Appendix A

Outline of the model of Pitzer

A very brief outline of the model of Pitzer introduced by Pitzer [168] is given below. For an electrolyte solution containing \( \overline{m}_{SH} \) kilograms of solvent, with molalities \( m_i, m_j, \ldots \), of solute species \( i, j, \ldots \), Pitzer [168] introduced the equation for the excess Gibbs energy:

\[
\frac{G^{ex}}{RT \overline{m}_{SH}} = f(I_m) + \sum_i \sum_j m_i m_j B_{ij} + \sum_i \sum_j \sum_k m_i m_j m_k C_{ijk} + \ldots \tag{A.1}
\]

where \( S_H \) is any amphoteric solvent and can be pure water, an alcohol-water mixture, or a pure alcohol. Pitzer [168] further derived the expression for the activity coefficient. For the dissolved species \( i, j \), the activity coefficients were estimated by:

\[
\ln(\gamma_{ij|m}) = -A \phi \left[ \frac{\sqrt{I_m}}{1 + b \sqrt{I_m}} \right] + m B_{ij} + 3m^2 C_{ij} \tag{A.2}
\]

where \( I_m \) is defined as:

\[
I_m = \frac{1}{2} \sum_{q=i,j} \overline{m}_{q} z_q^2 \tag{A.3}
\]

and \( b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2} \). The Debye-Hückel term was given as:

\[
A_\phi = \frac{1}{3} \sqrt{2\pi N_A \rho} \left( \frac{e^2}{4\pi \varepsilon_0 \varepsilon_{SH} kT} \right)^{1.5} \tag{A.4}
\]

where the specific density, \( \rho \), and the relative dielectric constant, \( \varepsilon_{SH} \), of the (solute-free) solvent mixture, as well as the parameter \( b \) given above, are solvent composition dependent parameters. \( \rho \) was taken from Saul & Wagner [55], Eastal & Woolf [169], Westmeier [170], and Kipkemboi & Eastal [171] for water, the methanol-water solvent, the ethanol-water solvent, and the \( t \)-butanol-water solvent, respectively. \( \varepsilon \) was taken from Bradley & Pitzer [72], Albright & Gosting [73], and Akerlof [74] for water, the methanol-water solvent, the ethanol-water solvent, and the \( t \)-butanol-water solvent. The parameter \( b \) was set to \( 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2} \) for aqueous solutions by Pitzer [168], and this value was assumed to be independent of the solvent composition and the value for pure water was applied [172]. The second virial coefficient is given:

\[
B_{ij} = 2\beta(0)_{ij} + \left( \frac{2\beta(1)_{ij}}{\alpha^2 I_m} \right) \left[ 1 - \frac{\alpha I_m^{1/2} - \alpha^2 I_m}{2} \exp \left( -\alpha I_m^{1/2} \right) \right] \tag{A.5}
\]
where \( \beta^{(0)}_{ij} \), \( \beta^{(1)}_{ij} \) and \( C_{ij} \) are salt specific interaction parameters. For the case considered here, \( \alpha = 2.0 \) kg\(^{-1}\) mol\(^{-1/2}\). The activity of the solvent mixture followed from the Gibbs-Duhem equation in the form of:

\[
\ln (a_{SH}) = \frac{M_{SH}^*}{1000} \left( 2A_0 + \frac{1}{1 + \lambda a_{SH}} \sum_{i \neq SH} \mu_i \right) \tag{A.6}
\]

where \( M_{SH}^* \) was the molecular weight of the solvent mixture.

### A.1 Interaction parameters for KCl in the model of Pitzer

The following section reports the temperature dependence of the ion interaction parameters for KCl given by Pabalan & Pitzer [10]. The interaction parameters are calculated from equation (A.7) and Table A.1.

\( T \) is the temperature in Kelvin, \( T_R = 298.15 \) K, \( p \) is the pressure in bar and \( p_R = 179 \) bar. The density of water, \( \rho_W \), was taken from Saul & Wagner [55]. The pressure, \( p \), was set to 1 bar. The pressure dependence of the thermodynamic properties were calculated from equation (A.8) and Table A.2. A complete description of the equations below are given by Pabalan & Pitzer [10].

\[
f(T, p) = \frac{u_1 T^2}{6} + \frac{u_2 T^3}{2} + \frac{u_3 T^4}{12} + \frac{u_4 T^5}{20} + u_5 \frac{T^2}{12} + \frac{u_6 T^3}{20} + u_7 \frac{2(647 - T) \ln (647 - T) - \ln (647 - T)^2}{T^3} + K_1 + f_L(T, p) \tag{A.7}
\]

Table A.1: Parameters for equation (A.7)

<table>
<thead>
<tr>
<th>parameter</th>
<th>( \beta_{KCl}^0 ) kg·mol(^{-1})</th>
<th>( \beta_{KCl}^1 ) kg·mol(^{-1})</th>
<th>( C_{KCl} ) kg(^{-1}) mol(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_1 )</td>
<td>-2.10289 \times 10^{-2}</td>
<td>2.20813 \times 10^{-2}</td>
<td>0.0</td>
</tr>
<tr>
<td>( u_2 )</td>
<td>6.00967 \times 10^{-1}</td>
<td>-4.61849 \times 10^{-1}</td>
<td>7.64891 \times 10^{-4}</td>
</tr>
<tr>
<td>( u_3 )</td>
<td>3.67768 \times 10^{-3}</td>
<td>-1.0176 \times 10^{-2}</td>
<td>0.0</td>
</tr>
<tr>
<td>( u_4 )</td>
<td>7.05537 \times 10^{-6}</td>
<td>1.10445 \times 10^{-4}</td>
<td>-1.12131 \times 10^{-8}</td>
</tr>
<tr>
<td>( u_5 )</td>
<td>1.97968 \times 10^{-9}</td>
<td>-4.73196 \times 10^{-8}</td>
<td>1.72256 \times 10^{-11}</td>
</tr>
<tr>
<td>( u_6 )</td>
<td>-2.47588 \times 10^{-3}</td>
<td>-2.74210 \times 10^{-2}</td>
<td>0.0</td>
</tr>
<tr>
<td>( u_7 )</td>
<td>1.44160 \times 10^{-1}</td>
<td>3.3288 \times 10^{-1}</td>
<td>-5.71188 \times 10^{-3}</td>
</tr>
<tr>
<td>( f_L(T, 1\text{bar}) )</td>
<td>6.77136 \times 10^{-4}</td>
<td>9.67584 \times 10^{-4}</td>
<td>-4.12364 \times 10^{-3}</td>
</tr>
<tr>
<td>( f_L(T, p_R) )</td>
<td>6.58083 \times 10^{-4}</td>
<td>9.76584 \times 10^{-4}</td>
<td>-4.12364 \times 10^{-3}</td>
</tr>
<tr>
<td>( f_{L}(T, p) )</td>
<td>4.8080 \times 10^{-3}</td>
<td>2.16752 \times 10^{-1}</td>
<td>-3.94 \times 10^{-4}</td>
</tr>
<tr>
<td>( K_1 )</td>
<td>-2941.25816</td>
<td>6535.355434</td>
<td>28.172180</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>-31.933433</td>
<td>193.004959</td>
<td>-0.125567</td>
</tr>
</tbody>
</table>
$$\ln \gamma_\pm (p_2) - \ln \gamma_\pm (p_1) =$$

