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Protonation constants and thermodynamic properties of amino acid salts for CO_2 capture at high temperatures

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Abstract:

Amino acid salts have greater potential for CO_2 capture at high temperatures than typical amine-based absorbents due to their low volatility, high absorption rate and high oxidative stability. The protonation constant (pK_a) of amino acid salts is crucial for the CO_2 capture as it decreases with the increase of absorption temperatures. However, published pK_a values of amino acid salts were usually determined at ambient temperatures. In this study, pK_a values of 11 amino acid salts were determined in the temperature range of 298−353 K using a potentiometric titration method. The standard state molar enthalpies (ΔH_m^o) and entropies (ΔS_m^o) of the protonation reactions were also determined by the van't Hoff equation. It has been found that sarcosine can maintain a higher pK_a than the other amino acids studied at high temperatures. We also found the CO_2 solubility and overall mass transfer coefficients of 5 m' sarcosinate (mol sarcosine/kg solution) at 333−353 K are higher than those of 30% MEA at 313−353 K. These results show that some of the possible benefits can be produced from use of sarcosine as a fast solvent for CO_2 absorption at high temperatures. However, the

pronotation reaction of sarcosine is the least exothermic among all amino acids studied. This could lead to a high regeneration energy consumption in the sarcosinate–based CO_2 capture process.

Keywords: CO_2 capture, amino acid salts, protonation constants (pK_a), standard molar enthalpy of protonation, standard molar entropy of protonation, high temperature absorption, sarcosine.

1 Introduction

Post-combustion capture (PCC) of CO_2 has potential to reduce power plant emissions, because PCC units can be easily retrofitted to existing power plants and integrated into new ones.[1,2] The temperatures of flue gas emitted from coal–fired power stations needs to be reduced from more than 393 K to 313 K to allow amine–based absorbents to react with CO_2. In most power stations, flue gases are cooled by the flue gas desulphurisation (FGD) process, which can remove impurities such as SO_2 before the discharge of flue gases to the atmosphere. However, FGD is not performed in Australian power stations, due to the low sulphur content of the Australian coal. To cool flue gases, additional cooling systems and equipment are therefore required for Australian PCC processes, which will increase the capital cost, water and energy consumption of PCC processes. To develop a more economical and energy efficient PCC technology for Australian power plants, absorbents are needed that can absorb CO_2 at temperatures as close to flue gas temperature as possible.[3,4]

Monoethanolamine (MEA) and aqueous ammonia (NH_3) are the typical absorbents for the commercial PCC processes and they have been reported many times in literature.[5,6] However, MEA and aqueous NH_3 are corrosive, volatile and MEA can be easily oxidised in flue gas, especially at high temperatures. Amino acid salts are promising candidates for CO_2 capture at high temperatures due to their high absorption rate, low vapour pressure and low

deterioration in the presence of oxygen.[7-10] Since the concept of the solution–based PCC process is to absorb acidic CO_2 by using alkaline absorbents, the basicity of the amino acid salts or the protonation constant (pK_a), plays an important role.[11] A high absorption temperature can result in the decrease of the pK_a values of amino acid salts and a decrease in the CO_2 absorption capacity. Therefore, it is important to find amino acid salts with high pK_a at high temperatures for the CO_2 capture process. The protonation reaction of an amino acid is exothermic, with a negative reaction enthalpy. This reaction enthalpy defines the rate of change of the pK_a with temperature.[12] Thus, knowledge of the temperature dependence of the pK_a values allows determination of the enthalpy and accompanying entropy, the values of which play important roles in the selection of amino acid salts for CO_2 capture at high temperatures.[13]

Most previous studies determined the pK_a values of amino acid salts at ambient temperatures. Few studies have presented the change of pK_a values at temperatures above 333 K. To fill this knowledge gap, we used potentiometric titrations to determine pK_a values of 11 amino acid salts at temperatures ranging from 298 to 353 K. The amino acid salts tested were L–alanine, glycine, L–proline, L–valine, DL–2–aminobutyric acid, 2–aminoisobutyric acid, sarcosine, L–norleucine, L–norvaline, taurine and cycloleucine. These amino acid salts have relatively high solubility in water and relatively low vapour pressures, indicating the potential for CO_2 absorption at high temperatures. The standard state molar enthalpy (ΔH_m^0) and entropy (ΔS_m^0) changes of the amino acid salts were determined using the van't Hoff equation. Based on the pK_a and the standard molar free energy (ΔG_m^0) values of amino acids obtained in this study, we selected 5 m' sarcosinate (mol sarcosine/kg solution) and compared its CO_2 solubility and CO_2 absorption kinetics with 30% MEA, the benchmark absorbent for PCC process. We also measured the overall mass transfer coefficients of CO_2 in 5 m' sarcosinate with various CO_2 loadings, and density and viscosity of solutions, to

determine the potential of sarcosinate to absorb CO_2 at high temperatures.

