Density, Viscosity, Solubility, and Diffusivity of N2O in Aqueous Amino Acid Salt Solutions
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Introduction

Aqueous solutions of amines are extensively used in the removal of acid gas components such as CO$_2$ and H$_2$S from a variety of industrial gas streams. In particular, alkanolamines and blends of alkanolamines are widely used amines in the gas-treating industry. Alkanolamines undergo degradation in oxygen-rich atmosphere, usually encountered in the treatment of flue gases, resulting in very toxic degradation products. Amino acid salts can be a possible alternative to alkanolamines in certain areas of gas treating, although they are more expensive than alkanolamines. The ionic nature of these salt solutions makes them more stable to oxidative degradation along with certain other desirable properties such as low volatility, higher surface tension, and so forth. Salts of amino acids have been of considerable interest in the development of hybrid solvents, especially as promoters to conventional solvents. Some of the amino acids used commercially are glycine, alanine, and diethy or dimethyl glycine. Numerous processes based on the use of sterically and nonsterically hindered amino acids have been reported in the recent past. Amino acids containing a sulfonic acid group have greater stability to degradation and are less corrosive than alkanolamines and amino acids with a carboxylic acid group. Taurine (2-aminoethanesulfonic acid) is one such compound, and its potential for use in gas treating is being explored.

Design of gas–liquid contactors, to be used in acid gas treating processes, requires information on mass-transfer coefficients, interfacial area, reaction kinetics, and physicochemical properties such as solubility and diffusivity of the relevant gases in the solvents. As the acid gases react with the solvents mentioned above, properties such as diffusivity and solubility need to be estimated by an indirect way, using gases with similar properties. In the case of alkanolamines, N$_2$O is often used as a nonreacting gas to estimate the physicochemical properties of CO$_2$ in a reactive liquid. Because the aqueous salt solutions of amino acids are ionic in nature, the "N$_2$O analogy" proposed by Laddha et al. for the estimation of the solubility of CO$_2$ in aqueous alkanolamine solutions, cannot be simply extended for the present situation. Instead, the experimental data on the solubility of N$_2$O in amino acid salt solutions can be interpreted using the van Krevelen–Hoijtizer model or the model of Schumpe. Applying these models to the N$_2$O solubility data, the ionic specific constants as defined by these models can be estimated. Using these constants, the solubility of CO$_2$ in amino acid salt solutions can now be reliably estimated for the amino acid salt solution. Gubbins et al. suggest that the ratio of the diffusivity of the solute gas in an aqueous electrolyte solution to the diffusivity in water is marginally affected by the species of the diffusant. As the properties of N$_2$O are very similar to those of CO$_2$ with regard to configuration, molecular volume, and electronic structure, the diffusivity of N$_2$O in aqueous amino acid salt solutions can be used to estimate the diffusivity of CO$_2$ in these solutions. In the present work, the density, viscosity, solubility, and diffusivity of N$_2$O in aqueous potassium taurate solutions are reported at various temperatures. Also, the solubility of N$_2$O in aqueous potassium glycinate solutions at 295 K is reported.

Experimental Section

The potassium salt of a selected amino acid was prepared by neutralizing the amino acid (99.9% purity, Merck), dissolved in deionized, distilled water, with an equimolar quantity of potassium hydroxide (Merck) in a standard flask. The neutralization reaction was carried out with constant cooling. The amino acid dissolved in water exists as a zwitterion, with the amino group completely protonated. The ionic equilibrium of the amino acids exists as follows:

\[
\text{HO}_2\text{CRNH}_3^+ + \text{H}^+ \rightarrow \text{O}_2\text{CRNH}_3^+ \quad \text{and} \quad \text{HO}_2\text{CRNH}_2^- + \text{H}^+ \rightarrow \text{O}_2\text{CRNH}_2^- \]

Addition of KOH results in deprotonation of the amino group, corresponding to the second equilibrium. The deprotonated amine species can react with the acid gases. The concentration of the deprotonated amine (amino acid salt) was estimated potentiometrically, by titrating with standard HCl solutions. The end point is the isoelectric point of the chosen amino acid. The experimentally determined amine concentrations were accurate to within 0.5%.
**Density and Viscosity.** The density was measured using a commercial density meter (DMA 58, Anton Paar GmbH), and the viscosity using a Haake microviscometer (Haake MessTechnik GmbH). In both cases, the measurement temperature could be controlled within ±0.05 K.

**Solubility.** The solubility was measured in a thermostatic stirred vessel, provided with a pressure transducer (0–1500 mbar, Druck) and a gas-inducing impeller. A known volume of solution was transferred into the vessel. The temperature of the solution was allowed to adjust to the temperature at which the measurement had to be done. The contents of the vessel above the liquid as well as the dissolved gas in the solution were removed by the application of vacuum, until the gas bubbles ceased to evolve and vapor–liquid equilibrium was attained. The pressure of the liquid was recorded. The gas was fed into the stirred vessel, until a desired pressure was attained and the pressure was recorded. The vessel was closed, and the agitator was turned on. The equilibrium was attained in around 30 min when the pressure inside the vessel remained constant. The final equilibrium pressure value was recorded. From the values of pressures and volumes recorded, the solubility of the gas in the liquid could be calculated. The reliability of the experimental data was verified by measuring the solubility of CO₂ and N₂O in water. The measured values were in agreement with those reported in the literature⁹ and the accuracy of the experiments was within ±2%.

