}(TAU^{-}) + CO_2 \xrightarrow[k_9,k_9]{} NH(COOH)C_2H_4O_2SO^{-}(TAU^{-}(CO_2H))$$
 (R9)

$$\mathrm{NH}(\mathrm{COO}^{-})\mathrm{C}_{2}\mathrm{H}_{4}\mathrm{O}_{2}\mathrm{SO}^{-}(\mathrm{TAU}^{-}(\mathrm{CO}_{2}^{-})) + \mathrm{H}^{+} \xleftarrow{\mathrm{K}_{10}} \mathrm{NH}(\mathrm{COOH})\mathrm{C}_{2}\mathrm{H}_{4}\mathrm{O}_{2}\mathrm{SO}^{-}(\mathrm{TAU}^{-}(\mathrm{CO}_{2}\mathrm{H}))$$
(R10)

$$\mathrm{NH}_{2}\mathrm{C}_{2}\mathrm{H}_{4}\mathrm{O}_{2}\mathrm{SO}^{-}(\mathrm{TAU}^{-}) + \mathrm{H}^{+} \xleftarrow{\mathrm{K}_{11}} \mathrm{NH}_{3}^{+}\mathrm{C}_{2}\mathrm{H}_{4}\mathrm{O}_{2}\mathrm{SO}^{-}(\mathrm{TAUH})$$
(R11)

$$NH_{3}^{+}C_{2}H_{4}O_{2}SO^{-} (TAUH) + H^{+} \xleftarrow{K_{12}} NH_{3}^{+}C_{2}H_{4}O_{2}SOH(TAUH_{2}^{+})$$
(R12)

As part of the global analysis the protonation reactions of the acid-base indicators (IND) and hydroxide ion, as shown in reactions (R13) and (R14), are included in the chemical model. Equilibrium constants for the protonation reaction of hydroxide were obtained from Maeda et al. ⁴⁷.

$$IND + H^+ \xleftarrow{K_{13}} INDH$$
 (R13)

$$H^+ + OH^+ \xrightarrow{K_{14}} H_2O$$
 (R14)

3. Experimental

Analytic grade aqueous NH₃ with weight concentrations of 25–30% was supplied by Scharlau and the exact NH₃ concentration was titrated by the standard 0.1M hydrochloric acid solution from Fluka. Taurine with a mass purity of 99% from Sigma–Aldrich was neutralized by an equal molar amount of potassium hydroxide (KOH, 85.9%) from VWR, Australia to generate the active form of taurine (taurate, TAU⁻). The exact concentration of KOH was determined by titration using potassium hydrochloric phthalate (Ajax Chemicals; 0.999 minimum mass fraction) as a reference solution and phenolphthalein (Hopkin & Williams Ltd) as an indicator. Thymol blue sodium salt (TB) as pH indicators was obtained from Sigma–Aldrich. All solutions were prepared using Milli–Q water which was boiled to remove CO₂ prior to use. The CO₂ solutions at various concentrations were prepared by bubbling mixture gases containing N₂(99.95%, BOC, Australia) and CO₂(99.5%, BOC, Australia) into Milli–Q water for more than 1 hour in order to reach saturation. The experimental conditions for stopped–flow measurements related to the TAU⁻– CO_2 – H_2O system and the TAU⁻– NH_3 – CO_2 – H_2O system are summarized in Table 1.

Reactions	Temperature (K)	Concentration of species in column A (mM)	Concentration of species in column B
	288.0	[CO ₂]= 8.10	[TAU ⁻]=4,6,8,12,14mM; 25.0μM TB
CO ₂ with taurate	298.0	[CO ₂]= 6.4	[TAU ⁻]=4,6,8,12,14mM; 25.0μM TB
	308.0	[CO ₂]= 5.30	[TAU ⁻]=4,6,8,10mM; 25.0μM TB
	318.0	[CO ₂]= 4.42	[TAU ⁻]=4,6,8,10mM; 25.0µM TB
CO ₂ with the blended solutions of taurate and NH ₃	298.0	[CO ₂]=6.4	[TAU ⁻]=6mM; [NH ₃]=2,4,6mM; 25.0μM TB
		[CO ₂]=6.4	[TAU ⁻]=2,3,4mM; [NH ₃]=6mM; 25.0µM TB
CO ₂ with NH ₃	298	[CO ₂]=6.4	[NH ₃]=4,6mM 25.0μM TB

Table 1. A summary of the experimental conditions for stopped-flow measurements.