2 Theory

In aqueous solutions, amino acids can exist in three forms: protonated acidic form, neutral form, or deprotonated base form, as shown in reactions (R1) and (R2).[14] Only the deprotonated base form can react with CO_2.

$$NH_2^+R_1R_2COO^- + H^+ <=> NH_2^+R_1R_2COOH \quad (R1)$$

(neutral form) (acidic form)

$$NH_2^+R_1R_2COO^- <=> NHR_1R_2COO^- + H^+ \quad (R2)$$

(neutral form) (base form)

The reaction mechanism of amino acid salts and CO_2 is similar to those of alkanolamine and CO_2 due to the presence of identical amino functional groups in their molecular structure,[15] as shown in reaction (R2) and (R3) to (R5).[16] CO_2 dissolves in water to form bicarbonate and release a proton (R3). The base form of amino acid (represented as $NHR_1R_2COO^-$) reacts with dissolved CO_2 to form carbamic acid ($NCOOH\ R_1R_2COO^-$) (R4). Depending on the acidity of the carbamic acid, it may give up a proton and form a carbamate ($NCOO^-R_1R_2COO^-$) (R5). Reaction (R5) is also dependent on the stability of carbamate, which is sensitive to pH value in the solution. The termination reaction is the base form of the amino acid molecule, which accepts protons from the hydration reaction of CO_2 (R3) or from the formation reaction of carbamate (R5).

$$CO_2+H_2O<=>HCO_3^-+H^+ \quad (R3)$$

$$CO_2 + NHR_1R_2COO^- <=> NCOOHR_1R_2COO^- \quad (R4)$$

$$NCOOHR_1R_2COO^-<=> NCOO^-R_1R_2COO^-+ H^+ \quad (R5)$$

The chemical absorption reactions of CO_2 by amino acids follow two pathways. The first pathway includes reaction (R2) and (R3); the second pathway includes reactions (R2), (R4) and (R5). Both pathways depend on the availability of an unprotonated base to accept a

proton. The basic strength or protonation constant of the amine group in the amino acid influences how far both of these reaction pathways can proceed, and may also influence the reaction rate of (R4).

3 Methodology

3.1 Solution preparation

The main physical properties and source of amino acids used in this work are listed in Table 1 of the Supporting Information.[17] For pK_a value measurements, 10 M standard sodium hydroxide (NaOH) (VWR; ~9.998−10.002 M) was diluted to 0.10 M, and its concentration 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. Standard HCl solution (Titripur; 99.98%) of 0.10 M concentration was diluted to 0.02 M for initial acidification of amino acids and 0.005 M for glass electrode calibration. Amino acid solutions of 0.01 M concentration were pretreated by addition of dilute standard HCl solution (0.02 M) at a molar ratio of amino acid to HCl of 1:2 to completely convert the amino acids to their acidic form. Milli–Q water (Millipore) was boiled to release CO_2 and used to prepare solutions and potentiometric titrations. For the wetted–wall column study and viscosity measurement, a 5m' deprotonated base form of sarcosinate was prepared by neutralising sarcosine with an equimolar amount of potassium hydroxide (Sigma-Aldrich; 85.9% KOH basis, pellets). 5 m' sarcosinate solutions with various CO_2 loadings (mol CO_2/mol sarcosinate) were prepared by bubbling CO_2 (99.5%, BOC Gas Australia) from a gas cylinder through a fritted bubbler into a batch of CO_2 free solution. A glass bottle with the fresh solution was immersed in a water bath which was placed on a balance (GX-6100, A&D weighing), so the amount of CO_2 loaded was determined by CO_2 added mass. The top of the glass bottle was connected to a cooling condenser to condense

any vapour produced during the exothermic absorption reaction.

3.2 Potentiometric titration

CO_2 can be absorbed from the air into a basic solution, resulting in the formation of carbonate which can affect the measurement of pK_a of amino acids. To avoid this, pK_a values were obtained by titrating the amino acid solutions from an acidic form to a basic form.

Potentiometric titrations were carried out using a 665 Metrohm dosimat automated burette system and a Metrohm combined micro-pH glass electrode (Model 6.0234.100). The electrode was interfaced with a National Instruments NI-DAQ 7 board to amplify and translate the electrode signal, which was recorded in mV and used directly in the analysis of the titration data. The details of the titration set-up were reported in the previous study. [13] Prior to potentiometric titration of acidified amino acids, the electrode potential was calibrated by titrating 10.00 ml HCl solution with 0.10 M standardised sodium hydroxide. The GLEE[18] computer program was used to fit the standard electrode potential. It is based on a modified Nernst equation (E1) and transfers electrode potential to the hydrogen ion concentration (p[H]). The pK_w values of water at different temperatures were provided by GLEE.

$$E=E^0+s \lg[H^+] \quad \text{(E1)}$$

where E is the electrode potential for measurement, E^0 is the standard electrode potential, s is the parameter of the refinement and also represents the slope, and $[H^+]$ represents the hydrogen ion concentration.