$$- [A_\phi (p_2) - A_\phi (p_1)] \left( \frac{\beta_{0ij}}{1 + \beta_{0ij}^2} + \frac{2}{7} \ln \left( 1 + \beta_{0ij}^2 \right) \right) + \int_{p_1}^{p_2} \left( 2m \left( \frac{\beta_{0ij}}{\delta p} \right) \right) \frac{\partial \beta_{0ij}}{\partial p} \right) \frac{1}{T} \left( 1 - \left( 1 + \alpha I_{1/2} - \alpha^2 I_{1/2}^2 \right) \exp \left( -\alpha I_{1/2}^2 \right) \right)$$

$$+ 3m^2 \left( \frac{\beta_{0ij}}{\delta p} \right) \frac{\partial \beta_{0ij}}{\partial p} \right) \frac{\partial \beta_{0ij}}{\partial p} \right) \frac{1}{T} \left( 1 - \left( 1 + \alpha I_{1/2} - \alpha^2 I_{1/2}^2 \right) \exp \left( -\alpha I_{1/2}^2 \right) \right)$$

where $$\left( \frac{\beta_{0ij}}{\delta p} \right) = B_{ij}^0$$ and $$B_{ij}^0$$ is calculated from equation (A.9) and Table A.2. Further, in this case, $$\left( \frac{\beta_{0ij}}{\delta p} \right) = 0$$ and $$\left( \frac{\beta_{0ij}}{\delta p} \right) = 0$$.}

$$f_\chi (T, p) = q_1 + \frac{q_2}{T} + q_3 T + q_4 T^2 + \frac{q_5}{(647 - T)}$$

$$+ p \left[ q_6 + \frac{q_7}{T} + q_8 T + q_9 T^2 + \frac{q_{10}}{(647 - T)} \right]$$

$$+ p^2 \left[ q_{11} + \frac{q_{12}}{T} + q_{13} T + q_{14} T^2 + \frac{q_{15}}{(647 - T)} \right] \quad \text{(A.9)}$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_1$</td>
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</tr>
<tr>
<td>$q_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$q_3$</td>
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</tr>
<tr>
<td>$q_4$</td>
<td>-2.96741 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$q_5$</td>
<td>3.26205 $\times 10^{-6}$</td>
</tr>
<tr>
<td>$q_6$</td>
<td>8.39662 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$q_7$</td>
<td>0.0</td>
</tr>
<tr>
<td>$q_8$</td>
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</tr>
<tr>
<td>$q_9$</td>
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</tr>
<tr>
<td>$q_{10}$</td>
<td>-4.42327 $\times 10^{-5}$</td>
</tr>
<tr>
<td>$q_{11}$</td>
<td>-7.57437 $\times 10^{-10}$</td>
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<td>$q_{13}$</td>
<td>4.12771 $\times 10^{-12}$</td>
</tr>
<tr>
<td>$q_{14}$</td>
<td>-7.2496 $\times 10^{-15}$</td>
</tr>
<tr>
<td>$q_{15}$</td>
<td>4.16221 $\times 10^{-8}$</td>
</tr>
</tbody>
</table>

### A.2 Interaction parameters for HCl in the model of Pitzer

The following section reports the density, pressure, and temperature dependence on the ion interaction parameters for HCl given by Holmes et al. [9]. The ion interaction parameters are
given by equation (A.11) and Table A.3. \( T \) is the temperature in Kelvin, \( T^* \) is 1 K, \( p^* \) is 1 MPa and \( \rho^* \) is 1 kg \( \cdot \) m\(^{-3} \). \( T_R, p_R \) and \( \rho_R \) are the reference temperature, pressure and density and are set to 298.15 K, 0.101325 MPa and 997.062 kg \( \cdot \) m\(^{-3} \), respectively. The pressure and density, \( p \) and \( \rho \), were set equal to the reference pressure and reference density. For HCl, the interaction parameter, \( C \) in equation (A.2), is defined:

\[
C = \frac{1}{2} C_{\text{HCl}}
\]

\[
f(\rho, T, p) = q_1 + q_2 \rho \ln \left( \frac{\rho}{\rho_R} \right) + q_3 \left( \frac{\rho - \rho_R}{\rho^*} \right) + q_4 \left( \frac{T - T_R}{T^*} \right) + q_5 \left( \frac{p - p_R}{p^*} \right)
\]

Table A.3: Parameters for equation (A.11)

<table>
<thead>
<tr>
<th>parameter</th>
<th>( \beta_{\text{HCl}} )</th>
<th>( \beta_{\text{HCl}} )</th>
<th>( C_{\text{HCl}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_1 )</td>
<td>0.17690</td>
<td>0.2973</td>
<td>0.362 ( \cdot ) 10(^{-3} )</td>
</tr>
<tr>
<td>( q_2 )</td>
<td>-0.09140</td>
<td>16.147</td>
<td>0.0</td>
</tr>
<tr>
<td>( q_3 )</td>
<td>0.0</td>
<td>-17.631 ( \cdot ) 10(^{-3} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( q_4 )</td>
<td>-4.034 ( \cdot ) 10(^{-4} )</td>
<td>0.0</td>
<td>-3.036 ( \cdot ) 10(^{-5} )</td>
</tr>
<tr>
<td>( q_5 )</td>
<td>0.620 ( \cdot ) 10(^{-4} )</td>
<td>7.20 ( \cdot ) 10(^{-4} )</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Appendix B

Diffusion Coefficients of N₂O in Aqueous Piperazine Solutions using the Taylor Dispersion Technique from 293 to 333 K and 0.3 to 1.4 mol·dm⁻³

Abstract

The diffusion coefficients of N₂O in aqueous piperazine (PZ) solutions have been determined using the Taylor dispersion technique over a temperature range from 293 to 333 K and a concentration range from 0.3 to 1.4 mol·dm⁻³. The experimental results have been compared to literature values. Diffusion coefficients of N₂O in aqueous PZ solutions can be estimated by using a modified Stokes-Einstein relation with sufficient accuracy for engineering purposes. The diffusion coefficient of CO₂ in an aqueous PZ solution can be estimated by means of the "N₂O analogy".