A typical stopped–flow instrument, shown in Figure 2, incorporates a rapid mixing device which forces two solutions (contained in syringes) together through a high efficiency mixing chamber into an absorption cell after which the flow is abruptly stopped.



RNH₂ = amine/amino acid salt, IND = coloured acid base indicator to observe pH changes during reactions.

Figure 2. General schematic diagram of the stopped-flow reactor.

The CO₂ saturated solutions and the amines solutions with 12.5 μ M (after mixing) thymol blue sodium salt were placed into two columns A and B, respectively. In the beginning of the experiments, two solutions are mixed together in a 1:1 v/v ratio and the mixture was impelled into the absorption cell instantaneously. pH values in the mixture solution change with the increase of the reaction time, which results in the color change of the solution. Absorbance values of the mixture were recorded over the wavelength range 400–700 nm by an applied photophysics DX–17 spectrophotometer equipped with a J&M Tidas MCS 500–3 diode–array detector. To obtain overall profiles, the absorbance values were totally measured for 15.0s in this study. Various initial concentration of taurate were mixed with different CO₂ solution at four temperatures 288.0, 298.0, 308.0, 318.0 K and the temperatures were controlled by a thermocouple located within the stopped–flow instrument. All of samples and the reservoir part of instruments were submerged in the water bath for 1h prior to mixing. The absorbance values at 590 nm were selected to do the data fitting using Reactlab Kinetics (http://www.jplusconsulting.com) and in house extensions of the software written in Matlab. Each stopped–flow measurement was repeated at least four times to obtain four independent values for each parameters. Instead of depending on standard deviation provided by the data fitting program, the average of the four independently obtained values at each temperature are reported here together with the standard deviation of these average values.

4. Results and discussion

4.1 Stopped-flow spectrophotometric studies of reactions of CO_{2(aq)}

The kinetics of the reaction of taurate with CO₂ were investigated at four temperatures under the conditions listed in Table 1. As an example, Figure 3 shows the experimental results and the data fitting results for the reaction of 3.2 mM aqueous CO₂ and taurate with various initial concentrations of taurate (2, 3, 4, 5, 6, 7 mM) in the presence of 12.5 μ M TB at 298 K. As displayed in Figure 3, the dotted markers and solid lines present the measured and calculated absorbance profiles as a function of the reaction time from the experimental and data fitting results, respectively. The good agreement between the experimental and data fitting results confirms the validity of the reaction scheme proposed for the TAU⁻-CO₂-H₂O system here. The absorbance values were recorded at an interval of 0.0025 s and were measured for a duration of 15.0 s in order to obtain overall profiles, as shown in Figure 3(a). It is evident that the absorbance values decreased promptly upon mixing and then changed slowly after the initial rapid drop. To understand how taurate reacted with CO_{2(aq)} in the beginning of reactions, the absorbance values (pH values) of the mixtures occurred in the initial 0.05 -0.1 s after which the extent of decrease with reaction time become smaller. At the same reaction time, the

absorbance values (pH values) are generally higher in the mixture with a higher taurate concentration and the same CO₂ concentration.



Figure 3. Absorbance at 590 nm versus time in the reaction of 3.2 mM $CO_{2(aq)}$ with different initial concentrations of taurate in the presence of 12.5 μ M thymol blue. (a) total 15 s; (b) initial 0.2 s. Solid markers are measured data and the lines are calculated profiles.

As part of the fitting program, we calculated the species distribution in the solution as a function of reaction time. As an example, Figure 4 shows the calculated concentration profiles and pH change curve in the reaction of 4 mM taurate with 3.2 mM $CO_{2(aq)}$ in the present of 12.5 μ M thymol blue at 298K (refer to the measured absorbance profiles in this reaction presented by the blue curve in Figure 3). Figure 4(a) show the overall profiles up to 15.0 s (note - the time axis is presented as a logarithm scale) and Figure 4(b) is an enlargement of the first 0.4 s from Figure 4(a). The variation of species concentration with reaction time can be divided into two stages which is consistent with the trend observed for the absorbance shown in Figure 3. The first stage of the reaction took place within the initial 0.1 s. The concentrations of reactants (taurate and $CO_{2(aq)}$) dropped dramatically and most of reactants were consumed. The pH values decrease rapidly from about 10.2 to 8.6. In the second stage, pH values changed only slightly and were around 8.4 after 15.0 s reaction time. The changes of concentration of

reactants in this stage were very slow.