The same glass electrode was used to measure the change of potential in the titration process of acidified amino acids. For each set of titrations on an acidified amino acid solution, 10.00 ml solution was added to the titration vessel at different temperatures from 298 to 353 K. The required titration temperatures were set up by a Julabo water bath (Model ED& F25), which circulated water between the bath and the jacketed titration vessel. To

eliminate interference from CO_2 in the air, nitrogen was bubbled through the acidified solutions for at least 10 minutes prior to the titrations and subsequently passed over the solutions during the titrations to ensure a CO_2 free atmosphere. Every acidified amino acid was titrated twice to ensure reproducibility. The electrode potential values (as a function of NaOH solution volume) and basic information from the electrode at different temperatures were input into the Hyperquad program, [19] which fitted the equilibrium constants from the potentiometric data. In this study, the protonation constant of the base form of amino acids (K_{prot} values), which are expressed as pK_a values for the protonated species (neutral form) were fitted by Hyperquad.

Acid dissociation can be divided into two processes. The first acid dissociation occurs on the acid group and the second on the base group. Acid dissociation constants ($k_{a,1}$ and $k_{a,2}$) are defined in equations (E2) and (E3), respectively. They are the reciprocal of the protonation constant of conjugate base form, respectively, as shown in equation (E4) and (E5). Figure 1 displays the change of electric potential as a function of the volume of NaOH solution added during the titration of sarcosine at 298 K. In this study, we investigated the protonation of the base group of the amino acids, which is represented by pK_a, as shown in equation (E6). pK_a values can be obtained by fitting the data from electric potential as a function of the volume of NaOH solution added.

$$k_{a,1} = [NH_2^+R_1R_2COO^-][H^+] / [NH_2^+R_1R_2COOH] \quad (E2)$$

$$k_{a,2} = [NHR_1R_2COO^-][H^+] / [NH_2^+R_1R_2COO^-] \quad (E3)$$

$$K_{prot,1} = 1/ k_{a,1} \quad (E4)$$

$$K_{prot,2} = 1/ k_{a,2} \quad (E5)$$

$$pK_a = -\log_{10} k_{a,2} = \log_{10} K_{prot,2} \quad (E6)$$

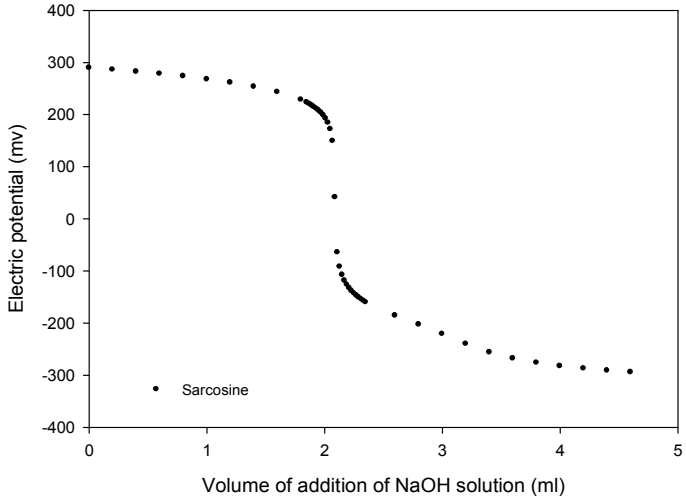

Figure 1. Electric potential as a function of volume of NaOH solution added sarcosine at 298 K.

The concentrations of all species in the solution can also be obtained from the Hyperquad fitting results. The ionic strengths are calculated by equation (E7):

$$\mathbf{I = 0.5 \sum_{i=1}^{n} C_i Z_i^2} \qquad \text{(E7)}$$

where C_i is the molecular concentration of an ion, i, and Z is its valency.

The standard state molar enthalpy and entropy changes (ΔH_m° and ΔS_m°) of the protonation(s) of each amino acid were obtained by plotting the $\log_{10}K_{prot,2}$ against 1/T, following by the equation (E8).[13]

$$2.303\log_{10}K_{prot,2}=2.303pK_a=-\Delta H_m^{\circ}/RT+\Delta S_m^{\circ}/R \qquad \text{(E8)}$$

The molar standard state free energy (ΔG_m°) was calculated from ΔH_m° and ΔS_m° by equation (E9).[13]

$$\Delta G_m^{\circ}=\Delta H_m^{\circ}-T\Delta S_m^{\circ} \qquad \text{(E9)}$$

3.3 Wetted–wall column

Measurements of CO_2 absorption flux in sarcosinate–based solutions were performed using a wetted-wall column and its associated facilities. As shown in Figure 2, the setup consists of a gas mixture system to control different CO_2 partial pressure, a water bath to adjust absorption temperatures, a condenser to remove water vapour from the gas phase, a Horiba (VA3000) CO_2 gas analyser to measure the CO_2 concentration in the inlet and outlet gas mixture, a saturator, a solution reservoir and a wetted–wall column with 41 cm^2 surface area where the gas phase, and liquid phase contact. A detailed description of circulation of gas phase and liquid phase in a wetted–wall column, gas mixture system, and liquid system has been reported in the previous work.[20] The absorbent flow rates were 100–120 ml/min, and were controlled by a rotameter to form a thin, ripple free film on the surface of the column. The total gas flow rates of N_2 and CO_2, controlled by Bronkhorst mass flow controllers, were fixed at 5 L/min at atmospheric pressure at absorption temperatures of 313−353 K. The absorption temperatures were measured using a K-type thermocouple. CO_2 and N_2 concentrations in the inlet and outlet system were recorded by the Horiba gas analyser (VA3000). The overall mass transfer coefficients (K_G) of CO_2 in the absorbents were obtained by:

