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Kinetic study of CO_2 with various amino acid salts in aqueous solution☆

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ABSTRACT

A study towards the kinetics of CO_2 with several aqueous salts of amino acids was performed at a temperature of 298 K. Absorption rate experiments were carried out in the pseudo-first-order regime, enabling the determination of the kinetic rate constant from the flux. In a preliminary screening at a concentration of 0.5 mol L^{-1} the potassium salts of 6-aminohexanoic acid, β-alanine, l-arginine, l-glutamic acid, dl-methionine, l-proline and sarcosine were investigated. Based on the results of this screening the aqueous potassium salts of sarcosine and proline were considered to be the most promising solvents. For these solvents, and the corresponding lithium solvents, the physical distribution coefficient of N_2O was determined for various temperatures and concentrations. Subsequently for these same solvents the kinetics were more extensively studied at 298 K in which the concentration of the amino acid salts was varied between 0.5 and 3 mol L^{-1}.

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1. Introduction

One of the most alarming global environmental problems of today is the increase of global temperatures. This problem is most likely caused by the increasing atmospheric carbon dioxide concentration due to the burning of fossil fuels for, among others, power generation. To minimize these effects, the carbon dioxide emissions from combustion and gasification processes in power plants have to be decreased by efficiency improvements and carbon dioxide capture.

The removal of acid gases such as CO_2, H_2S or COS by absorption in aqueous alkanolamine solutions is widely used in the chemical industry. This process is based on the reversible chemical absorption of CO_2 using an acid–base reaction in an absorption–desorption loop (Kohl and Nielsen, 1997). In the absorber at relatively low temperature and/or high pressure the acid gases are absorbed, while in the desorber the loaded solvent is regenerated at elevated temperatures and/or reduced pressure. Typical alkanolamines used for this process are monoethanolamine, diethanolamine or *N*-methyldiethanolamine. A problem with the use of alkanolamines for the CO_2 removal from flue gas is that they degrade as a result of long exposure or repeated use, because of side reactions with carbon dioxide, oxygen and other contaminants. Because the desire to separate CO_2 from flue gas streams is gaining momentum as a result of environmental concerns, there is an urgent need to develop new solvent systems that are stable in the presence of oxygen. Amino acids have the same functional groups as alkanolamines, and can be expected to behave similarly towards carbon dioxide, but do not deteriorate in the presence of oxygen (Hook, 1997). Kumar et al. (2003) have proven this assumption to be valid. An additional advantage of amino acids is the possibility of adding a salt function. The carboxylate group can be neutralized with potassium or lithium hydroxide, in order to produce the corresponding salts of the amino acids. This salt function ensures the non-volatility of the substance (Goan et al., 1960), which is helpful when working at stripper conditions (lowered pressure and elevated temperature). A third advantage of the use of aqueous solutions of amino acid salts is their high surface tension, which makes them interesting for gas–liquid membrane applications. In contrast with MEA, which can only be used in combination with expensive membranes due to wetting problems, they can be used in conjunction with simple polyolefin membranes, like polypropene (Kumar et al., 2002).

Design of gas–liquid contactors, used in acid gas treating processes, requires information on mass-transfer coefficients, interfacial area, reactions kinetics and physicochemical properties such as density, viscosity of the solvents and the solubility of the relevant gases in the solvents. The physicochemical properties of several amino acid salt solutions have been reported in a previous study (van Holst et al., 2008).This study will focus on the determination of the reaction kinetics of carbon dioxide with several amino acid salt solutions using a stirred cell set-up at 298 K. The first phase of this study will concentrate on the initial screening of various amino acid salt solutions with respect to the forward reaction kinetics. For this purpose kinetic experiments have been carried out at only one concentration,

☆ In memory of Jacco van Holst who suddenly passed away at the young age of 28.

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being 0.5 mol L^{-1}. The amino acid salts that have been studied are the potassium salts of 6-aminohexanoic acid, β-alanine, L-arginine, L-glutamic acid, DL-methionine, L-proline and sarcosine. Based on the results of this initial screening a more extensive study on the reaction kinetics has been carried out for the potassium and lithium salts of the two of the most promising amino acid salts, being the salts of sarcosine and L-proline.

2. Theory

The amino acids dissolved in water exist as zwitterions with the amino group completely protonated. The ionic equilibrium of the amino acids exists as follows:

$$HO_2CRNH_3^+ \leftrightarrow H^+ + {}^-O_2CRNH_3^+ \leftrightarrow 2H^+ + {}^-O_2CRNH_2 \quad (1)$$

Addition of KOH or LiOH to an aqueous amino acid solution will result in the deprotonation of the zwitterion into the deprotonated amino acid salt solution KO_2CRNH_2 or LiO_2CRNH_2, respectively. This deprotonation step is necessary in order to make the amino group reactive towards CO_2.

A good reference in the determination of the reaction mechanism and kinetics of CO_2 with amino acids is the reaction of CO_2 with alkanolamines. Apart from the backbone of the molecules, the functional groups of amino acids is basically the same as that of alkanolamines and the reaction mechanism can be expected to be similar. Indeed Kumar et al. (2003) has shown that the reaction of two amino acids, taurine and glycine (see Fig. 1), can be described using the same reaction mechanism as used for alkanolamines.

The initial step in the reaction is the formation of the carbamate which can then undergo hydrolysis to the bicarbonate and, if conditions such as pH are suitable, the carbonate species. The degree of hydrolysis of the carbamate is determined by parameters such as amine concentration, solution pH, and the chemical stability of the carbamate (Caplow, 1968; Kumar et al., 2003).

In aqueous solutions, carbon dioxide reacts with primary and secondary alkanolamines to the corresponding carbamate according to the following overall reaction (Blauwhoff et al., 1984):

$$CO_{2(G)} + 2RNH_{2,L} \leftrightarrow RNH_{3,L}^+ + RNHCOO_L^- \quad (2)$$

The zwitterion reaction mechanism is generally accepted as the reaction mechanism for this step (Caplow, 1968; Danckwerts, 1979):

$$CO_{2,L} + RNH_{2,L} \underset{k_{-1}}{\overset{k_2}{\leftrightarrow}} RN^+H_2COO_L^- \quad (3)$$

$$RN^+H_2COO_L^- + B_L \underset{k_{-B}}{\overset{k_B}{\leftrightarrow}} RNHCOO_L^- + HB_L^+ \quad (4)$$

Reaction (4) is the base-catalyzed deprotonation of the zwitterion by any base existing in the solution. According to this reaction mechanism the base can be the amine, water, or a hydroxyl ion. Assuming a quasi-steady state condition for the zwitterion concentration, and a first-order behaviour of CO_2, the reaction rate between CO_2 and the amine can be expressed as (Danckwerts, 1979)

$$r_{CO_2} = k_{app} c_{CO_2,L} \quad (5)$$

with

$$k_{app} = \frac{k_2 c_{RNH_2,L}}{1 + \frac{k_{-1}}{\sum k_B c_{B,L}}} \quad (6)$$

where $\sum k_B c_{B,L}$ is the contribution of all the bases present in the solution for the removal of proton. In lean aqueous solutions, the species amine, water and OH^- can act as bases as shown by Blauwhoff et al. (1984). Because the hydroxyl concentration is typically low in the reaction of CO_2 with the amines, its contribution to the deprotonation of the zwitterions is generally assumed to be negligible (Blauwhoff et al., 1984; Versteeg and Oyevaar, 1989; Xu et al., 1996). However, in some of the concentrated amino acid salt solutions, the pH can rise up to considerable values so its contribution to the deprotonation of the zwitterion might not be negligible in these cases. For few asymptotic situations, Eq. (6) can be simplified as follows.