Figure 4. Calculated reactants and products species concentration profiles and pH in the reaction of 4 mM taurate with 3.2 mM $CO_{2(aq)}$ at 298K. (a) total 15 s; (b) initial 0.4 s.

Based on reaction R(9), the reaction of taurate with $CO_{2(aq)}$ generated taurine carbamic acid, TAU⁻(CO₂H) firstly but its concentration was extremely low and only taurine carbamate, TAU⁻ (CO₂⁻) is observed in Figure 3. This suggests that once the intermediate TAU⁻(CO₂H) was formed, it instantaneously released proton to form TAU⁻(CO₂⁻), resulting in almost complete consumption of TAU⁻(CO₂H) and an instant decrease on pH in the first stage. In the second stage, the taurate concentration remains low and almost unchanged, but the concentration of $CO_{2(aq)}$ continued to decrease, accompanied by a decrease in pH and concentration of taurine carbamate, TAU⁻(CO₂⁻) and an increase in HCO₃⁻ and TAUH. The reason for that observation is that the concentration of taurate was very low in the second stage, its contribution to the consumption of $CO_{2(aq)}$ became less important. In comparison, the reactions between $CO_{2(aq)}$ and OH⁻/water played a more important role in consumption of $CO_{2(aq)}$, leading to a continued decrease in pH and an increase in HCO₃⁻. Decreasing $CO_{2(aq)}$, concentration caused the decomposition of carbamate as a shift of reaction 9 to left. The generated taurate (TAU⁻) was instantly protonated to taurine (TAUH). As a result, the concentration of TAUH increased accordingly.

Four unknown parameters $(k_9, k_{.9}, \log(K_{10}), \log(K_{12}))$ in the developed reaction scheme were determined by Global data fitting over the temperature range 283–298K. The equilibrium constant for reaction 9, K₉ was calculated by k₉ and k_{.9}. The corresponding rate and equilibrium constants are listed in Table 2.

Table 2. Calculated unknown rate and equilibrium constants in the reaction scheme for the TAU⁻–CO₂–H₂O system at different temperatures.