$$N_{CO_2} = K_{G,CO_2} A \, (P_{CO_2} - P^*_{CO_2}) \qquad (1)$$

where P_{CO_2} is the partial pressure of CO_2 in the bulk gas, which can be expressed by the natural log mean of the inlet and outlet partial pressure in the wetted–wall column; $P^*_{CO_2}$ is the CO_2 partial pressure that is in equilibrium with the liquid phase (all pressures are

expressed in kP_a). N_{CO_2} is the CO_2 absorption rate in mmol/s; K_{G,CO_2} is the overall mass transfer coefficient of CO_2 in mmol/(m^2·s·kP_a); and A is the effective interfacial surface area in m^2.

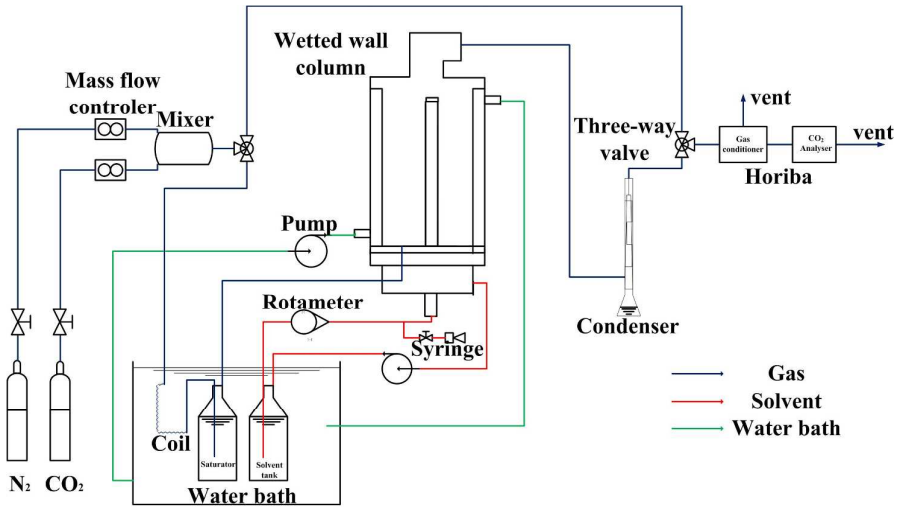

Figure 2. A schematic diagram of the wetted–wall column and associated apparatus.

3.4 Density and viscosity measurement

The densities of unloaded and loaded 5 m' sarcosinate solutions at temperatures ranging from 303−353 K were determined by a traditional method of measuring the mass and the volume of the solution. Sarcosinate solutions were added to a volumetric flask (Pyrex) which volume was calibrated at temperatures from 313−353 K using deionized water. The mass of the certain volume of solution was weighted using a balance (GR 300, A&D Weighing).

Dynamic viscosities of sarcosinate were measured using an AMVn automated micro viscometer (Anton Paar), at temperatures from 313−353 K, with a specified repeatability of <0.1%. The temperature meters are integrated in the viscosity meter, with an error limit of

±0.05 K.

4 Results and discussion

4.1 Protonation constants of amino acids

The pK_a values of 11 amino acid salts were determined in this study. The pK_a values of sarcosine, L–norvaline and 2–aminoisobutyric acid at different temperatures shown in Figure 3 were also compared with data from literatures[21-23] to validate the methodology of this work. The pK_a of sarcosine determined by Bunting and Stefanidis[21] at temperatures of 268−328K were lower than the pK_a values of this work. The pK_a values of L–norvaline and 2–Aminoisobutyric acid determined by Sovago et al.[22] and Chen and Lin[23] at temperatures of 268−328K were slightly higher than the pK_a values of this work. The small differences between them were most likely due to the difference of the ionic strength (IS).