B.1 Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO₂ and H₂S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating. [1] Recently, blends of a primary or secondary (alkanol)amine with an aqueous solution of a tertiary (alkanol)amine has found application in the removal and absorption of CO₂ due to higher reaction rates and lower heats of regeneration in the desorber section. There is a growing interest in the use of piperazine (PZ) blended with aqueous solutions of N-methyldiethanolamine (MDEA) as a tertiary alkanolamine for gas treating processes. This type of solution is also called the activated MDEA solvent. PZ is known as the activator or promotor and enhances the reactivity towards CO₂, whereas MDEA contributes to the lower heats of regeneration. In these solvents, the concentration of MDEA is usually kept at about 3 to 4 mol·dm⁻³ and typically a maximum PZ concentration of about 1.0 mol·dm⁻³ is applied. [173-177]

Knowledge of diffusion coefficients is needed for the design of absorbers and desorbers in a commercial CO₂ capture plant, as they are related to the mass transfer coefficients. They are also essential for a correct and accurate interpretation of many (lab scale) absorption rate experiments, e.g. the experiments aimed at the determination of the intrinsic kinetics in a gas-liquid process. The diffusion coefficients of N₂O in aqueous PZ solutions are presented in this work, and these values can be used to estimate the diffusion of CO₂ in aqueous PZ solutions by means of the "N₂O analogy".

Measurements of gas diffusivities in liquids have previously, in a large part, been carried out with the use of experimental techniques like laminar liquid jet, diaphragm cell, or wetted
wall absorber. The Taylor dispersion technique has primarily been used to determine liquid diffusivities in liquid systems. However, some literature sources have reported gas diffusivities in liquids using the Taylor dispersion technique. [178,179] These literature sources determined the diffusivity of gases in single component liquids, e.g. N\textsubscript{2}O + H\textsubscript{2}O system. In the present work, diffusivities of a gas in binary liquid mixtures are determined, e.g. N\textsubscript{2}O + (PZ + H\textsubscript{2}O) system. These types of chemical systems contain three compounds, e.g. N\textsubscript{2}O, PZ, and H\textsubscript{2}O, and there are experimental challenges with these types of systems when determining diffusivities using the Taylor dispersion technique. The advantages of using the Taylor dispersion technique over the other experimental techniques aforementioned is the fast measuring time, readily automation of the setup, possibility of measurements at elevated temperatures and/or pressures, and that the setup consists of standard HPLC components.

B.2 Theory and experimental procedures

The diffusivities were determined using the Taylor dispersion technique. A square pulse of a solute solution is injected into a solvent solution showing laminar flow through a capillary tube. The solute solution contains the same amounts of liquid components as the solvent, but with additional N\textsubscript{2}O gas absorbed. As an example; for measurements of N\textsubscript{2}O diffusivity in an aqueous PZ solution of 1.0 mol dm\textsuperscript{-3}, the solute and solvent solution would contain 1.0 mol dm\textsuperscript{-3} PZ. The solute solution would additionally contain N\textsubscript{2}O gas absorbed, and a square pulse of this solution would be injected into the flowing solvent solution. The combined action of axial convection and radial and axial molecular diffusion will eventually change the shape of the solute pulse into a gaussian shaped curve. The theory and mathematical description of such a measurement have been in detail described by Taylor [180,181] and Aris [182].

The experimental setup used is shown schematically in Figure B.1. Two vessels containing the solute solution and the solvent solution were kept under a constant 5 \times 10\textsuperscript{3} kPa pressure of saturated helium in order to create a constant flow of the solute and solvent solution. Saturated helium was used in order to prevent any concentration changes in the solute and solvent solution as the liquid level in the two closed vessels containing the solutions decrease during a measurement due to the solution outflow. Introduction of a solute square pulse was done by switching an air actuated six-way valve back and forth within a few seconds. The capillary tube was elliptical coiled and placed in a water bath for temperature control. The flow velocity was controlled by mass flow controllers (Rosemount Flowmega 5881), located behind the refractive index (RI) detector (Varian 350 RI) and the six-way pulse valve in order to obtain a constant pulsation-free solute and solvent solution flow throughout the measurement. In order to avoid bubble formation from the absorbed gas and thus a disturbance of the laminar fluid flow profile, especially at higher temperatures, pressure reducers were located behind the RI detector and the six-way pulse valve. These reducers pressurized the fluids inside the tubing to 4 \times 10\textsuperscript{3} kPa. The influence of the pressure on the diffusion coefficients was neglected for the pressure applied. [183,184] Prior to each experiment, both the solute and the solvent solution were degassed by applying vacuum for a while, and N\textsubscript{2}O was further absorbed into the solute solution by bubbling the gas up to 1.5 \times 10\textsuperscript{3} kPa into the closed vessel containing the solution. The vessel was kept at room temperature (298.15 K) at all time, and the concentration of N\textsubscript{2}O in the solute solution was determined based on the solubility of N\textsubscript{2}O in aqueous PZ solutions [185] and the ideal gas law. A computer was connected to the setup for control and data acquisition. The output signal from the RI detector was recorded as a function of time and used to determine the diffusion coefficients. The RI detector showed a linear response to concentration changes of absorbed N\textsubscript{2}O in the solutions investigated. Depending on the residence time and the dispersion rate of the injected N\textsubscript{2}O pulse, the average concentration of the detected N\textsubscript{2}O was lower than the concentration of the N\textsubscript{2}O absorbed into the solute solution. The determined diffusivities are characterized to be at infinite dilution, since the average concentration of the injected N\textsubscript{2}O
A disturbance of the laminar fluid flow profile can occur due to the helical coiling of the tube. The varying path lengths traversed by the fluid at different radial positions in the tube and the secondary flows present in the flow can contribute additionally to the dispersion process. This topic has been extensively discussed by Alizadeh et al. [186] and Snijder et al. [92]. In order to avoid this disturbance, the critical \((De)^2Sc\) was determined for each system. The dimensionless \((De)^2Sc\) number is defined as:

\[
De = Re \left( \frac{R_C}{R} \right)^{-1/2} \tag{B.1}
\]

\[
Sc = \frac{\mu}{\rho D} \tag{B.2}
\]

where Re is the well-known Reynolds number and \(\mu\) and \(\rho\) are the solvent viscosity and density. The other parameters are defined in Table B.1. The measurements had to be carried out at a value of \((De)^2Sc\) lower than the critical one.

### B.2.1 Chemicals

PZ [110-85-0] (Sigma-Aldrich), \(N_2O\) [10024-97-2], and helium [7440-59-7] (Linde Gas) were used as supplied. Water was demineralized and further purified by vacuum distillation. The actual PZ concentration in the prepared solutions was determined by volumetric titration.