T (K)	Reaction	Constants	1	2	3	4	Average
288		k ₉ [M ⁻¹ s ⁻¹]	2.35×10 ³ ±3.23	2.36×10 ³ ±3.71	2.63×10 ³ ±4.48	2.28×10 ³ ±9.28	2404.25
	(R9)	k-9 [s ⁻¹]	3.46×10±0.21	33.8×10±0.13	36.1×10±0.12	3.58×10±0.34	35.08
		K ₉ [M ⁻¹]	67.95	69.94	72.74	63.58	68.55
	(R10)	$log(K_{10})$	7.05±2.88×10 ⁻³	7.10±1.95×10 ⁻³	7.13±1.26×10 ⁻³	7.04±4.41×10 ⁻³	7.08
	(R12)	$log(K_{12})$	2.02±1.32×10 ⁻²	1.98±1.44×10 ⁻²	2.05±1.42×10 ⁻²	2.02±1.65×10 ⁻²	2.02
298		k9 [M ⁻¹ s ⁻¹]	$4.30 \times 10^{3} \pm 12.92$	4.35×10 ³ ±12.41	$4.21 \times 10^{3} \pm 10.41$	$4.29 \times 10^{3} \pm 10.92$	4286.50
	(R9)	k-9 [s ⁻¹]	6.48×10±0.56	6.70×10±0.54	6.57×10±0.62	6.70×10±0.51	66.13
		K ₉ [M ⁻¹]	66.34	64.91	64.09	63.99	64.82
	(R10)	$log(K_{10})$	7.07±3.89×10 ⁻³	7.11±3.93×10 ⁻³	7.08±4.22×10 ⁻³	7.09±3.67×10 ⁻³	7.09
	(R12)	$log(K_{12})$	$1.89 \pm 2.88 \times 10^{-2}$	1.90±7.27×10 ⁻³	1.86±1.87×10 ⁻²	1.90±1.44×10 ⁻²	1.89
308		k9 [M ⁻¹ s ⁻¹]	$7.11 \times 10^3 \pm 8.61$	7.16×10 ³ ±9.31	7.07×10 ³ ±9.53	$7.11 \times 10^{3} \pm 8.95$	7114.00
	(R9)	k.9 [s ⁻¹]	$1.17 \times 10^{2} \pm 1.10$	$1.21 \times 10^{2} \pm 0.70$	$1.17 \times 10^{2} \pm 0.66$	1.19×10 ² ±0.51	118.45
		$K_9[M^{-1}]$	60.96	59.15	60.40	59.76	60.06
	(R10)	$log(K_{10})$	7.05±4.03×10 ⁻³	7.03±2.66×10 ⁻³	7.05±3.20×10 ⁻³	7.05±2.37×10 ⁻³	7.05
	(R12)	$log(K_{12})$	1.70±1.40×10 ⁻²	1.70±1.03×10 ⁻²	1.70±1.36×10 ⁻²	1.70±1.42×10 ⁻²	1.70
318		k ₉ [M ⁻¹ s ⁻¹]	9.90×10 ³ ±15.66	$1.08 \times 10^{4} \pm 17.92$	$1.10 \times 10^{4} \pm 18.43$	$1.14 \times 10^{4} \pm 17.50$	10792.75
	(R9)	k.9 [s ⁻¹]	$1.74 \times 10^{2} \pm 3.06$	$2.14 \times 10^{2} \pm 3.09$	$2.19 \times 10^{2} \pm 2.22$	$2.10 \times 10^{2} \pm 0.57$	204.25
		K ₉ [M ⁻¹]	56.90	50.69	50.27	54.36	52.84
	(R10)	$log(K_{10})$	6.91±7.60×10 ⁻³	6.90±6.41×10 ⁻³	6.90±4.55×10 ⁻³	6.90±2.65 ×10 ⁻³	6.90
	(R12)	$log(K_{12})$	1.62±2.94×10 ⁻²	1.62±2.20×10 ⁻²	1.64±1.83×10 ⁻²	1.64±1.63×10 ⁻²	1.63

Temperature Dependence

The Arrhenius equation (E1) and the van't Hoff equation (E2) were used to analyse the relationship between temperature and rate constants or equilibrium constants.

Arrhenius:
$$k(T) = A \cdot \exp(-\frac{E_a}{RT})$$
 (E4)

van't Hoff:
$$K(T) = \exp(-\frac{\Delta H^{\varnothing}}{RT} + \frac{\Delta S^{\varnothing}}{R})$$
 (E5)

Where, A is a pre-exponential factor, R is the molar gas constant, T is the absolute temperature, Ea is the activation energy, H^{\emptyset} is the enthalpy, and S^{\emptyset} is the entropy of the reaction.

Figure 5 shows the Arrhenius plots for the natural log values of rate constants k_9 , $k_{.9}$ for the reaction of taurate with $CO_{2(aq)}$ as a function of 1/T. The linear correlation coefficients (R^2) for $ln(k_9)$ and $ln(k_{.9})$ versus 1/T are 0.997 and 0.998, respectively. Figure 6 plots log K_{10} , log K_{12} and ln K_9 as a function of 1/T and shows the good linear relationship. Based on the linear relationship in Figures 5 and 6, the activation parameters, reaction enthalpies and the reaction entropies are calculated and are listed in Table 3.



Figure 5. Arrhenius plots of $ln(k_9)$ and $ln(k_{-9})$ versus 1/T for the forward and backward reaction of TAU⁻ with CO₂(aq)



Figure 6. van't Hoff plots of $ln(K_9)$, $log(K_{10})$ and $log(K_{12})$ versus 1/T.