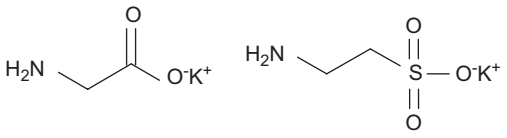

Fig. 1. Potassium salt of glycine and taurine.

I. $k_{-1}/(\sum k_B c_{B,L}) \ll 1$: This results in a 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 the amine.

$$r_{CO_2} = k_2 c_{CO_2,L} c_{RNH_2,L} \quad (7)$$

II. $k_{-1}/(\sum k_B c_{B,L}) \gg 1$: This results in a somewhat more complex kinetic rate expression.

$$r_{CO_2} = k_2 c_{CO_2,L} c_{RNH_2,L} \left(\sum \frac{k_B}{k_{-1}} c_{B,L} \right) \quad (8)$$

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

III. In the absorption of CO_2 in alkanolamines dissolved in non-aqueous solvents (say alcohols), the deprotonation of the zwitterion is solely due to amine. For, this case, Eq. (5) in combination with Eq. (6) reduces to

$$r_{CO_2} = \frac{k_2 c_{CO_2,L} c_{RNH_2,L}}{1 + \frac{k_{-1}}{k_{RNH_2} c_{RNH_2,L}}} \quad (9)$$

At low concentrations of the 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 $(k_{-1}/(k_{RNH_2} c_{RNH_2,L}) \gg 1)$) and this reduces to one at very high amine concentrations.

When working with aqueous solutions of amines it is necessary to take the hydration of CO_2 into account in the interpretation of the absorption rate experiments. The hydration reaction of CO_2 with OH^- is relatively fast and can enhance mass transfer:

$$CO_{2,L} + OH_L^- \overset{k_{OH^-}}{\rightarrow} HCO_{3,L}^- \quad (10)$$

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

$$k_{ov} = k_{app} + k_{OH^-} c_{OH^-,L} \quad (11)$$

Both Pohorecki and Moniuk (1988) and Haubrock et al. (2007) have shown that for hydroxide solutions the rate constant k_{OH^-} is

dependent on the OH^- concentration, ionic strength I and counterions in the solutions (Li^+, K^+, Na^+). Based on these studies it is very likely that k_{OH^-} will vary with the type and concentration of the amino acid-salt solution used and the cation, however, this dependence is not known. In this study the dependence of k_{OH^-} on the ionic strength and counterion according to Pohorecki and Moniuk (1988) will assumed to be valid. For KOH solutions Pohorecki and Moniuk found that

$$k_{OH^-,K^+} = k^{\infty}_{OH^-} \times 10^{(0.287 \cdot I - 0.013 \cdot I^2)} \tag{12}$$

with

$$k^{\infty}_{OH^-} = 10^{(11.895 - 2382/T)} \tag{13}$$

For LiOH solutions Pohorecki and Moniuk and Haubrock et al. (2007) found a much lower reaction rate constant for k_{OH^-} as a function of the ionic strength of the LiOH solutions:

$$k_{OH^-,Li^+} = k^{\infty}_{OH^-} \times 10^{(0.111 \cdot I - 0.006 \cdot I^2)} \tag{14}$$

in which $k^{\infty}_{OH^-}$ is calculated by Eq. (13).

The use of $k_{OH}-$ calculated for amino acid salt solutions, either potassium or lithium, is probably just a rough approximation of the actual rate constant k_{OH^-} in these solutions, but in the context of this study it will suffice. This is because in general the contribution of $k_{OH^-} c_{OH^-,L}$ to k_{ov} is relatively small (maximum about 20% for the experiments carried out), so a possible uncertainty in k_{OH^-} will have a limited influence on the value of k_{app}.

In the initial screening experiments of the various amino acid salt (AmA) solutions, only the k_{ov} (Eq. (11)) will be used. This is because for the screening experiments a relatively low concentration of amino acid salt was chosen (0.5 mol L^{-1}), resulting in a relatively low pH, and therewith a low contribution (smaller than a few percent) of $k_{OH^-} c_{OH^-,L}$ to k_{ov}.

The reaction kinetics can be determined from the absorption rate in the solution when measuring in the pseudo-first-order reaction regime, which is the case when the following conditions are satisfied (Westerterp et al., 1984):

$$2 < Ha \ll E^{\infty}_A \tag{15}$$

with

$$Ha = \sqrt{\frac{k_{ov} D_{CO_2,L}}{k_L^2}} \tag{16}$$

and assuming the penetration model to be applicable and the reactions to be irreversible:

$$E^{\infty}_A = \sqrt{\frac{D_{CO_2,L}}{D_{AmA,L}}} + \sqrt{\frac{D_{AmA,L}}{D_{CO_2,L}}} \frac{c_{AmA,L}}{\nu_{AmA} m_{CO_2} c_{CO_2,G}}$$
$$= \sqrt{\frac{D_{CO_2,L}}{D_{AmA,L}}} + 1.10^3 \times \sqrt{\frac{D_{AmA,L}}{D_{CO_2,L}}} \frac{c_{AmA,L} RT}{\nu_{AmA} m_{CO_2} P_{CO_2,G}} \tag{17}$$

As the reaction of CO_2 with amino acid salts is basically reversible, the infinite enhancement factor becomes lower than suggested by Eq. (17). A method to calculate the infinite enhancement factor for reversible reactions is given by Secor and Beutler (1967) and is also described by Hogendoorn et al. (1997). As the calculation of the infinite enhancement factor taking into account reversibility needs an equilibrium constant—which is not available for the systems under consideration—it is of little practical use to apply the equilibrium based infinite enhancement factor expression in this study. For irreversible reactions, normally the Hatta number should at least be five times smaller than the infinite enhancement factor to meet the condition of a pseudo-*n*-th order regime as indicated by Eq. (15). However, for reversible reactions this margin should be even higher than that. In the pseudo-first-order regime the carbon dioxide absorption rate can then be described by

$$J_{CO_2} = \sqrt{k_{ov} D_{CO_2,L}} \frac{m_{CO_2} P_{CO_2,G}}{RT} \tag{18}$$

For absorption rate experiments carried out in the pseudo-first-order regime, the flux should be independent on k_L and thus the stirrer speed. This is always a good check on the fulfilment of pseudo-first-order condition of Eq. (15). Besides this, in the pseudo-first-order regime a linear relation between the flux and the CO_2 partial pressure is to be expected. So, even if the exact value of the infinite enhancement factor for reversible reactions cannot be calculated, the independency of the flux on the stirrer speed and a linear relationship between the flux and the CO_2 partial pressure gives enough certainty that Eq. (15) is fulfilled.