### B.2.2 Diffusivity of \(N_2O\) in \(H_2O\)

Figure B.2 shows a typical experimental result from a pulse recorded using the Taylor dispersion technique. The figure shows a dimensionless result from a \(N_2O + H_2O\) system. The recorded
pulse is the response from absorbed N\textsubscript{2}O in the solution flowing through the RI detector. The experimental result of the diffusion coefficient from this typical experiment is derived from curve fitting Equations (B.3) and (B.4) \[180–182\] to the experimental data where \(N_{\text{inj}}(\text{N}_2\text{O})\), \(u\) and \(D_{\text{N}_2\text{O}}(\text{in H}_2\text{O})\) are the independent variables:

\[
e_{\text{cm}} = \frac{N_{\text{inj}}(\text{N}_2\text{O})}{2\pi R^2 \sqrt{2K(\text{N}_2\text{O}) t}} \exp \left( \frac{(L-ut)^2}{4K(\text{N}_2\text{O})t} \right) \tag{B.3}
\]

\[
K(\text{N}_2\text{O}) = \frac{u^2R^2}{48D_{\text{N}_2\text{O}}(\text{in H}_2\text{O})} + D_{\text{N}_2\text{O}}(\text{in H}_2\text{O}) \tag{B.4}
\]

where \(e_{\text{cm}}\) is the measured concentration profile, \(t\) is the time, \(N_{\text{inj}}(\text{N}_2\text{O})\) is the number of moles of \(\text{N}_2\text{O}\) injected, and \(D_{\text{N}_2\text{O}}(\text{in H}_2\text{O})\) is the diffusion coefficient of \(\text{N}_2\text{O}\). The other parameters are defined in Table B.1.

![Figure B.2: Typical result from a N\textsubscript{2}O + H\textsubscript{2}O system](image)

**Figure B.2**: Typical result from a N\textsubscript{2}O + H\textsubscript{2}O system: –, exp. result; · · · · , fit

### B.2.3 Diffusivity of N\textsubscript{2}O in (PZ + H\textsubscript{2}O)

Figure B.3 shows a dimensionless recorded experimental result from a N\textsubscript{2}O + (PZ + H\textsubscript{2}O) system. It is shown that a combination of two pulses appears. The degassed solvent and solute solutions used were prepared containing a specific and equal concentration of PZ. \(\text{N}_2\text{O}\) was further absorbed into the solute solution as aforementioned. As \(\text{N}_2\text{O}\) was absorbed into the solution, a small liquid volume increase would take place because of the volume occupied by the \(\text{N}_2\text{O}\) molecules. Consequently, the concentration of PZ is decreased in the solute solution, compared to the solvent solution. The ‘negative’ peak in Figure B.3 must be attributed to this phenomena. The ‘positive’ peak is the effect of the \(\text{N}_2\text{O}\) present in the solution.

The RI detector showed a higher sensitivity towards concentration changes of liquid compounds than concentration changes of absorbed gas compounds in the fluid under investigation. This lead to an amplification of the recorded RI signal from concentration changes of liquid compounds relative to concentration changes of absorbed gas compounds. The concentration peak responsible for the ‘negative’ pulse in Figure B.3 was found to be in the order
Figure B.3: Typical result from a $\text{N}_2\text{O} + (\text{PZ} + \text{H}_2\text{O})$ system: $\cdot \cdot \cdot \cdot$, exp. result; $\cdot \cdot \cdot \cdot \cdot$, fit; $\cdot \cdot \cdot \cdot \cdot$, $\text{N}_2\text{O}$ response; $\cdot \cdot \cdot \cdot \cdot$, $\text{PZ}$ response.

of $10^{-6}$ mol dm$^{-3}$ after calibration of a $\text{PZ} + \text{H}_2\text{O}$ system, whereas the ‘positive’ peak was found to be in the order of $10^{-3}$ mol dm$^{-3}$. The concentration differences between the ‘positive’ and ‘negative’ peaks were thus in the order of $10^{-3}$ mol dm$^{-3}$, and the ‘negative’ peak in Figure B.3 appears thus to be larger than the actual in relation to the ‘positive’ peak. As the dispersion of the ‘positive’ and ‘negative’ pulse were unequal, apparent molecular diffusion coefficients could be determined from the recorded experimental data by the principle of superposition. The total response of the RI detector is the sum of two separate gaussian curves.

The experimental measured result was curve fitted to Equations (B.5) to (B.7):

$$c_m = \frac{N_{\text{inj}}(\text{N}_2\text{O})}{2\pi R^2 \sqrt{\pi K(\text{N}_2\text{O})}} \exp \left( -\frac{(L - ut)^2}{4K(\text{N}_2\text{O})t} \right)$$

$$+ \frac{N_{\text{inj}}(\text{PZ})}{2\pi R^2 \sqrt{\pi K(\text{PZ})t}} \exp \left( -\frac{(L - ut)^2}{4K(\text{PZ})t} \right)$$

$$K(\text{N}_2\text{O}) = \frac{u^2 R^2}{48D_{\text{N}_2\text{O}}(\text{in PZ sol.})} + D_{\text{N}_2\text{O}}(\text{in PZ sol.})$$

$$K(\text{PZ}) = \frac{u^2 R^2}{48D_{\text{PZ}}(\text{in H}_2\text{O})} + D_{\text{PZ}}(\text{in H}_2\text{O})$$

where $c_m$ is the measured concentration profile, $t$ is the time, $N_{\text{inj}}(\text{N}_2\text{O})$, and $N_{\text{inj}}(\text{PZ})$ are the respective number of moles of $\text{N}_2\text{O}$ and excess number of moles of $\text{PZ}$ injected. The fluid flow, $u$, is identical for both injected $\text{N}_2\text{O}$ and $\text{PZ}$. $D_{\text{N}_2\text{O}}(\text{in PZ sol.})$ and $D_{\text{PZ}}(\text{in H}_2\text{O})$ are the respective binary diffusion coefficients of $\text{N}_2\text{O}$ and $\text{PZ}$. The parameters $N_{\text{inj}}(\text{N}_2\text{O}), N_{\text{inj}}(\text{PZ}), u,$ and $D_{\text{N}_2\text{O}}(\text{in PZ sol.})$ in Equations (B.5) to (B.7) are the independent variables used to fit the equations to the experimental data. $D_{\text{PZ}}(\text{in H}_2\text{O})$ was taken from Derks [177], and the influence of $\text{N}_2\text{O}$ present in the current work on this value was neglected. The value of
\( D_{D2}(in \ H_2O) \) represents the dispersion of the 'negative' pulse in Figure B.3 through Equation (B.7). The other parameters are defined in Table B.1.