Table 3. Calculated activation parameters, enthalpies, and entropies for the reaction of TAU⁻ with CO_{2(aq)} and taurine carbamate protonation.

reactions	Arrhenius		van's Hoff		
	Ea [kJ mol ⁻¹]	А	ΔH^{\varnothing} [kJ mol ⁻¹]	ΔS^{\varnothing} [J mol ⁻¹ K ⁻¹]	
r1	38	2.1×10 ¹⁰			
r2	45	4.5×10^{9}			
r3			-6	13	
r4			-10	101	
r5			-24	-44	

$NH_2C_2H_4O_2SO^{-}(\mathrm{TAU}^{-}) + \mathrm{CO}_2 \xrightarrow{k_9} NH(COOH)C_2H_4O_2SO^{-}(\mathrm{TAU}^{-}(\mathrm{CO}_2\mathrm{H}))$	(r1)
$NH_2C_2H_4O_2SO^{-}(TAU^{-}) + CO_2 \leftarrow NH(COOH)C_2H_4O_2SO^{-}(TAU^{-}(CO_2H))$	(r2)

$$NH_{2}C_{2}H_{4}O_{2}SO^{-}(TAU^{-}) + CO_{2} \xleftarrow{\kappa_{0}} NH(COOH)C_{2}H_{4}O_{2}SO^{-}(TAU^{-}(CO_{2}H))$$
(r3)

$$NH(COO^{-})C_{2}H_{4}O_{2}SO^{-}(TAU^{-}(CO_{2}^{-})) + H^{+} \xleftarrow{k_{10,Tau}} NH(COOH)C_{2}H_{4}O_{2}SO^{-}(TAU^{-}(CO_{2}H))$$
(r4)

$$NH_{3}^{+}C_{2}H_{4}O_{2}SO^{-} (TAUH) + H^{+} \xleftarrow{^{K_{12}Tau}} NH_{3}^{+}C_{2}H_{4}O_{2}SOH(TAUH_{2}^{+})$$
(r5)

1

As described in introduction, the kinetics of the reaction of $CO_{2(aq)}$ with aqueous taurate salts have been studied at various taurate concentrations and temperatures and the rate constants for the forward reaction of taurate and $CO_{2(aq)}$ reported have been reported. Figure 7 shows the comparison of the rate constants reported in literature and those obtained in this study. The values reported by Kumar et al. are significantly higher than those from the other three sources. The rate constants obtained from this study are similar to those from Sodiq et al. ³⁴and Wei et al. ³⁷, suggesting the results in this study are reasonable.



Figure 7 Comparison of the rate constants for the forward reaction of taurate with $CO_{2(aq)}$ reported in literature and those obtained in this study.

4.2 Stopped-flow spectrophotometric studies of reactions of CO_{2(aq)} with blended NH₃/TAU⁻ solution

To study the mechanism involved in the reaction of NH₃ and taurate blends with $CO_{2(aq)}$, we assumed the reaction scheme for the TAU⁻–NH₃–CO₂–H₂O system was the simple combination of the TAU⁻–CO₂–H₂O and the NH₃–CO₂–H₂O individual reaction system. Since the kinetic parameters for all reaction in the TAU⁻–NH₃–CO₂–H₂O system were determined, the absorbance values in the reaction of $CO_{2(aq)}$ with the mixture can be calculated. To verify the assumption, we designed the CO₂ absorption experiments using the blended solutions of NH₃ and taurate under conditions shown in Table 1. The experimental absorbance curve were recorded and compared to the calculated curve, as shown in Figure 8. In addition, separate experiments on the reaction of 3.2 mM $CO_{2(aq)}$ with 2 and 3 mM NH₃ alone solutions were also carried out and the absorbance curves are compared between the experimental and calculated. The objective is to confirm the reaction scheme for the NH₃–CO₂–H₂O system obtained previously can be used to satisfactorily predict the experimental results for the reaction of NH₃ with $CO_{2(aq)}$ in this study.



Figure 8. Absorbance at 590 nm as a function of time in the reactions of $CO_{2(aq)}$ with different concentrations of NH₃/TAU⁻ mixtures at 298K. (a) total 15s, (b) initial 0.5s. Solid markers are measured data and the lines are calculated profiles.

Figure 8 shows the absorbance at 590 nm as a function of time in the reactions of $CO_{2(aq)}$ with different concentrations of NH₃ and taurate blended solutions at 298 K. The excellent agreement between the experimental and calculated profiles confirms our assumption for the reaction mechanism involved in the reaction of $CO_{2(aq)}$ with the mixture of NH₃ and taurate. To show a general picture of how taurate affects CO_2 absorption in the mixture, we present the experimental and calculated absorbance profiles for the reaction of $CO_{2(aq)}$ with NH₃ alone,

taurate alone and mixture of NH₃ and taurate in Figure 9.