As can be seen in Eq. (18) the calculation of k_{ov} from the absorption flux requires, amongst others, knowledge about the physical distribution coefficients of CO_2 in these reactive solutions. In a previous study (van Holst et al., 2008) the physical distribution coefficient of N_2O in various amino acid salt solutions was measured for one concentration (0.5 mol L^{-1}) and one temperature (298 K). For the two amino acid salts, which have been studied in more detail in this study (sarcosine and proline), additional distribution coefficients have been measured in this work.

3. Experimental procedure and interpretation of results

3.1. Chemicals

The potassium or lithium salts of the selected amino acids were prepared by neutralizing the amino acid, with purities of at least 98% (Sigma Aldrich) dissolved in demineralized water, with an equimolar amount of potassium or lithium hydroxide (Riedel-de Haën, $\geqslant$85%, pellets[1]). The actual concentration of the aqueous amino acid salt solutions was measured potentiometrically with a standard 1.000 mol L^{-1} hydrochloride acid solution (Merck). The experimentally determined concentrations were within 0.5%. The pH of the absorbent solution was measured after each experiment with a Metrohm 3 M KCl pH-electrode. The hydroxyl ion concentration was calculated from this pH, and used to calculate the contribution of $k_{OH^-} c_{OH^-}$ in Eq. (11).

3.2. Experimental procedure

Experiments were performed in a (closed) stirred cell reactor (see Fig. 2). Carbon dioxide could be fed to the reactor from two supply vessels that had volumes of ~325 and ~85 ml, respectively, or directly from the gas cylinder. The pressure in the reactor, which has a volume of ~ 720 ml, could be kept constant by a pressure controller model. The stirred cell, a double walled glass reactor with thermostat, was closed by two stainless steel flanges. Two separate operating stirrers were used to stir the gas and liquid phase separately. A pressure transducer was connected to the reactor for

[1] The total amount of impurities other than water was around 1% (mostly as carbonates, product analysis by Riedel-de Haën). The actual purity of the KOH pellets was determined by acid titration. This number was used for the determination of the weight of KOH/LiOH pellets required for the deprotonation of the amino acids.

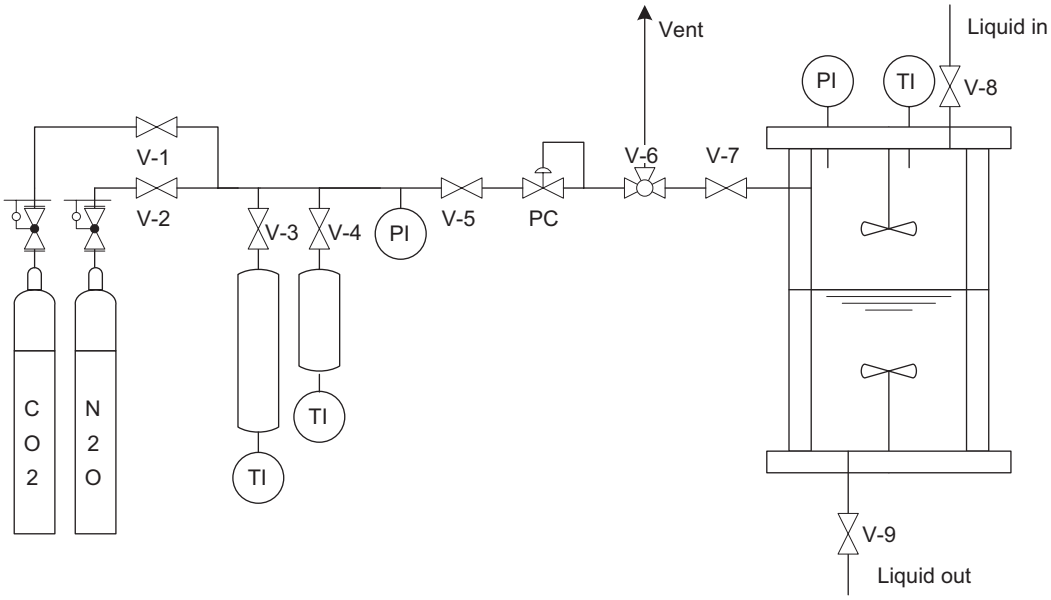

Fig. 2. Schematic representation of the stirred cell set-up.

monitoring the pressure in the reactor, and a second one was connected to the gas supply vessels for determining the pressure in these vessels.

The experimental set-up allowed two operating modes:

1. Semi-batch operation. In this operation mode the pressure in the reactor was kept constant, and the pressure drop against time was measured in the supply vessel. In the pseudo-first-order regime, the relation between the pressure and time in the supply vessel can be obtained from an instationary mass balance (Hogendoorn et al., 1995)

$$P_{CO_2,G_{\text{Supply Vessel}}}|_t = P_{CO_2,G_{\text{Supply Vessel}}}|_{t=0} - \sqrt{k_{ov}D_{CO_2,L}}\frac{m_{CO_2}P_{CO_2,G_{\text{Reactor}}}A}{V_{G_{\text{Supply Vessel}}}}\cdot t \qquad (19)$$

2. Total batch operation. After admittance of a batch of gas, the reactor was closed (valve V7), and the pressure drop in the reactor against time was measured. The relation between the pressure and time in the reactor, when closed, is given by (Blauwhoff et al., 1984)

$$\text{In } P_{CO_2,G_{\text{Reactor}}}|_t = \text{In } P_{CO_2,G_{\text{Reactor}}}|_{t=0} - \sqrt{k_{ov}D_{CO_2,L}}\frac{m_{CO_2}A}{V_{G_{\text{Reactor}}}}\cdot t \qquad (20)$$

When the reaction rate of CO_2 with the amino acid salt is high (as is expected for these amino acid salt solutions), large Hatta numbers will be obtained. A large Hatta number has the consequence that the CO_2 partial pressure in the reactor must be very low (and hence the total pressure close to the water vapor pressure), to satisfy the second condition as stated by Eq. (15) ($Ha \ll E_A^\infty$). When working in operation mode 2, the pressure drop in time in the reactor would be quite hard to measure accurately at total pressures just above the vapour pressure of water. The initial screening experiments were carried out using operation mode 2 (batch wise operation) because of its simplicity and speed. The first operation mode was chosen for the amino acid salts selected for the more extensive kinetic study, viz. sarcosine and proline.