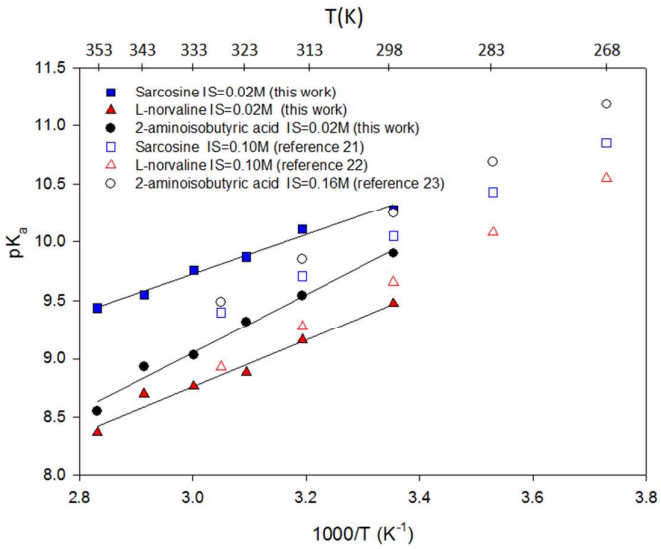

Figure 3. Comparison of measured amimo acid salt pK_a values with published values as a function of temperature.

Table 2 of the Supporting information shows the pK_a values of the amino acid salts obtained from this work and literatures[13, 24-43] at 298 K. In this work, the ionic strength of taurine and other amino acid salts were 0.01 and 0.02, respectively. The difference of ionic strength was very small and the effect of ionic strength can be negligible.

In general, the pK_a values were in good agreement with the literature data[21-23] and the methodology used was deemed reliable.

The pK_a values of 11 amino acid salts and their standard deviations and ionic strength are shown in Table 3 of the Supporting Information. The pK_a value of monoethalamine[13] is also listed in Table 3 of the Supporting Information as a benchmark.

Figure 4 shows the pK_a values as a function of temperature (1/T) for each amino acid in the temperature range of 298−353 K. The correlation between pK_a and 1/T was linear. Most of the linear correlation coefficients (R^2) were higher than 0.99, except for 2–aminoisobutyric acid, which had an R^2 of 0.95. The molar standard enthalpies and entropies were calculated from the slope and intercept of the plots in equation (E8). ΔG_m^0 of the protonation reaction was calculated by equation (E9). Amino acids were divided into two groups by the variation of pK_a values. Figure 4(a) shows that sarcosine, cycloleucine, L–norvaline and L–norleucine had a relatively small variation in pK_a values with increasing temperature. Of these amino acids, sarcosine had the highest pK_a at temperatures of 313–353 K. The pK_a variations of L–proline, 2–aminoisobutyric acid, DL–2–aminobutyric acid, L–alanine, L–valine, glycine, taurine in Figure 4(b) were larger than those in Figure 4(a). Although the pK_a values of a few amino acids in Figure 4(b) were similar to those in Figure 4(a) at low temperatures, they decreased more than those in Figure 4(a) at high temperatures. For example, the pK_a values of L–proline and sarcosine were 10.38 and 10.37 at 298 K, respectively. The pK_a values of L–proline and sarcosine were 9.1 and 9.4 when the temperature increased from 298 K to 353 K. Similar observations could be found in 2–

aminoisobutyric acid and cycloleucine solution. Initially, the pK_a values of 2–aminoisobutyric acid was higher than cycloleucine by 0.1 at 298 K, but it was lower than cycloleucine by 0.2 at 353 K.

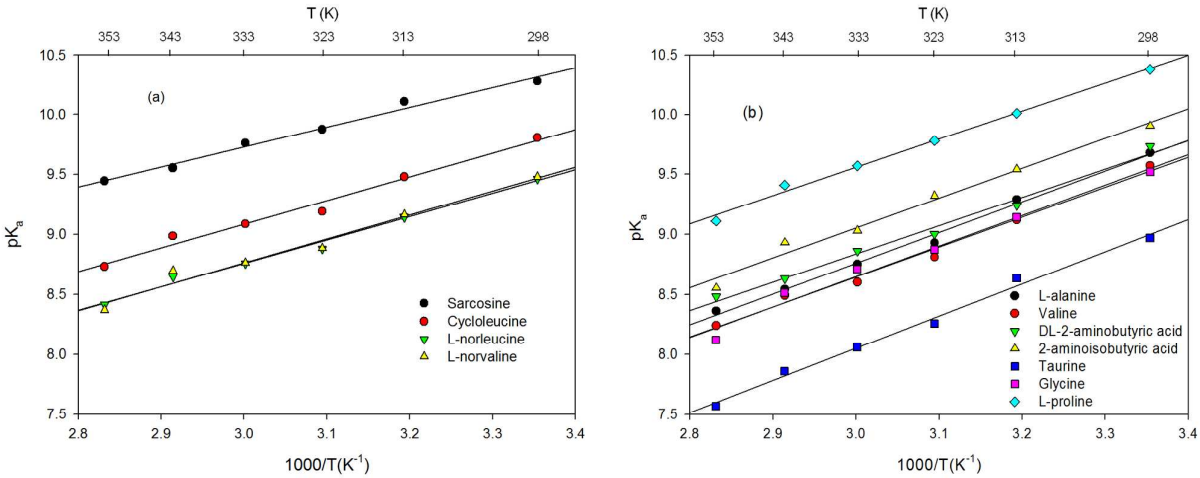

Figure 4. Plots of pK_a vs 1/T for the protonation of amino acids. (a) Protonation of amino acids with a small change of pK_a values; (b) Protonation of amino acids with a large change of pK_a values.