**Diffusivity.** The diffusion coefficient of N₂O in aqueous potassium taurate solutions was determined using a diaphragm diffusion cell. In the diaphragm cell, a porous, nonpermselective sintered glass membrane separates the liquid and gas phases. The pores of the glass membrane are completely filled with the liquid in which the diffusion coefficient is to be measured (Figure 1). The solution inside the pores of the diaphragm can be related to the diffusion coefficient, using the film theory. From the time versus gas-phase pressure, the diffusion coefficient can be calculated using overall and gas-phase mass balances as given below.

**Overall mass balance:**

\[ V_0 \frac{P_0}{RT} + V_L C_{L,0} = V_G \frac{P(t)}{RT} + V_L C_L(t) \]  

(1)

**Gas-phase balance:**

\[ \frac{V_G}{RT} \frac{dP}{dt} = -k_L A \left( m \frac{P}{RT} - C_L \right) \]  

(2)

**Initial condition:**

\[ t = 0; \quad P = P_0; \quad C_L = C_{L,0} = 0 \]  

(3)

where \( A \) is the interfacial area for mass transfer, \( C_L \) and \( C_{L,0} \) are the concentration of gas in the liquid at time \( t \) and at \( t = 0 \), respectively, \( k_L \) is the mass-transfer coefficient, \( m \) is the dimensionless solubility defined as the ratio of the liquid-phase concentration to the gas-phase concentration of the solute at equilibrium conditions, \( P(t) \) and \( P_0 \) are the gas-phase pressures at time \( t \) and \( t = 0 \), respectively, \( R \) is the universal gas constant, \( T \) is the temperature of the diaphragm cell, and \( V_G \) and \( V_L \) are the volume of gas and liquid phase, respectively, of the diaphragm cell. The \( k_L \) in eq 2 can be defined using the film theory by

\[ k_L = \frac{D}{\delta} \]  

(4)

where \( D \) is the diffusion coefficient of gas in the liquid. For the case where the entire mass resistance is located inside the diaphragm, the effective film thickness (\( \delta \)) depends on the thickness of the membrane \( (d_m) \), its porosity \( (\epsilon) \), and the tortuosity of the pores \( (\tau) \). Because the values of these properties are not known beforehand, a membrane calibration factor \( (f) \) as defined in the equation below has to be determined experimentally

\[ k_L A = \frac{D}{d_m} \frac{\epsilon}{\tau} = Df \]  

(5)

The calibration factor, \( f \), can be determined by absorbing gas into a liquid, for which the diffusion coefficient is known.
accurately. In the present case, the absorption of N₂O and CO₂ in water was used as a calibration system, because, for these systems, a considerable amount of information on diffusion coefficients is available in the literature.

Solving the mass balance equations (eqs 1 and 2) with the initial condition (eq 3), the following equation can be obtained.

\[
\ln \left( \frac{(V_G + mV_L)P(t)}{P_0} - V_G \right) = -k_L A \left( \frac{1}{V_L} + \frac{m}{V_G} \right) t \tag{6}
\]

A plot of eq 6 yields the value of \(k_L A\). Using eq 5, the diffusion coefficient can be calculated if the calibration factor, \(f\), is known or vice versa.

**Diffusion Cell.** The diaphragm diffusion cell used for the measurements is shown in Figure 1. The liquid chamber (volume 282.5 mL) was equipped with a magnetic stirrer. The gas chamber was divided into two parts. The upper chamber (170.5 mL) was the reference chamber and consisted of a pressure transducer (0–1000 mbar, Druck) connected to the lower measuring chamber (187.5 mL) by two valves. The valves can be used to disconnect the two gas chambers. A differential pressure transducer (range 0–0.305 m H₂O; accuracy 1% of full scale; Druck 600DP series) was connected between the reference and measuring chamber. It was used to measure the pressure drop in the measuring chamber, with respect to the constant pressure in the reference chamber. This method of measuring the pressure drop during gas absorption significantly reduces the duration of the experiment, in comparison to that for an earlier version of the instrument containing a gas chamber without a partition. The whole apparatus was thermostated, and the temperature was controlled within ±0.1 K.

**Calibration of Diaphragm.** The calibration factor, \(f\), for the diaphragm [P4 type; pore diameter (10–16) μm; area (33 ± 0.5) cm²; thickness 4 mm] was determined by carrying out experiments on the absorption of N₂O and CO₂ in water in the temperature range 292–310 K, using different liquid stirrer speeds. The values of diffusion coefficient of N₂O and CO₂ in water obtained from the literature were used to determine the calibration factor, \(f\). The factor of the diaphragm used for the measurements was 0.48. The accuracy of the estimated calibration factor was within ±3% for the two gases studied and over the temperature range mentioned above. There was no influence of the stirrer speed between 30 and 60 rpm. At temperatures above 310 K, this operational window reduced and considerable scatter of the estimated \(f\) values occurred at the higher and lower ends of the stirrer speed. Therefore, no experiments above 308 K are presented on the diffusivity.