4. Additionally required physicochemical constants

4.1. Density and viscosity

The densities and viscosities of the different amino acid salt solutions with concentrations ranging from 0.25 up to 3.5 mol L^{-1} (depending on the solubility of the amino acid salt) were measured with an AP Paar DMA 58 density meter and an Ubbelohde viscometer and are reported by van Holst et al. (2008).

4.2. Physical solubility

The physical solubility of N_2O has been measured and from that the physical solubility of CO_2 can be estimated using the CO_2–N_2O analogy (Laddha et al., 1981) or the method of Schumpe (1993) as shown by van Holst et al. (2008). van Holst et al. showed that both the CO_2 analogy and the method of Schumpe gave comparable results in the prediction of the physical solubility of CO_2 in amino acid salt solutions. In this work the method of Schumpe will be used to predict the physical distribution coefficients of CO_2 as it allows the estimation of the distribution coefficients at arbitrary concentrations and temperatures.

Schumpe's models states that the distribution coefficient m of a gas j can be related to the physical distribution coefficient in water according to

$$\log\left(\frac{m_{j,H_2O}}{m_{j,L}}\right) = \sum(h_i + h_G)c_{i,L} \qquad (21)$$

where h_i is the ion-specific parameter, h_g is the gas-specific parameter and $c_{i,L}$ is the concentration of ion i. The reference distribution coefficient of CO_2 in water (m_{CO_2,H_2O}) can be derived from the following relation based on the use of the N_2O/CO_2 analogy for water (Versteeg and van Swaaij, 1988):

$$m_{CO_2,H_2O} = C_1 \cdot m_{N_2O,H_2O} \qquad (22)$$

with

$$C_1 = 3.04 \cdot \exp\left(\frac{-240}{T}\right) \qquad (23a)$$

$$m_{N_2O,H_2O} = 1.17 \times 10^{-7} \cdot RT \cdot \exp\left(\frac{2284}{T}\right) \quad (23b)$$

In 1996 Weissenberger and Schumpe extended the model given by Eq. (21) to a wider temperature range. The temperature dependency was found gas-specific, and the gas-specific constant was assumed to be a linear function of the temperature:

$$h_G = h_{G,0} + h_T(T - 298.15) \quad (24)$$

The Schumpe parameters for h_i^+, $h_{G,0}$ and h_T are given in Table 1. In a previous study the interaction parameter h_i^- for the amino acid salts has already been reported, however, in the previous study the concentration and temperature were restricted to 0.5 mol L^{-1} and T=298 K, respectively (see Table 2). For the amines used in the initial kinetic screening this is sufficient, however, for the amines studied in more detail (sarcosine and proline) some extra data on the distribution coefficient were considered necessary to make the determination of k_{ov} (and therewith k_{app}) from Eq. (19) or (20) more reliable. Therefore, for the potassium and lithium salts of sarcosine and proline additional physical distribution measurements of N_2O were carried out to get more reliable information on h_i^-. The experimental set-up and procedure were identical to the one described in the previous study (van Holst et al., 2008) and experiments were carried out in the range of 0.5–3 mol L^{-1} and 298–333 K using both the lithium and potassium salts of proline and sarcosine, respectively. It should be noted that the temperature range is partly outside the temperature range for which values of h_G are reported (from 273 to 313 K) but still relation 22 together with the $h_{G,0}$ and h_T values from Table 1 were used. The previously determined parameter h^- for proline (0.074 L mol^{-1}, see Table 2 and van Holst et al., 2008) proved to be well suited to represent the data over a more extensive concentration and temperature range for both the lithium as the potassium salt (see Figs. 3 and 4). However, for sarcosine an adapted parameter value for h^- (0.0680 L mol^{-1} instead of 0.0819 L mol^{-1} as reported in the previous study of van Holst et al., 2008) did yield a better agreement between the predicted and theoretical physicals solubility of N_2O in these solutions. In Fig. 5 the physical solubility in potassium and lithium sarcosine salt solutions is given. The parity plot for both the lithium and potassium salt of sarcosine is given in Fig. 6.

As can be seen the prediction of the physical solubility of N_2O is generally within 10% although especially at higher concentrations of the amino acids and higher temperatures (low distribution coefficients) the inaccuracy seems to be somewhat higher. It is expected that the predictions of the physicals solubility of CO_2 using the method of Schumpe and the data given in Tables 1 and 2 will yield the same trends and accuracy as observed for N_2O.

Table 1
Schumpe model parameters (Weisenberger and Schumpe, 1996).

Cation	h_i^+ (L mol^{-1})	Gas	h_G (L mol^{-1})	$10^3 \cdot h_T$ (L mol^{-1} K^{-1})	Temp. range (K)
K^+	0.0922	N_2O	−0.0085	−0.479	273–313
Li^+	0.0744	CO_2	−0.0172	−0.338	273–313

Table 2
Ion-specific Schumpe parameters h_i^- for several amino acid salts.

Potassium salt of amino acid	Range of c_{AmA} (mol L^{-1})	Range of T (K)	h_i^- (L mol^{-1})
β-Alanine	0.5	298	0.0715
6-Aminohexanoic acid	0.5	298	0.0968
L-Arginine	0.5	298	0.1452
L-Aspartic acid	0.5	298	0.2236
L-Glutamic acid	0.5	298	0.2162
LL-Methionine	0.5	298	0.0846
L-Phenylalanine	0.5	298	0.0875
L-Proline	0.5–3	298–333	0.0740
Sarcosine	0.5–3	298–333	0.0680

The values for proline and sarcosine have been (re)determined in this work, while the other interaction parameters have been taken from van Holst et al. (2008).