4.2 Thermodynamic properties of amino acids

The ΔH_m^o, ΔS_m^o and ΔG_m^o values of the protonation reaction of amino acids are listed in Table 4 of the Supporting Information. The ΔH_m^o, ΔS_m^o and ΔG_m^o values of monoethalamine[13] are also listed in Table 4 of the Supporting Information as a benchmark. The ΔH_m^o and the ΔS_m^o values of amino acids are negative and positive, respectively. This indicates that the protonation reactions of amino acids are all significantly exothermic, and enthalpically driven. The protonation reaction of sarcosine was the least exothermic, with ΔH_m^o being −31.92 kJ/mol; while taurine was the most exothermic at −51.36 kJ/mol. The negative ΔG_m^o values indicate that the protonation reactions of amino acids are spontaneous

from 298 to 353 K. We also found the ΔG_m^o values of sarosine and L–proline were larger in magnitude than those of the other amino acids and MEA.

4.3 Comparative study of monoethanolamine and sarcosinate for CO_2 absorption

4.3.1 Comparison of CO_2 solubility in monoethanolamine and potassium sarcosinate

The previous thermodynamic study showed that the pK_a value of sarcosine was 9.44 at 353 K, which is the same as the published pK_a value of MEA at 298 K[13]. Since the pK_a of sarcosine can also maintain high values when the temperature increases, this implies that sarcosine has a greater ability to accept protons i.e. a higher CO_2 solubility, at high temperatures. We compared CO_2 solubility in 5m' sarcosinate (mol sarcosine/kg-total solution)[44] and 30% MEA[45] respectively, at temperatures of 313−353 K. Figure 5 shows the CO_2 partial pressure as a function of CO_2 loading in 5m' sarcosinate and 30% MEA with different CO_2 loading at a temperature range of 313 to 353 K. For both of solutions, the CO_2 equilibrium partial pressure in the gas phase increased with increasing CO_2 loading and temperature. The CO_2 partial pressure in 5m' sarcosinate is lower than that in 30% MEA at the same loading and the same temperatures. What is more, the CO_2 equilibrium partial pressures in 5m' sarcosine at 333 and 353 K are even lower than those in 30% MEA at lower temperatures (313 and 333 K, respectively). In other words, the solubility of CO_2 in 5 m' sarcosinate at 333 and 353 K is greater than in 30% MEA at 313 and 333 K, respectively.

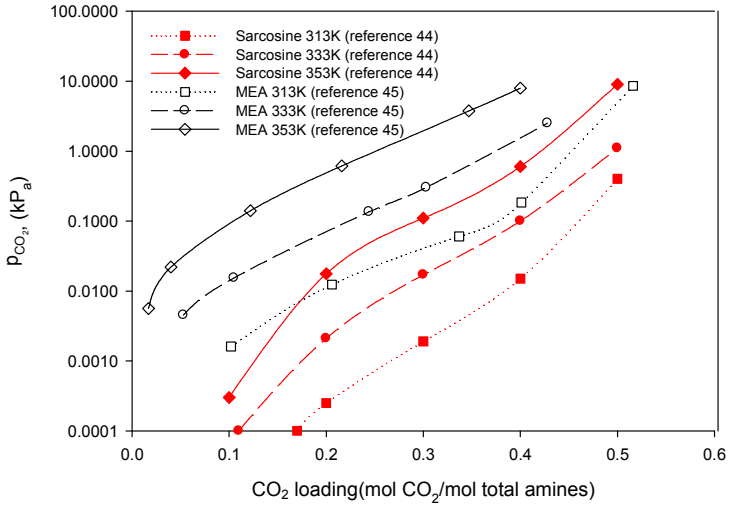

Figure 5. The comparison of equilibrium solubility of CO_2 in 5m' sarcosinate and 30% monoethanolamine (MEA) as a function of CO_2 loading at three temperatures.

4.3.2 Comparison of reaction rate constant and mass transfer coefficient

The kinetics of CO_2 absorption in solutions is a very important parameter for PCC processes. The reaction rate of CO_2 with amines is a critical parameter for determination of the CO_2 absorption rate. Figure 6 shows the rate constants of sarcosinate (k_{Sar})[46], piperazine (k_{PZ})[47] and MEA (k_{MEA})[48] with CO_2. We selected piperazine and MEA as reference absorbents because the fast CO_2 absorption rate of piperazine is well recognised[47], and MEA is a well-known benchmark CO_2 absorbent. As shown in Figure 6, the rate constants for the reactions of amines with CO_2 increased according to the order of k_{PZ} > k_{Sar}> k_{MEA} at temperatures below 330 K. At temperatures above 330 K, the k_{Sar} increased dramatically and was the highest. This implies that sarcosinate has the potential to absorb CO_2 at relatively

higher temperatures from a kinetic point of view.