### B.3 Results and Discussion

#### B.3.1 Diffusivity of \( \text{N}_2\text{O} \) in \( \text{H}_2\text{O} \)

Measurements were conducted on the system \( \text{N}_2\text{O} + \text{H}_2\text{O} \) from 293 to 368 K to evaluate the accuracy of the equipment used. The critical \( (Dc)^2Sc \) number was found to be 130 for this system. Figure B.4 shows the experimental results of \( \text{N}_2\text{O} \) diffusion in \( \text{H}_2\text{O} \), and the results are tabulated in Table B.2. The experimental uncertainty was estimated to be \( \pm 10 \% \). The values are the average value of at least three measurements, and the reproducibility of the measurements was within \( \pm 2 \% \). The concentration of \( \text{N}_2\text{O} \) in the injected square pulse was calculated [185] to be 0.036 mol\cdot dm\(^{-3}\). The results of the present study are in agreement with the results reported by previous authors using different experimental techniques. [90, 110, 187–192]

![Figure B.4: Experimental results of \( D_{\text{N}_2\text{O}}(\text{in } \text{H}_2\text{O}) \): •, exp. results present work with error bars representing the uncertainty of \( \pm 10 \% \); ▽, Davidson & Cullen [187]; △, Duda & Vrentas [188]; ◄, Haimour & Sandall [110]; □, Sada et al. [189]; ◆, Joosten & Dasshwers [190]; □, Versteeg & Van Swaaij [90]; +, Thomas & Adams [191]; *, Samanta et al. [192]

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( D_{\text{N}_2\text{O}}(\text{in } \text{H}_2\text{O}) ) ( \times 10^{-9} \text{ m}^2 \text{ s}^{-1} )</th>
<th>Reference</th>
<th>Method*</th>
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<td>1.39</td>
<td>Haimour &amp; Sandall [110]</td>
<td>LLJ</td>
</tr>
</tbody>
</table>

*LLJ = laminar liquid jet; DC = diaphragm cell; WWA = wetted wall absorber; TDT = Taylor dispersion technique

\[ \text{continued on next page} \]
### B.3.2 Diffusivity of N₂O in aqueous PZ solutions

The experimental determined diffusivities of N₂O + (PZ + H₂O) were measured and averaged over at least three measurements from 293 to 333 K and 0.3 to 1.4 mol·dm⁻³. These results were used to calculate the diffusion coefficients, and the results were averaged over the experimental data. The reference methods used are indicated in the table below.

<table>
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*LLJ = laminar liquid jet; DC = diaphragm cell; WWA = wetted wall absorber; TDT = Taylor dispersion technique*
Diffusivities of $\text{N}_2\text{O}$ in aqueous PZ solutions have been reported by Samanta et al. [192] and Sun et al. [193] at 303 K and 313 K. These data are compared to the results from the present work at 303.15 K and 313.15 K in Figure B.6 and the calculated values from the modified Stokes-Einstein relation. The values from the present work have a relative absolute average deviation of 2.4 % and 2.8 % from the calculated values at 303.15 K and 313.15 K, respectively. The values from Samanta et al. [192] deviates with 1.9 % and 5.6 % at 303 K and 313 K and the values of Sun et al. [193] deviates with 5.2 % and 3.0 %, respectively, from the calculated values. Samanta et al. [192] and Sun et al. [193] both used a wetted wall absorber to determine the diffusivities. Figure B.6 shows that the method developed and described in the present work can be used to determine gas diffusivities in binary liquid systems with sufficient accuracy.
Figure B.5: Logarithmic Stokes-Einstein plot for $D'_\text{N}_2\text{O}(\text{in PZ sol.})$: •, $T = 293.15$ K; ▼, $T = 298.15$ K; ▲, $T = 303.15$ K; ◀, $T = 313.15$ K; ◁, $T = 323.15$ K; ◆, $T = 333.15$ K. The solid line represents Equation (B.8) and the dashed lines represent ±10%.

Figure B.6: Comparison of $D'_\text{N}_2\text{O}(\text{in PZ sol.})$ to literature sources: •, $T = 303.15$ K present work with error bars representing the uncertainty of ±10%; ▼, $T = 303$ K Sun et. al. [193]; ▲, $T = 303$ K Samanta et al. [192]; ◀, $T = 303.15$ K modified Stokes-Einstein; ◆, $T = 313.15$ K present work with error bars representing the uncertainty of ±10%; ◂, $T = 313$ K Sun et al. [193]; △, $T = 313$ K Samanta et al. [192]; - - - , $T = 313.15$ K modified Stokes-Einstein.
than the Taylor dispersion technique. The diffusivity of N₂O in aqueous PZ solutions can be calculated with a modified Stokes-Einstein relation for engineering purposes. The results from the present work have an average and maximum deviation of 3.0 % and 6.4 % from the calculated values, whereas the results from the literature have an average deviation of up to 5.6 % for the results considered. As a result, the Taylor dispersion technique can be used as an experimental technique to determine gas diffusivities in binary liquid systems with sufficient accuracy.
Appendix C

Diffusivities in Aqueous Solutions of the Potassium Salt of Amino Acids

Abstract

Diffusion coefficients of the potassium salt of taurine, sarcosine, L-proline, and glycine have been determined in aqueous solutions using the Taylor dispersion technique over a temperature range from 293 to 368 K and salt concentrations ranging from 0 to 3.0 mol dm$^{-3}$. The diffusion coefficients of absorbed N$_2$O in aqueous solutions of the potassium salt of taurine, sarcosine, L-proline, and glycine have been determined over a temperature range from 293 to 333 K and salt concentrations ranging from 1.0 to 3.0 mol dm$^{-3}$. The experimental results have been compared to estimated values from a modified Stokes-Einstein relation and available literature data. The diffusivities can be estimated with sufficient accuracy for engineering purposes using a modified Stokes-Einstein relation. The diffusion coefficients of CO$_2$ in the aqueous amino acid salt solutions can be estimated by means of the ”N$_2$O analogy”.

C.1 Introduction

Aqueous solutions of amines are frequently used for the removal of acid gases, such as CO$_2$ and H$_2$S, from a variety of gas streams. In particular, aqueous solutions of alkanolamines and blends of alkanolamines are widely applied in gas treating. Alkanolamines can undergo degradation in oxygen atmosphere, usually encountered in the treatment of flue gases. The relative high volatility of alkanolamines also leads to losses of the compound during commercial operation of CO$_2$ capture plants. Aqueous solutions of salts of amino acids might be an attractive alternative to alkanolamines. They have been found to have better resistance to oxidative degradation, and their reactivity with CO$_2$ is comparable to aqueous alkanolamines of related classes. The ionic nature of the aqueous solutions of salts of amino acids result in a negligible volatility. [1, 194–197]

Knowledge of diffusion coefficients is needed for the design of absorbers and desorbers in a commercial CO$_2$ capture plant, as they are related to the mass transfer coefficients. They are also essential for a correct and accurate interpretation of many (lab scale) absorption rate experiments, e.g. experiments aimed to determine the intrinsic kinetics in a gas-liquid process. Diffusivities of the potassium salt of taurine, sarcosine, L-proline, and glycine in aqueous solutions determined by the Taylor dispersion technique at temperatures from 293 to 368 K and salt concentrations ranging from 0 to 3.0 mol dm$^{-3}$ are presented in this work. Diffusivities of N$_2$O in the same solutions determined with the same technique at temperatures from 293 to 333 K and salt concentrations ranging from 1.0 to 3.0 mol dm$^{-3}$ are also presented. The results are correlated and compared to literature values.
C.2 Theory and experimental procedures