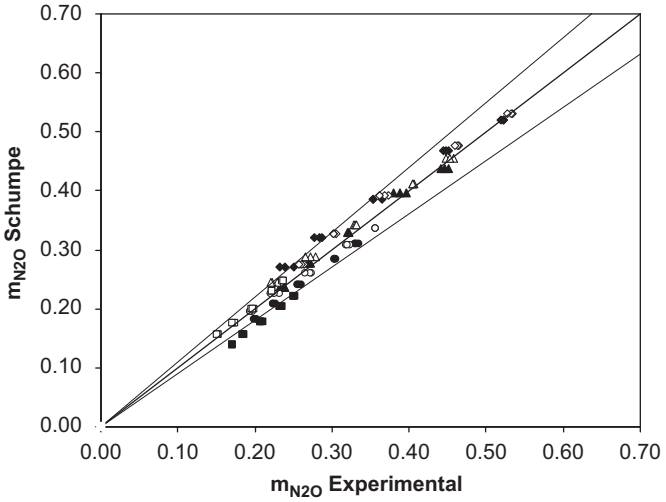

Fig. 4. Parity plot of the physical solubility m of N_2O in aqueous prolinate salt solutions. Closed symbols represent potassium salt, open symbols lithium salt. Diamonds: 0.5 mol L^{-1}; triangles: 1 mol L^{-1}; circles: 2 mol L^{-1} and squares 3 mol L^{-1}.

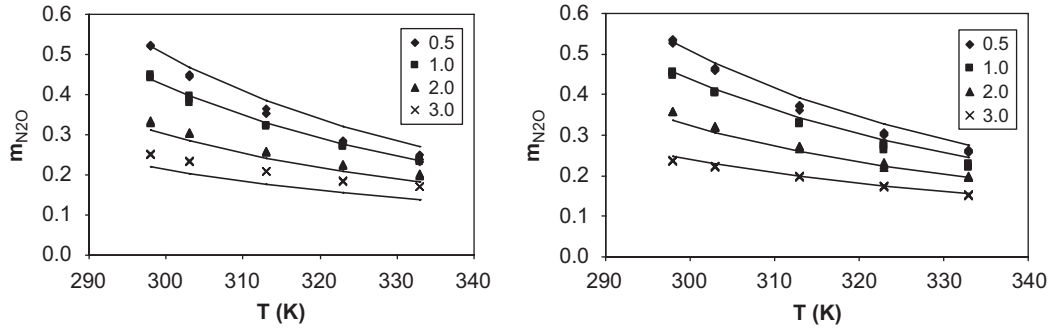

Fig. 3. Physical distribution coefficient m of N_2O in aqueous potassium prolinate solutions (left) and lithium prolinate solutions (right). Continuous lines give predictions according to method of Schumpe (see Tables 1 and 2 for interaction parameters).

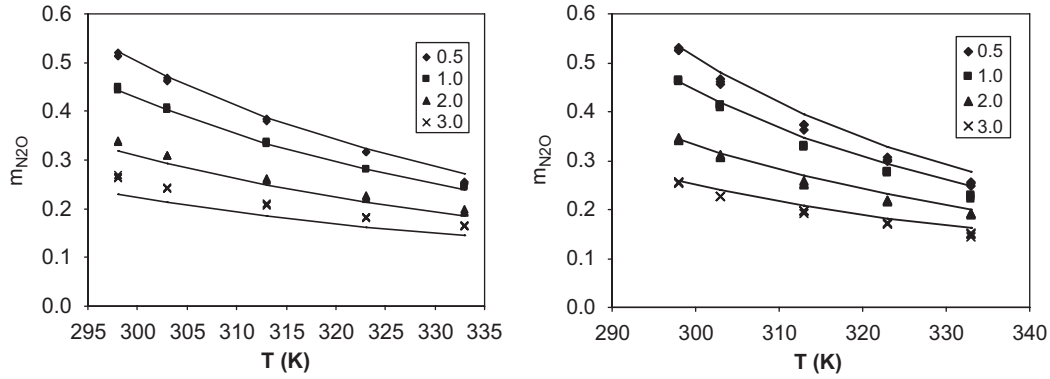

Fig. 5. Physical distribution coefficient m of N_2O in aqueous potassium sarcosinate solutions (left) and lithium sarcosinate solutions (right). Continuous lines give predictions according to method of Schumpe (see Tables 1 and 2 for interaction parameters).

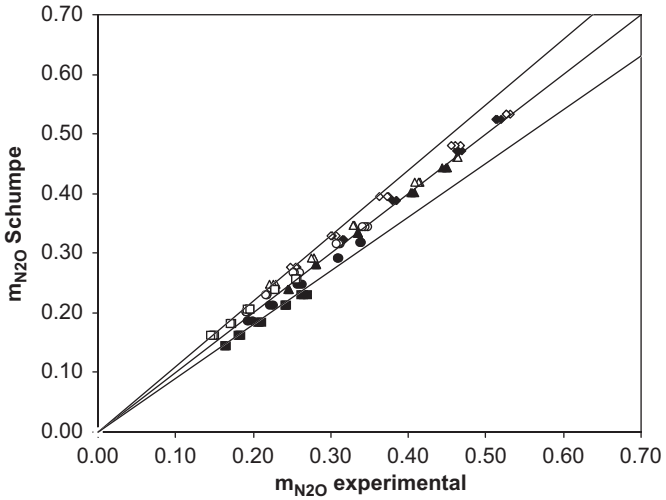

Fig. 6. Parity plot of the physical solubility m of N_2O in aqueous sarcosinate solutions. Closed symbols represent potassium salt, open symbols lithium salt. Diamonds: 0.5 mol L^{-1}; triangles: 1 mol L^{-1}; circles: 2 mol L^{-1} and squares 3 mol L^{-1}.

4.3. Estimation of CO_2 diffusion coefficient

A modified Stokes–Einstein relation, given by Eq. (25), was used to determine the diffusion coefficient as required in the determination of the kinetics (Eq. (19) or (20)).

$$(D_{CO_2,L} \cdot \eta^{0.74})_{H_2O} = (D_{CO_2,L} \cdot \eta^{0.74})_{AmA} \quad (25)$$

The diffusivity of CO_2 in water as needed in Eq. (25) was determined with the following relation (Versteeg and van Swaaij, 1988):

$$D_{CO_2,Water} = 2.35 \times 10^{-6} \cdot \exp\left(\frac{-2119}{T}\right) \quad (26)$$

The viscosity as reported by van Holst et al. (2008) for amino acid solutions was used in Eq. (25). As the viscosity of corresponding Li-amino acid solutions is not known, the viscosity for the Li-amino acid salt solutions was assumed to be identical to the ones for the corresponding potassium salt solutions.

5. Results and discussion

5.1. Screening experiments

The experimental procedure for the batch wise operation mode (method 2 in section *Experimental procedure*) was validated with CO_2 absorption experiments in diethanolamine (DEA) solutions with concentrations of 0.6, 1.0 and 2.0 mol L^{-1}. As already indicated for the screening experiments a concentration of 0.5 mol L^{-1} of potassium amino acid-salts was used at a temperature of 298 K. For these conditions the typical (estimated) contribution of $k_{OH^-} c_{OH^-,L}$ to k_{ov} was only a few percent, so it was decided to compare the results of the various amino acid salts with respect to only k_{ov} as a good indicator of k_{app}. The results of the screening experiments is given in Table 3 and graphically represented in Fig. 7. A high reaction rate is important to reduce the size and therewith capital costs of the absorber, while a low pK_a is of importance to minimize the energy requirement in the desorber.