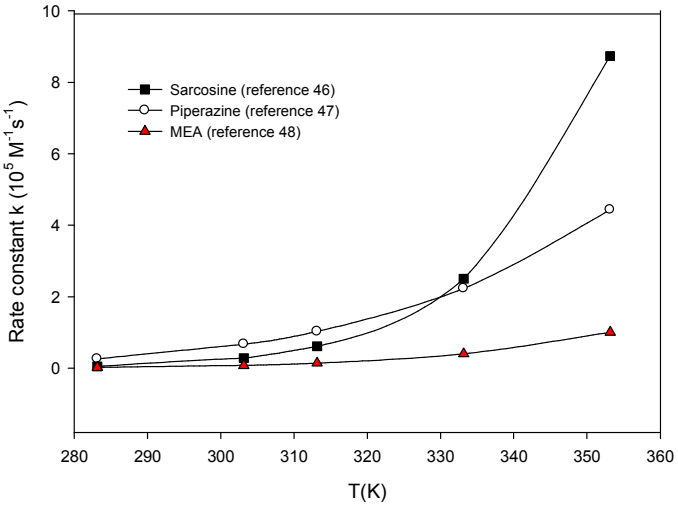

Figure 6. Comparison of CO_2 absorption rate constants of sarcosinate, piperazine and monoethanolamine (MEA).

To further identify the performance of CO_2 absorption using sarcosinate at high temperatures, we investigated the overall mass transfer coefficients (K_G) in 5 m' sarcosinate with various CO_2 loadings at the temperatures of 313−353 K using a wetted–wall column and also compared the results with the K_G of CO_2 absorption in MEA[49], as shown in Figure 7.

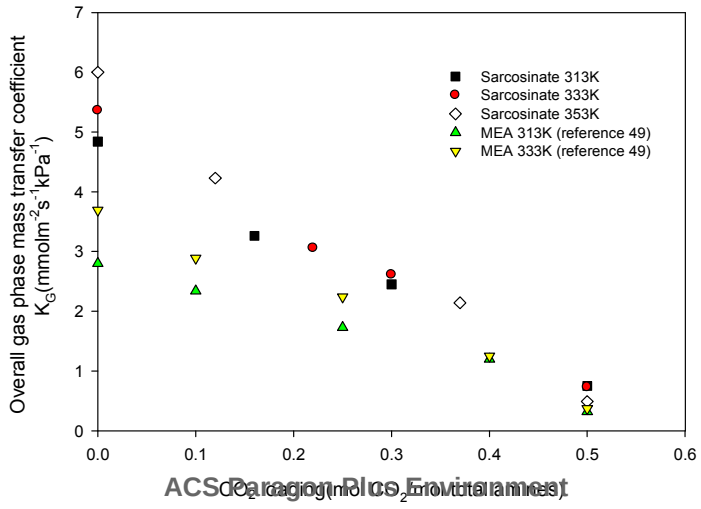

Figure 7. K_G of CO_2 absorption in 5m' sarcosinate and 30% monoethanolamine (MEA) as a function of CO_2 loading at different temperatures.

As shown in Figure 7, the K_G of CO_2 absorption in sarcosinate reached about 5 $mmol \cdot m^{-2} \cdot s^{-1} \cdot kPa^{-1}$ at 313 K, and was even higher at 353 K at zero CO_2 loading. This is about 1.5 times higher than the K_G of CO_2 absorption in 30% MEA at 353 K. It should be pointed out that the K_G of CO_2 absorption in 5 m' Sarcosinate at 313−353 K were higher than that in 30% MEA at 313−333 K with the same CO_2 loadings. The results of K_G further confirm that sarcosinate can be used to absorb CO_2 at the high temperatures.

4.3.3 Comparison of physical properties

The physical properties of solvents play important roles in absorbing CO_2 from flue gases. In this work, we have determined the densities of 5 m' sarcosinate at CO_2 loadings of 0, 0.3, and 0.5 (mol CO_2/mol sarcosinate) and temperatures of 303−353 K and compared the results with those of 30% MEA[50] at 298−353 K. Figure 8 shows the densities of 30% MEA solutions and 5 m' sarcosinate with different CO_2 loadings. The densities of 5m' sarcosinate are higher than those of 30% MEA.

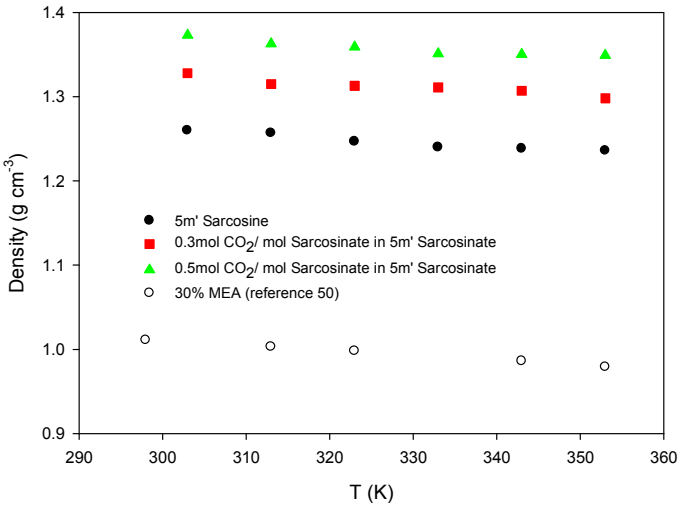

Figure 8. Density of 5m' sarcosinate−based solutions and 30% monoethanolamine (MEA) at different temperatures.