C.2.1 General theory of the Taylor dispersion technique

The diffusivities were determined using the Taylor dispersion technique. A square pulse of a solute solution was injected into a solvent solution showing laminar flow through a capillary tube. The solute solution contained the same components as the solvent solution, but with a slightly higher concentration of the compound of which diffusivities were to be determined (an addition of approx. 0.05 mol·dm⁻³). In the case of absorbed gas measurements; the solute solution contained the same amounts of liquid components as the solvent solution, but with additional N₂O gas absorbed. As an example of liquid measurements; for measurements of diffusivities in an approx. 1.00 mol·dm⁻³ solution of potassium taurate, the solvent solution contained 1.00 mol·dm⁻³ potassium taurate. The solute solution contained 1.05 mol·dm⁻³ potassium taurate, and a square pulse of this solution was injected into the flowing solvent solution. For gas measurements in aqueous solutions of potassium taurate at 1.00 mol·dm⁻³; both the solvent and solute solution contained 1.00 mol·dm⁻³ of potassium taurate. The solute solution contained additional absorbed N₂O, and a square pulse of this solution was injected into the flowing solvent solution. The combined action of axial convection and radial and axial molecular diffusion eventually changed the pulse into a gaussian curve. The theory, mathematical description and procedure of such diffusivity measurements have been described in detail by Taylor [180,181], Aris [182], and in Appendix B.

The experimental setup used is shown schematically in Figure C.1. Two vessels containing the solute solution and the solvent solution were kept under a constant 5·10² kPa pressure of saturated helium in order to create a constant flow of the solute and the solvent. Saturated helium was used in order to prevent any concentration changes in the solute and solvent solution as the liquid level in the two closed vessels decreased during a measurement due to the solution outflow. Introduction of a solute pulse was done by switching an air actuated six way valve back and forth within a few seconds. The capillary tube was elliptical coiled and placed in a water bath for temperature control of ±0.1 K. The flow velocity was controlled with mass flow controllers (Rosemount Flowmega 5881), located behind the refractive index (RI) detector (Varian 350 RI) and the six way pulse valve in order to obtain a constant pulsation-free solute and solvent solution flow throughout the measurement. In order to avoid bubble formation inside the tubing and a disturbance of the laminar fluid flow profile, especially at higher temperatures and/or during absorbed gas diffusion measurements, pressure reducers were located behind the RI detector and the six-way pulse valve. These reducers pressurized the fluids inside the tubing to 4·10² kPa. The influence of the pressure on the diffusion coefficients could be neglected for the pressure applied. [183,184] Prior to each experiment, both the solute and solvent solution were degassed by applying vacuum for a while, and further the RI detector was calibrated. For absorbed gas diffusion measurements, N₂O was absorbed into the solute solution by bubbling the gas up to 1.5·10² kPa into the closed vessel containing the solution. A computer was connected to the setup for control and data acquisition. The output signal from the RI detector was recorded as a function of time and used to determine the diffusion coefficients. The RI detector showed a linear response to concentration changes of the potassium salt of amino acids and absorbed N₂O in the solutions investigated. The dimensions of the experimental setup and the flow conditions are given in Table C.1.

A disturbance of the laminar fluid flow profile can occur due to the elliptic coiling of the tube. The varying path lengths traversed by the fluid at different radial positions in the tube and the secondary flows present in the flow can contribute additionally to the dispersion process. This topic has been extensively discussed by Alizadeh et al. [186] and Snijder et al. [92]. In order to avoid this disturbance, the critical \((De)^{2}Sc\) was determined for each system. The dimensionless \((De)^{2}Sc\) number is defined as:
Figure C.1: Schematic representation of the Taylor dispersion setup

Table C.1: Dimensions of the experimental setup and flow conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of the capillary tube ($L$)</td>
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</tr>
<tr>
<td>Inner radius of the capillary tube ($R$)</td>
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</tr>
<tr>
<td>Radius of the helical coil ($R_C$)</td>
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</tr>
<tr>
<td>Injection volume ($V_{inj}$)</td>
<td>$(2.5 \text{ to } 4.1) \times 10^{-8}$ m³</td>
</tr>
<tr>
<td>Liquid flow velocity ($u$)</td>
<td>$(2 \text{ to } 6) \times 10^{-3}$ m·s⁻¹</td>
</tr>
</tbody>
</table>

\[
D_c = Re \left( \frac{R_C}{R} \right)^{-1/2} \quad (C.1)
\]

\[
Sc = \frac{\mu}{\rho D} \quad (C.2)
\]

where $Re$ is the well-known Reynolds number and $\mu$ and $\rho$ are the solvent viscosity and density. The other parameters are defined in Table C.1. The measurements had to be carried out at a value of $(Dc)^2 Sc$ lower than the critical one.

C.2.2 Chemicals

Taurine [107-35-7], sarcosine [107-97-1], glycine [56-40-6], L-proline [147-85-3], KOH [1310-58-3] (Sigma-Aldrich), $N_2O$ [10024-97-2], and helium [7440-59-7] (Linde Gas) were used as supplied. Water was demineralized and further purified by vacuum distillation.

C.2.3 Salt preparation

The respective aqueous solutions of the potassium salt of the amino acids were prepared by adding equimolar amounts of KOH and amino acid based on weight. The aqueous amino acid zwitterion will be deprotonated according to:

\[
-\text{OOC} - R - \text{NH}_2^+ + \text{KOH} \rightarrow \text{K}^+ + -\text{OOC} - R - \text{NH}_2 + \text{H}_2\text{O} \quad (C.3)
\]

and form a potassium salt of the amino acid. The salt concentration was checked by means of titration.
C.2.4 Salt diffusivity measurements

The results of salt diffusivity measurements can be described by [180–182]:

\[
c_m = \frac{N_{\text{inj,SAA}}}{2\pi R^2 \sqrt{\pi K_{\text{SAA}}}} \exp \left( \frac{(L - ut)^2}{4K_{\text{SAA}}t} \right)
\]  

(C.4)

\[
K_{\text{SAA}} = \frac{u^2 R^2}{8D_{\text{SAA}}} + D_{\text{SAA}}
\]  

(C.5)

where \(c_m\) is the measured concentration profile at the end of the capillary tube, \(N_{\text{inj,SAA}}\) is the excess number of moles of the salt of amino acid injected, \(t\) is the time, and \(D_{\text{SAA}}\) is the binary diffusion coefficient. The subscript SAA refers to the salt of the amino acid. The other parameters are defined in Table C.1. \(N_{\text{inj,SAA}}, u, \) and \(D_{\text{SAA}}\) are the independent parameters used to curvefit Equations (C.4) and (C.5) to the experimentally recorded results. Since the concentration of the solute pulse decreases because of dispersion while the solute pulse is traversing with the solvent through the tubing, an average concentration value had to be determined. Alizadeh et al. [186] referred to this as the reference concentration \(c_{\text{ref}}\) given by:

\[
c_{\text{ref}} = \frac{c_{\text{solv}} + N_{\text{inj,SAA}} \left( \frac{5}{16} - \frac{1}{8\sqrt{\pi}} \right)}{\pi R^2 \sqrt{2K_{\text{SAA}}}}
\]  

(C.6)

where \(c_{\text{solv}}\) is the solvent concentration and \(t'\) is the time at which the measurement ends.