From the amino acid salt solutions studied in this work, especially sarcosine, proline and glycine exhibit a relatively high reaction rate constant at a relatively low pK_a of the amino acid salts. Although arginine also exhibits a fairly high apparent rate constant, it's pK_a is high. This will probably require a larger and economically prohibitive energy input in the desorber, and therefore arginine was excluded for further study. The salts of glycine have been studied previously (see, e.g. Kumar et al., 2003), and therefore only the salts of sarcosine and proline were selected for further study in this work.

It must be noted that this analysis and selection is based on the use of just one concentration (0.5 mol L^{-1} at one temperature (298 K)). For alkanolamines it has been shown that the overall reaction order in the amine can be between 1 and 2, depending on the governing mechanisms in the deprotonation of the zwitterion as indicated by Eq. (6). This also means that the current results on the preference in amino acid salts cannot be extrapolated to other (higher) concentrations as the reaction order per amine is not known. Still, based on this screening study, the salts of glycine, proline and sarcosine, seem to be promising amino acid salts for CO_2 capture from the viewpoint of kinetics and pK_a.

5.2. Kinetics of CO_2 with potassium and lithium salts of sarcosine and proline

First, experimental validation of the set-up was carried out using operation mode 1 (see section *Experimental procedure*) and various DEA solutions. Experiments were repeated using different pressures in the reactor. This way a plot like in Fig. 8 could be

Table 3
k_{ov} values for potassium amino acid salts.

Amino acid salt	pK_a	c_{AmA} (mol L^{-1})	k_{ov} (s^{-1})	k_{ov} normalized at 0.5 mol L^{-1} (s^{-1})
Taurine	9.06[a]	0.486	1240	1276
Methionine	9.2[b]	0.498	809	812
Glutamic acid	9.98[b]	0.492	1419	1442
Sarcosine	10.21[a]	0.501	2979	2973
β-alanine	10.33[a]	0.499	1496	1499
Proline	10.64[b]	0.495	7146	7218
6-Aminohexanoic acid	10.95[a]	0.502	1271	1266
Arginine	12.48[b]	0.444	3732	4203

[a]Hamborg et al. (2007).
[b]Perrin (1972).

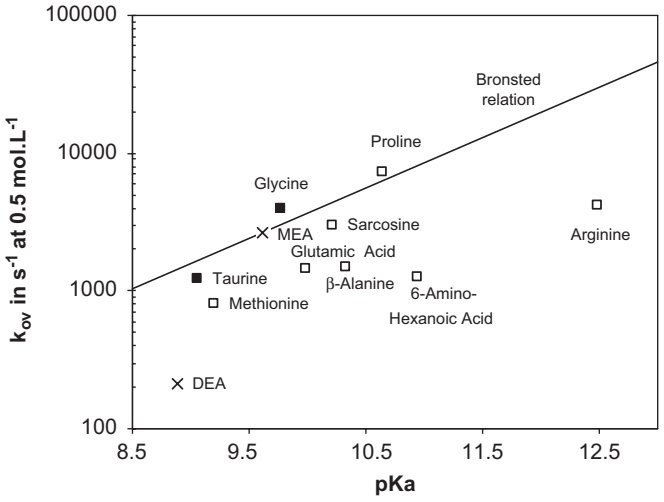

Fig. 7. k_{ov} vs. pK_a for various potassium salts of amino acids. The data for taurine and glycine have been taken from Kumar et al. (2003) MEA and DEA data are from Blauwhoff et al. (1984). (Brønsted relation taken from Penny and Ritter, 1983 with $k_{app} = \exp(0.844 \cdot pK_a - 6.44) \times c_{AmA}$.)

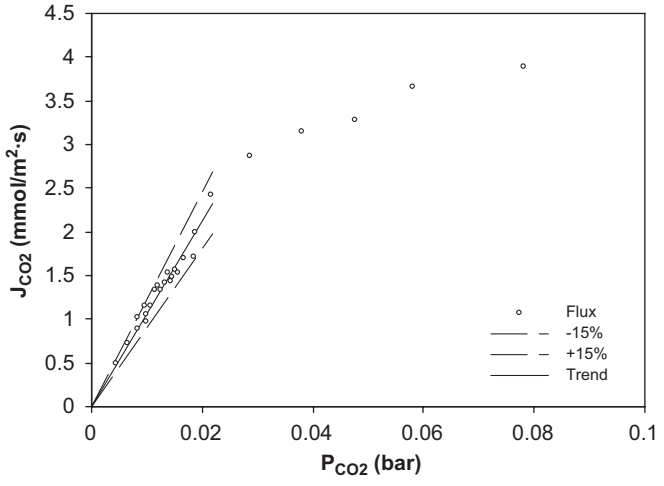

Fig. 8. Typical plot of the flux vs. the partial pressure obtained for experiments carried out in operation mode 1.

obtained. Only experiments obtained in the regime where a linear relationship existed between pressure and flux were used in the interpretation of the experiments, as these experiments were carried out in the pseudo-first-order regime. The results for DEA agreed well

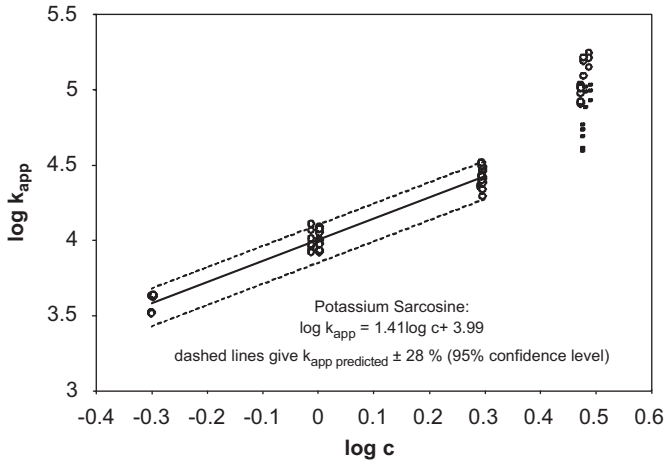

Fig. 9. Results for k_{app} (s^{-1}) as a function of the potassium sarcosine concentration (c in mol L^{-1}). Symbol -: CO_2 physical solubility increased with 20% as compared to Schumpe prediction (see also Fig. 5).