We also determined the viscosities of 5 m' sarcosinate at CO_2 loadings of 0, 0.3 and 0.5 (mol CO_2/mol sarcosinate) and temperatures of 313, 333 and 353 K since the viscosity of an absorbent affects the diffusion coefficient of CO_2 into solution and subsequently can affect CO_2 absorption rate. Figure 9 illustrates that the viscosities of sarcosinate increased with the increasing of CO_2 loading. Although the viscosities of sarcosinate solutions were higher than those of 30% MEA, the viscosities of sarcosinate decreased dramatically with increasing temperature. When the temperature increased to 353 K, the viscosity of 5 m' sarcosinate were similar to that of 30% MEA at 313 K.

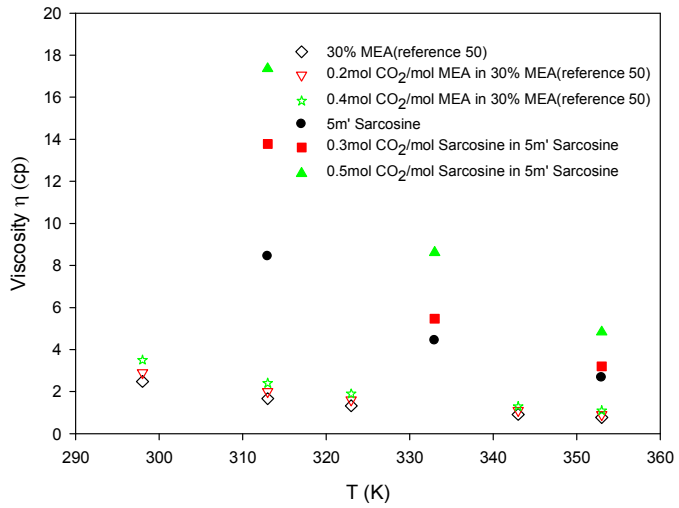

Figure 9. Viscosities of 5m' sarcosinate based solutions and 30% monoethanolamine (MEA) at temperatures of 298−353 K.

It has been pointed that the pK_a value of sarcosine is a weak function of temperature and the pronotation reaction of sarcosine is the least exothermic among all amino acids studied. It is very likely that the low protonation heat of sarcosine will lead to a low heat of

CO_2 absorption. Oexmann et al.[51] found that if two solvents have the same capacity, the one showing the larger heat of absorption can profit from a greater temperature swing between absorber and desorber. Solvents with low heat of absorption might benefit from regeneration below atmospheric pressure (vacuum desorption) and at low temperatures. It is very likely that the regeneration energy would be high for sarcosine based CO_2 capture if the regeneration is carried out under pressure (conditions similar to the typical MEA based processes). Wang et al.[52,53] studied the vacuum regeneration using hollow fibre membrane contactor and suggested that this technology could improve the CO_2 membrane stripping performance due to the lower regeneration pressure. They found that potassium sarcosinate has a less tendency of increasing membrane resistance than MEA and 2−amino−2−hydroxymethyl−1,3−propanediol, although this advantage is not as significant as that at lower temperature. Therefore, the low pressure membrane stripping could be used for sarcosinate based solvents for reducing regeneration energy.

5 Conclusions

The basicity of amino acid salts is crucial to CO_2 capture at high temperatures, since their basicity decreases with the increase of the absorption temperatures. 11 amino acids with pK_a values in a suitable range for CO_2 capture at 313 K have been identified. To determine their suitability for use at higher absorption temperatures, we have determined their pK_a values at 298−353 K using the potentiometric titration method. The ΔH_m^o, ΔS_m^o and ΔG_m^0 of the protonation reactions for the amino acids were calculated by using the van't Hoff equation. Based on the pK_a and ΔH_m^o values of the amino acids, sarcosine was selected for further thermodynamic and kinetic study. It has been found that CO_2 solubility and the mass transfer coefficients of CO_2 in 5 m' sarcosinate at temperatures of 313−353 K were higher than those of 30% MEA at temperatures of 313−353 K. The viscosities and densities of 5 m' sarcosinate at high temperatures were similar to those of 30% MEA. The results suggested

that use of sarcosine for CO_2 absorption at high temperatures could bring some benefits. However, the pronotation reaction of sarcosine is the least exothermic among all amino acids studied. This could lead to a high regeneration energy consumption in the sarcosinate−based CO_2 capture process. Further studies are required to establish if the sarcosinate−based solvent is a suitable one for CO_2 capture at high temperatures.

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