Figure 9. Absorbance at 590 nm as a function of time in the reactions of $CO_{2(aq)}$ with different initial concentration of NH₃/TAU⁻ mixtures, NH₃-based solutions and TAU⁻-based solutions 298K. (a) total 15 s, (b) initial 0.2 s.

The good agreement between the experimental and calculated absorbance profiles in the reaction of $CO_{2(aq)}$ (3.2 mM) with NH₃ alone (2 and 3 mM) confirms the previous work can be reproduced and provides additional evidence to show the approach and methodology in this work is sound and consistent with previous work. Comparison of absorbance profiles (indication of pH values and extent of reaction)) shown in Figure 9(b) indicates the extent of absorbance change in the initial stage of the reaction (0.1 s) decreased in the following order: Taurate alone > NH₃/Taurine mixture > NH₃ alone. After the initial rapid change, the absorbance in the taurate alone solutions decreased very slowly and absorbance in the NH₃ alone solutions dropped to a larger extent while the extent of decrease in absorbance in the mixture fell between those for taurate alone and NH₃ alone solutions. This clearly indicates the reaction rates of taurate with $CO_{2(aq)}$ are higher than those of NH₃ with $CO_{2(aq)}$ at the same reactants conditions and temperature. This is consistent with the rate constants for these two

reactions. The rate constants for the forward reaction of $CO_{2(aq)}$ and taurate is 4286 M⁻¹s⁻¹ which is more than 10 times higher than that for the reaction of $CO_{2(aq)}$ with NH₃ (394 M⁻¹s⁻¹) ⁴⁶. With the reaction model for the TAU⁻–NH₃–CO₂–H₂O system developed in this work, we can further calculate the concentrations of all species in the solution at any reaction time and has a detailed understanding of how the CO₂ absorption reaction takes place. As an example, the concentration changes of reactants (NH₃, TAU⁻, CO₂) and pH values, and the concentration changes of key products (NH₂CO₂⁻, TAU⁻(CO₂⁻), HCO₃⁻, NH₄⁺, TAUH) and pH variation in the reaction of 3.2 mM CO_{2(aq)} with the blended solution of 3 mM NH₃ and 1 mM taurate at 298 K are shown in Figures 10 and 11 respectively. The time axis of Figure 10(a) and Figure 11(a) is in common logarithm scale. The species profiles in the initial 0.4 s are presented in Figure 10(b) and Figure 11(b).

Figure 10(b) shows that the concentrations of TAU⁻, NH₃ and CO₂ drop considerably in the initial 0.1s, followed by slower consumption. After approximate 0.3-0.4s, the majority of TAU⁻ was consumed and its concentration remained low while the NH₃ concentration remained relatively high and continued to decrease although in a very slow pattern. The concentrations of $CO_{2(aq)}$ were higher than both those of TAU⁻ and NH₃ and kept decreasing during reaction. The variation of pH was in a similar trend to that of $CO_{2(aq)}$.



Figure 10. Calculated reactants concentration profiles and pH in the reaction of 3mM NH₃/1mM TAU⁻. (a) total 15 s; (b) initial 0.4 s



Figure 11. Calculated products concentration profiles in the reaction of 3mM NH₃/1mM TAU⁻. (a) total 15 s; (b) initial 0.4 s.

TAU⁻(CO₂⁻) was the major carbon-containing product in the initial stage of the reaction despite the lower concentration of taurate than NH₃. This is due to much higher rate constants for the forward reaction of taurate with CO₂ than those for NH₃ and CO_{2(aq)}. The concentration of TAU⁻(CO₂⁻) peaked at about 0.4-0.6 s and was around 0.0084 M. Theoretically 0.001 M taurate can react with 0.0005 M $CO_{2(aq)}$ to produce 0.0005 M TAU⁻(CO₂⁻) because the protons released from TAU⁻CO₂H will combine with taurate. In the presence of NH₃, more protons will combine with NH₃ instead of taurate because NH₃ has a higher pKa value (9.25 at 298 K) that taurate (8.97 at 298 K) and the concentration of free NH₃ is higher than that of taurate in the mixture ^{48, 49}. As a result, more taurate is available for reaction of $CO_{2(aq)}$ which can lead to a higher CO₂ reaction rate compared to NH₃ alone and better utilization of taurate.