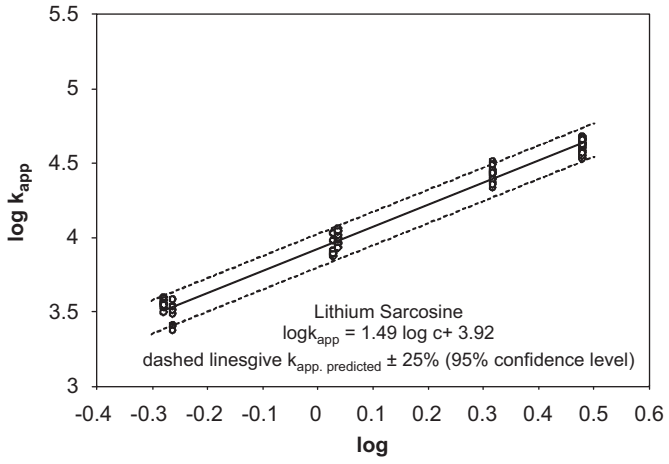

Fig. 10. Results for k_{app} (s^{-1}) as a function of the lithium sarcosine concentration (c in mol L^{-1}).

with literature results of, e.g. Blauwhoff et al. (1984) and Versteeg and Oyevaar (1989). The same procedure was followed for the actual sarcosinate and prolinate solutions, in which not only the potassium salts of these amino acids were used but also the lithium salts.

Pohorecki and Moniuk (1988) but also Haubrock et al. (2007) have shown that for the reaction between OH^- and CO_2 the rate constant is very much dependent on the "environment" of the reactants (ionic strength, type of ions present), and not only on the concentrations of the reactants. This phenomenon was also studied for the current amino acid salt solutions: if the reaction rate between CO_2 and the amino acid salts is affected by the type of counter ion (lithium or potassium), it is an effective tool to increase the overall reaction rate per m^3 of solution.

The results for potassium sarcosine and lithium sarcosine solutions are given in Figs. 9 and 10, respectively (dashed lines give uncertainty with 95% confidence levels for k_{app}). As can be seen in Fig. 9 for potassium sarcosinate, the points at lower concentration are very well in line with each other. In contrast, the data points at 3 mol L^{-1} are clearly above this trend line. However, if the physical distribution coefficient of N_2O in potassium sarcosinate solutions is considered at 3 mol L^{-1} and 298 K, it can clearly be seen that the Schumpe predictions at lower concentrations are quite good, but for

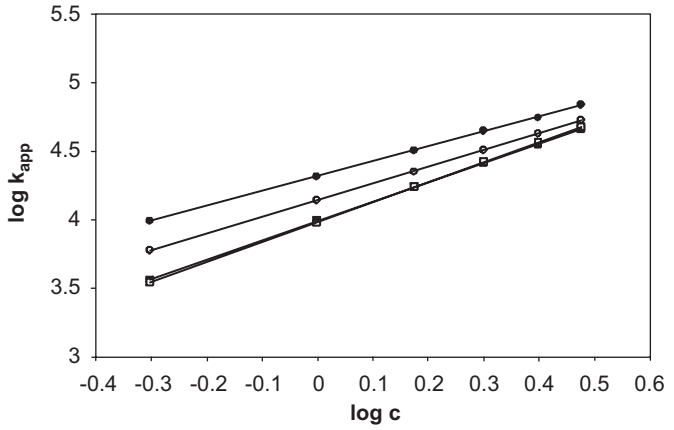

Fig. 11. Prediction of k_{app} (s^{-1}) as a function of concentration (c in mol L^{-1}). Squares: sarcosine; points: proline. Open symbols lithium salt; closed symbols: potassium salt.

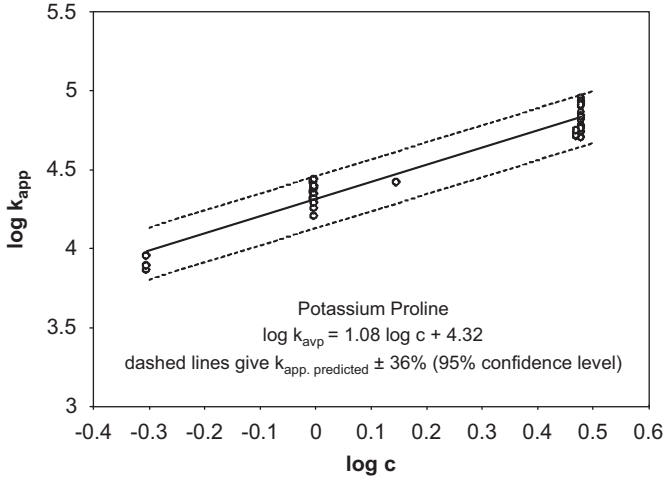

Fig. 12. Results for k_{app} (s^{-1}) as a function of the potassium proline concentration (c in mol L^{-1}).

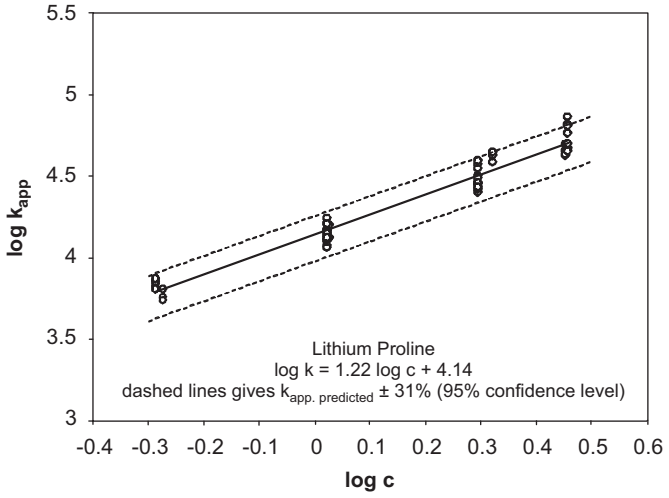

Fig. 13. Results for k_{app} (s^{-1}) as a function of the lithium proline concentration (c in mol L^{-1}).

3 mol L^{-1} there is an under-prediction of about 20% (see also Fig. 5). If the Schumpe predicted CO_2 physical distribution coefficient would be increased by 20% then the horizontal symbols in Fig. 9 are obtained. These data are much better in line with the trend line as obtained for the lower concentrations. For this potassium sarcosinate solution the following kinetic expression can be given at 298 K (fitted from 0.5 to 2 mol L^{-1}):

$$r_{CO_2} = k_{app} c_{CO_2,L} = 9.77 \times 10^3 c^{1.41}_{Sarcosinate,L} c_{CO_2,L} \quad (27)$$

Of course, it would be possible to separately fit k_2, k_{-1}, k_{B,H_2O}, k_{B,OH^-} $k_{B,AmA}$—which would be in line with the zwitterions mechanism as described by Eq. (6)—but at this point the accuracy and therewith the physical meaning of the fitted parameters would be doubtful. The overall reaction order of 1.41 in sarcosine suggests that the experiments have been carried out in reaction regime II, where not only the amino acid but also other bases have an influence on the deprotonation rate of the zwitterion.