C.2.5 Absorbed gas diffusivity measurements

The experimental procedure used to determine diffusivities of absorbed N\(_2\)O in aqueous solutions by the Taylor dispersion technique has been given in detail in Appendix B. The recorded pulses are described by Equations (C.7) to (C.9):

\[
c_m = \frac{N_{\text{inj,N}_2\text{O}}}{2\pi R^2 \sqrt{\pi K_{\text{N}_2\text{O}}}} \exp \left( \frac{(L - ut)^2}{4K_{\text{N}_2\text{O}}t} \right)
\]  

\[
+ \frac{N_{\text{inj,SAA}}}{2\pi R^2 \sqrt{\pi K_{\text{SAA}}}} \exp \left( \frac{(L - ut)^2}{4K_{\text{SAA}}t} \right)
\]  

(C.7)

\[
K_{\text{N}_2\text{O}} = \frac{u^2 R^2}{8D_{\text{N}_2\text{O}}} + D_{\text{N}_2\text{O}}
\]  

(C.8)

\[
K_{\text{SAA}} = \frac{u^2 R^2}{8D_{\text{SAA}}} + D_{\text{SAA}}
\]  

(C.9)

where \(c_m\) is the measured concentration profile, \(N_{\text{inj,N}_2\text{O}}\) and \(N_{\text{inj,SAA}}\) are the respective numbers of moles of absorbed N\(_2\)O and excess number of moles of salt of amino acid injected, \(t\) is the time, and \(D_{\text{N}_2\text{O}}\) and \(D_{\text{SAA}}\) are the respective diffusion coefficients of absorbed N\(_2\)O and the potassium salt of amino acid. The other parameters are defined in Table C.1. The parameters \(N_{\text{inj,N}_2\text{O}}, N_{\text{inj,SAA}}, u, \) and \(D_{\text{N}_2\text{O}}\) are the independent variables used to fit the equations to the experimental data. The value of \(D_{\text{SAA}}\) is from the previous measurement as aforementioned, and the influence of absorbed N\(_2\)O present in the current measurement on this value is neglected.
C.3 Results and discussion

C.3.1 Diffusivity of the potassium salt of amino acids in aqueous solutions

Values of the diffusivities of the potassium salt of taurine, sarcosine, L-proline, and glycine in aqueous solution were measured and averaged over at least three measurements at temperatures from 293 to 368 K and salt concentrations ranging from 0 to 3.0 mol dm\(^{-3}\). The results are presented in Table C.2. The experimental uncertainty was estimated to be ±5% at temperatures less than 333 K and ±10% at higher temperatures. The reproducibility was within 2%. The critical \((De)^2Sc\) number was found to be about 100 for these systems.

Table C.2: Diffusion coefficients, \(D\), of salts of amino acids in aqueous solutions at various temperatures, \(T\), and reference concentrations, \(c_{ref}\). Subscripts: \(PT = \) potassium taurate; \(PS = \) potassium sarcosinate; \(PP = \) potassium proline; \(PG = \) potassium glycinate.

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<th>(D_{PT}) (10(^{-9}) m(^2) s(^{-1}))</th>
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<th>(c_{ref,PS}) (mol dm(^{-3}))</th>
<th>(D_{PP}) (10(^{-9}) m(^2) s(^{-1}))</th>
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continued on next page
### APPENDIX C.DIFFUSIVITIES IN AQUEOUS SOLUTIONS OF THE POTASSIUM SALT OF AMINO ACIDS

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<th>Temperature (K)</th>
<th>$D_{pp}$</th>
<th>$c_{pp}$</th>
<th>$D_{pg}$</th>
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<td>2.36 · $10^{-1}$</td>
<td>3.30 · $10^{-3}$</td>
</tr>
</tbody>
</table>

continued on next page
The theory of diffusion of aqueous salts at low concentration is well developed. [198] For dilute solutions of a single salt, the diffusion coefficient can be estimated by the Nernst-Haskell equation:

\[
D^0 = \frac{RT}{(1/z^+ + 1/\lambda_0^+)} \left( \frac{1}{\lambda_0^+} + \frac{1}{\lambda_0^-} \right)
\]

where \(D^0\) is the diffusion coefficient at infinite dilution, \(R\) is the gas constant, \(T\) is the temperature, \(F\) is the faraday constant, \(\lambda_0^+\) and \(\lambda_0^-\) are the limiting ionic conductivities, and \(z^+\) and \(z^-\) are the respective valences of the cation and anion. In the case of the potassium salt of glycine at 298.15 K, limiting ionic conductivities have been reported by D’yachkova et al. [199], Miyamoto & Schmidt [200], and Mehl & Schmidt [201] for glycinate. These values are listed in Table C.3. The limiting ionic conductivity of the potassium ion is reported by Poling et al. [198] to be 73.5 cm\(^2\)·S·mol\(^{-1}\). By the use of these values and Equation (C.10), the respective estimated diffusivities at infinite dilution, \(D_{\text{est}, \text{potassium glycinate}}\), were calculated and listed in Table C.3. From Table C.2, the experimentally determined value at low salt concentrations, \(D_{\text{potassium glycinate}}\), is \(1.11 \times 10^{-9}\) m\(^2\)·s\(^{-1}\) at 298.15 K. The relative deviation between the estimated and the experimental values are listed in Table C.3. The limiting ionic conductivity of 39.2 cm\(^2\)·S·mol\(^{-1}\) from Mehl & Schmidt [201] is most likely too high [202] for an ion of the size of glycinate. This can explain the relative deviation of 22.5 %. In the absence of information on limiting ionic conductivities of taurate, sarcosinate, and prolinate, diffusivities at infinite dilution are not estimated for salts of these ions. At higher concentrations, salt diffusivities can be estimated [198] by the additional use of viscosities, solvent partial molar volume and molar density, and mean ionic activity coefficients. As some of these properties are not readily available for the considered salts, such estimations are not further investigated in the present work.

Table C.3: Limiting ionic conductivities, \(\lambda_0^\pm\), estimated and measured diffusivities, \(D_{\text{est}}\) and \(D\), and relative deviation. Subscripts: PG = potassium glycinate

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<th>(D_{\text{PG}})</th>
<th>rel. dev.</th>
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<td>1.11</td>
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C.3.2 Diffusivity of N\(_2\)O in aqueous solutions of the potassium salt of amino acids

The experimental determined diffusivities of N\(_2\)O in aqueous solutions of the potassium salt of taurine, sarcosine, L-proline, and glycine were measured and averaged over at least three measurements at temperatures from 293 to 333 K and salt concentrations ranging from 1.0
APPENDIX C. DIFFUSIVITIES IN AQUEOUS SOLUTIONS OF THE POTASSIUM SALT OF AMINO ACIDS

The results are presented in Table C.4. The experimental uncertainty was estimated to be 10 %, and the reproducibility was within 2 %. The critical ($De$) number was found to be about 80 for these systems.