**Results and Discussion**

The measured values of density and viscosity of the aqueous salt solutions studied are given in Table 1. The estimated accuracy of the density and viscosity measurements is within 0.01% and 0.5%, respectively.

**Solubility.** Tables 2 and 3 give the experimental data of the solubility of N₂O in aqueous potassium taurate and potassium glycinate solutions, respectively. The data show the typical "salting out effect" observed in electrolyte solutions for N₂O. For moderately high concentrations, the effect can be best described by the Sechenov relation

\[
\log(m_v/m) = KC_s \tag{7}
\]

\(m_v\) and \(m\) denote the solubility of N₂O in water and salt solution, respectively, and \(C_s\) is the molar salt concentration. Several empirical models have been proposed in the past to predict the Sechenov constant \((K)\). The most widely used models are the van Krevelen–Hoftijzer model and the one proposed by Schumaeke. For a single
salt, the Sechenov constant, based on the Schumpe model, is given by the following relation

$$K = \sum (h_i + h_G)n_i$$  \hspace{1cm} (8)

The Sechenov constant, as defined in the van Krevelen-Hoftijzer model, for a single salt is

$$K = (h_i + h_G)n_i$$  \hspace{1cm} (9)

with $n_i$ being the index of the ion $i$ in the formula of the salt. The parameter $K$ is specific to the gas and the salt. $h_i$ and $h_G$ are the ion and gas specific constants. On the basis of extensive study by Schumpe on the solubility of various gases in different salt solutions, it was found that the standard deviation of the experimentally determined Sechenov constant by the model of Schumpe was half as compared to that of the constant determined with the van Krevelen-Hoftijzer model. So, the model proposed by Schumpe was adopted for the present system.

The plot of eq 7 for the experimental data yields the Sechenov constants, and they are given in Table 4. The experimental data were found to be well fitted by eq 7 ($R^2 > 0.985$). From the Sechenov constants, the anion specific constant ($h_-$) can be estimated using eq 8 because the information on the cation specific constant ($h_+$) as well as the gas specific constant ($h_G$) and its dependence on temperature is available in the literature. The value of the constant corresponding to the anion is given at various temperatures in Table 4. The average values of $h_-$ for taurate and glycinate ions are 0.0249 (std dev 0.0026) and 0.0276, respectively. A parity plot between the experimental data and estimated values using eqs 7 and 8 is shown in Figure 2.

**Diffusivity.** The experimental data for the diffusivity of N$_2$O in potassium taurate solutions are given in Table 5. The values provided here are the arithmetic mean of three or four identical measurements. The standard deviation of the measured values was within ±5% of the mean value. The dependence of diffusion coefficient on the concentration and temperature can be described in terms of the viscosity of the solution ($\mu$), using a modified Stokes-Einstein equation. In the case of alkanolamines, the dependence has been reported as $D = \frac{kT}{6} \mu^{-0.6}$ = constant for various amines in aqueous solutions. Similarly, gas
diffusion in electrolyte solutions can be reasonably correlated with the modified Stokes–Einstein equation.\textsuperscript{8,12} Figure 2 shows the plot of \(D/D_w\) versus \((\\mu/\\mu_w)\). The data fit to the following equation within ±10% accuracy, as shown in Figure 3.

\[
(D/D_w) = (\\mu/\\mu_w) ^{-0.74}
\]

(10)

Here \(D_w\) is the diffusion coefficient of the gas in water and \(\\mu_w\) is the viscosity of water. The values of viscosity used to calculate \((\\mu/\\mu_w)\) in Table 5 at various concentrations and temperatures were interpolated from the experimental data given in Table 1.

Conclusions

1. The solubility of \(\text{N}_2\text{O}\) in aqueous potassium glycinate and taurate has been experimentally determined. The effect of temperature and concentration of the salt on the solubility of \(\text{N}_2\text{O}\) can be expressed by the Sechenov equation. The anion specific constant \((h_+)\) in the Sechenov equation has been determined for taurate and glycinate ions.

\[
\begin{align*}
\text{O}_3\text{SCH}_2\text{CH}_2\text{NH}_2: (h_+) &= 0.0249 \\
\text{O}_2\text{CCH}_2\text{NH}_2: (h_+) &= 0.0276
\end{align*}
\]

2. The diffusivity of \(\text{N}_2\text{O}\) in potassium taurate solution is reported in the range 0–3.5 M and 293–308 K. As expected, the modified Stokes–Einstein equation can be used for the estimation of the diffusion coefficient of \(\text{N}_2\text{O}\) in aqueous potassium taurate solution.

\[
D\\mu^{0.74} = \text{constant}
\]

Literature Cited


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