For lithium sarcosinate solutions the results are given in Fig. 10. The reaction rate for lithium sarcosinate can be expressed by

$$r_{CO_2} = k_{app} c_{CO_2,L} = 8.32 \times 10^3 c^{1.49}_{Sarcosinate,L} c_{CO_2,L} \quad (28)$$

As can be seen the overall reaction order is 1.49 and therewith quite close to the one as determined for the potassium salt of the same amino acid, the difference (1.49 vs. 1.41) not being statistically meaningful. Also the absolute value of the rate constants for both solutions is comparable as can be seen in Fig. 11. Based on the results of the study of Haubrock et al. (2007) this would imply that for these sarcosinate solutions the activity of the reactants is not (seriously) affected by the type of counter-ion in the solution.

The results for the potassium and lithium salts of proline are given in Figs. 12 and 13, respectively (again, dashed lines give uncertainty with 95% confidence levels for k_{app}). The kinetic rate expression for these solvents is expressed by, respectively:

Potassium prolinate:

$$r_{CO_2} = k_{app} c_{CO_2,L} = 2.09 \times 10^4 c^{1.08}_{Prolinate,L} c_{CO_2,L} \quad (29)$$

Lithium prolinate:

$$r_{CO_2} = k_{app} c_{CO_2,L} = 1.38 \times 10^4 c^{1.22}_{Prolinate,L} c_{CO_2,L} \quad (30)$$

Again, the reaction order in the amino acid salt is between 1 and 2, indicating a contribution of not only proline to the deprotonation of the zwitterions but also other bases. However, the reaction order for both the lithium and potassium salt of proline is much closer to 1 than for sarcosine indicating a relatively fast deprotonation of the zwitterion. Just like for sarcosine, the difference in reaction order between the potassium and lithium salt of proline is statistically not meaningful (1.08 vs. 1.22, respectively). In contrast, the fitted pre-exponential rate constant differs considerably which yields significantly different values of k_{app}, which can be clearly seen when comparing the predicted results of Eqs. (29) and (30) in Fig. 11.

Although Eq. (29) describes the experimental results for potassium prolinate solutions accurately at high concentrations, in all fairness it must be mentioned that, just like for potassium sarcosinate solutions, the physical distribution coefficient for CO_2 at high amino acid salt concentrations is probably underestimated (see Fig. 3). If a correction is applied and the physical distribution coefficient of CO_2 at high amino acid salt concentrations ($\geqslant 2$ mol L^{-1}) is increased, a lower k_{app} than obtained in Fig. 12 would be obtained. This means that at high amino acid concentrations ($\geqslant 2$ mol L^{-1}) Eq. (29) would predict values for k_{app} which are above this corrected k_{app}. If this is indeed true, the reaction order at high prolinate concentration would decrease with concentration, but such a change

in reaction order with concentration is not impossible for amine solutions (Danckwerts, 1979; Versteeg and Oyevaar, 1989).

Taking into account the uncertainty of Eqs. (29) and (30) (see Figs. 12 and 13, respectively), it cannot be concluded beyond doubt that the k_{app} values for potassium and lithium salt of proline are really different. However, the current results strongly suggest that for these solutions, the type of counter-ion *does* influence the activities of the reactants and therewith the overall reaction rate (but not the reaction order!). Also in case of hydroxide solutions, it was observed that potassium increased the reaction rate as compared to sodium (slower) and lithium (slowest) (Haubrock et al., 2007). Using an activity based rate expression might diminish the differences in the rate constants between the potassium and lithium prolinate solutions, but to realize this an appropriate method to estimate the activities of the reaction components present in the solution is needed. Although various equilibrium models can be used to described the activities in the aqueous solutions, the required interaction parameters for these models are not available for the components of interest in this study.

6. Conclusions

In a preliminary screening at a concentration of 0.5 mol L^{-1} the potassium salts of 6-aminohexanoic acid, β-alanine, L-arginine, L-glutamic acid, DL-methionine, L-proline and sarcosine were investigated. Based on the results of this screening the aqueous potassium salts of sarcosine and proline are considered to be the most promising solvents because they combine a relatively high apparent rate constant with a relatively low pK_a. For these solvents, and the corresponding lithium solvents, the physical distribution coefficient of N_2O was determined for various temperatures and concentrations. The results were interpreted using the model Schumpe, for which the interaction parameter h- had to be determined. Generally, the deviation between the theoretically predicted—and experimental values increased with temperature and salt concentration, but was typically within 10%. Subsequently for these same solvents the kinetics were determined at 298 K in which the concentration of the amino acid salts was now varied between 0.5 and 3 mol L^{-1}.

The results indicate that the kinetics for the sarcosine salts seem to be independent on the counter-ion (Li^+ or K^+), while for the prolinate solutions the potassium salt seems to have a substantially higher apparent rate constant than the lithium salt.

Notation

$c_{i,G}$	concentration component/ion i in gas phase, mol L^{-1}
$c_{i,L}$	concentration component/ion i in liquid phase, mol L^{-1}
$D_{i,G}$	diffusion coefficient of component i in gas phase, m^2 s^{-1}
$D_{i,L}$	diffusion coefficient of component i in liquid phase, m^2 s^{-1}
$E_{A,\infty}$	infinite enhancement factor defined by Eq. (17), dimensionless
h_i	interaction parameter Schumpe model for ions, L mol^{-1}
h_i^+	interaction parameter Schumpe model for cations, L mol^{-1}
h_i^-	interaction parameter Schumpe model for anions, L mol^{-1}
h_G	interaction parameter Schumpe model for gases, L mol^{-1}
h_T	temperature correction Schumpe model, L mol^{-1} K^{-1}
Ha	Hatta number defined by Eq. (16), dimensionless
I	ionic strength, mol L^{-1}
J	flux, mol m^{-2} s^{-1}
k_{app}	pseudo-first-order rate constant, s^{-1}
k_L	liquid side mass transfer coefficient, m s^{-1}
k_{OH^-}	reaction rate constant for reaction between CO_2 and OH^-, L mol^{-1} s^{-1}
k_{ov}	overall rate constant defined by Eq. (11)
$m_{i,j}$	physical distribution coefficient of component i in liquid phase j, dimensionless
P_{i,G_j}	gas phase pressure component i in vessel j, Pa
r_{CO_2}	rate of reaction of CO_2, mol L^{-1} s^{-1}
R	gas constant = 8.314, J mol^{-1} K^{-1}
T	temperature, K

Greek letters

η	dynamic viscosity, Pa s
ν	stoichiometric coefficient in Eq. (17), dimensionless

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