 $NH_2CO_2^-$ was another major carbon-containing product resulting from the reaction of NH_3 with $CO_{2(aq)}$. Despite high NH_3 concentration in the mixture, the concentration of $NH_2CO_2^-$ produced was lower that of the $TAU^-(CO_2^-)$. As explained above, NH_3 and taurate competed for reaction with $CO_{2(aq)}$. Much higher CO_2 reactivity resulted in more CO_2 reacting with taurate and more NH_3 being protonated. After the majority of taurate was consumed and $TAU^-(CO_2^-)$ reached its maximum concentration, more CO_2 became available for NH_3 leading to a continued increase in the concentration of $NH_2CO_2^-$.

Similar to the reaction of taurate with CO_2 , the formation of HCO_3^- was predicted in the reaction of CO_2 with the NH₃ and taurate mixture. Different from $TAU^-(CO_2^-)$ and $NH_2CO_2^-$ whose concentrations increased initially and then decreased in the remaining of the reaction, HCO_3^- was produced with its concentration increasing invariably with reaction time and became the major carbon-containing product after around 3 s' reaction. The reactions between $CO_{2(aq)}$ and OH^- /water are the direct reaction pathways leading to formation of HCO_3^- . In the beginning of the reaction, the majority of CO_2 reacted with taurate and NH_3 . With an decrease in the concentration of taurate and NH_3 , the reactions between $CO_{2(aq)}$ and OH^- /water became the main reactions consuming CO_2 in the solution. The decomposition of carbamates TAU^- (CO_2^-) and $NH_2CO_2^-$ also occurred (a shift of reactions 7 and 9 to left). The generated taurate (TAU^-) and NH_3 were instantly protonated to taurine (TAUH) and NH_4^+ . As a result, the concentration of TAUH and NH_4^+ increased accordingly.

Although the addition of taurate to the NH₃ solutions did not have a catalytic effect on CO₂ absorption and both taurate and NH₃ reacted with CO₂ individually, the above analysis does show that the different CO₂ reactivity and basicity of taurate and NH₃ can offer some positive impact on the performance of CO₂ absorption by the mixture of taurate and NH₃. The presence of taurate can significantly enhance CO₂ absorption rate and capacity and NH₃ can work as a proton sink allowing more taurate available for CO₂ and reduction of free ammonia concentration will also help reduce NH₃ evaporation. In all, the availability of the detailed reaction scheme for the TAU⁻-CO₂-H₂O system and the TAU⁻-NH₃-CO₂-H₂O system will allow us to have a detailed understanding of the CO₂ absorption kinetics, speciation and thermodynamics and support development of the process simulation.

5 Conclusions

This work investigated the reaction of CO₂ with taurate and blended NH₃ and taurate solutions over the temperature range 283.0 – 313.0 K using stopped-flow spectrophotometry, and developed details reaction mechanisms including all reactions for the two systems. All unknown rate and equilibrium constants for the reaction systems were determined over the studied temperature range by global data fitting. The corresponding activation parameters, reaction enthalpy and entropy of reactions were also obtained. The obtained rate constant for the forward reaction of $CO_{2(aq)}$ with taurate agree well with values reported in literature. The role of the taurate in NH₃-based CO₂ capture was elucidated. The reaction mechanism involved in the reactions of $CO_{2(aq)}$ with the blended taurate–NH₃ solution was a simple combination of the two individual systems for taurate–CO₂–H₂O and NH₃–CO₂–H₂O. However, high CO₂ reactivity of taurate and high basicity of NH₃ render the taurate and NH₃ mixture as an interesting CO₂ absorbent: The presence of taurate in the mixture can significantly enhance CO₂ absorption rate and NH₃ can work as a proton sink allowing more taurate available for CO₂ and reduction of free ammonia concentration and thus potentially ammonia loss. The availability of detailed reaction schemes for the taurate and mixed taurate-NH₃ systems will guide the understanding and further assessment of PCC absorbent systems involving use of taurate.

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