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>293.15</th>
<th>298.15</th>
<th>303.15</th>
<th>313.15</th>
<th>323.15</th>
<th>333.15</th>
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<td>$c_{PT}$ / mol·dm$^{-3}$</td>
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<td>$D_{N_{2}O}$ / 10$^{-9}$ m$^{2}$·s$^{-1}$</td>
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<td>$c_{PS}$ / mol·dm$^{-3}$</td>
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Several investigators have correlated the diffusivity of an absorbed gas in an aqueous salt solution to the viscosity or the salt concentration. [203–207] Ratcliff & Holdcroft [203], Brilman et al. [206], and Kumar et al. [207] correlated the diffusivities to the viscosities by a modified Stokes-Einstein relation:

$$D_{N_{2}O} = \frac{(H_{2}O)}{(SAA)}^{\alpha} = \text{constant} \quad (\text{C.11})$$

where $\alpha$ is a constant. Ratcliff & Holdcroft [203] found this value to be 0.637, whereas Brilman et al. [206] found it to be 0.6. Kumar et al. [207] found the value to be 0.74. A value of 0.6 was found to predict the diffusivities within an average and maximum absolute relative deviation of 5.6 % and 15.1 %, respectively. The viscosities were taken from Kumar et al. [207], van Holst [208], Portugal et al. [209], and Lide [93]. The diffusivity of $N_{2}O$ in $H_{2}O$ was taken from Versteeg & van Swaaij [90]. The correlation is presented in Figure C.2 for the aqueous solutions of the potassium salt of the amino acids considered. Diffusivities of $CO_{2}$ in aqueous solutions of the potassium salt of amino acids can be estimated by the "$N_{2}O$ analogy” [90].

Kumar et al. [207] reported diffusivities of $N_{2}O$ in aqueous solutions of the potassium salt of taurine at 293 K using a diaphragm cell technique. The results [207] are compared to the results from the present work at 293.15 K in Figure C.3 and the estimated values from the modified Stokes-Einstein relation at 293.15 K. The values from the present work have an average absolute and maximum deviation of 4.6 % and 6.1 % from the estimated values at 293.15 K, respectively. The results of Kumar et al. [207] deviates by 4.8 % and 10.5 % from the estimated values.

C.4 Conclusion

Diffusivities of the potassium salt of taurine, sarcosine, L-proline, and glycine have been determined in aqueous solutions at temperatures from 293 to 368 K and salt concentrations
Figure C.2: Logarithmic Stokes-Einstein plot relating diffusivities, $D$, and viscosities, $\mu$, in aqueous solutions of the potassium salt of amino acids: •, potassium taurate; ▼, potassium sarcosinate; ▲, potassium prolinate; ◀, potassium glycinate. The solid line represents Equation (C.11) and the dashed lines represent $\pm 10\%$.

Figure C.3: Comparison of the diffusivity of $N_2O$, $D_{N_2O}$, in aqueous solutions of the potassium salt of taurine to literature values as a function of concentration, $c$, at 293.15 K. •, exp. results present work with error bars representing the uncertainty of $\pm 10\%$; ▼, Kumar et al. [207]; ---, modified Stokes-Einstein relation.
ranging from 0 to 3.0 mol·dm$^{-3}$. The diffusivities at infinite dilution can be estimated by the Nernst-Haskell equation if limiting ionic conductivity data are available.

Diffusivities of $\text{N}_2\text{O}$ in aqueous solutions of the potassium salt of taurine, sarcosine, L-proline, and glycine have been determined at temperatures from 293 to 333 K and salt concentrations ranging from 1.0 to 3.0 mol·dm$^{-3}$. The diffusivities are in agreement with available literature values. The diffusivities can be estimated using a modified Stokes-Einstein relation, and the diffusivities of CO$_2$ in these solutions can be further calculated.
Appendix D

Patent: Method for Enhancing the Performance of Processes for the Removal of Acid Gas

D.1 Field of invention
The present invention relates to a method for enhancing the performance of processes for the removal of acid gas.

More particularly, the present invention relates to a method for enhancing the performance of processes for the removal of acid gas such as CO$_2$, H$_2$S, COS, CS$_2$, mercaptans.

D.2 Background to invention
Acid gases (also known as sour gases) include CO$_2$, H$_2$S, COS, CS$_2$, mercaptans, etc. The removal of these acid gases is an important step in many industrial processes.

A known technology which is frequently used to capture these sour gases is the absorber/desorber process, whereby (aqueous) solutions of basic reacting solvents, frequently encountered (alkane) amines, are used as solvents. These processes are, however, very energy intensive, because absorption takes place at about 20-40°C and desorption at about 100-120°C, thus a significant amount of energy is required to strip the acid gas from the solvent.

It is an object of the invention to suggest a method for enhancing the performance of processes for the removal of acid gas, which will assist in overcoming these problems.

D.3 Summary of invention
According to the invention, there is provided a method for enhancing the performance of processes for the removal of acid gas, which includes the step of adjusting the dielectric constant of a solvent associated with a process for removing acid gas. Also according to the invention, a process for the removal of acid gas, includes the steps

1. of passing a feed-stream through an absorber/desorber system;
2. of adding a solvent to the system; and
3. of adjusting the dielectric constant of the solvent in order to enhance the performance of the system.
Yet further according to the invention, an arrangement for the removal of acid gas in an acid gas removal process, includes
1. an absorber;
2. a desorber; and
3. adjustment means adapted to adjust the dielectric constant of a solvent added to the process in order to enhance the performance of the system.

The dielectric constant of the solvent may be changed in the absorber, desorber and/or somewhere else in the process.

The adjustment of the dielectric constant of a solvent may influence the thermodynamic equilibrium of the process.

A change of the dielectric constant of 10% may change the solubility of the acid gas by more than 30%.

The acid gas solubility may be increased in the absorber system, in order to increase the capacity of the solvent, resulting in smaller equipment and/or a lower solvent circulation rate.

The acid gas solubility may be decreased in the desorber system, in order to decrease the amount of energy required to strip the acid gas, decrease the size of the desorber and/or decrease the desorber temperature.

The dielectric constant of the solvent may be adjusted by at least one of the steps selected from the group consisting of:
1. adding additional components to the solvent prior to entering the absorber or desorber column;
2. applying an electric field to change the dielectric constant of the solvent; and
3. applying electromagnetic waves adapted to influence the dielectric constant of a solvent.

The added additional component may be removed downstream the absorber or respective desorber.

The dielectric constant of the solvent may be decreased by adding a component which has a dielectric constant lower than water.

The dielectric constant of the solvent may be increased by adding a component with a high dielectric constant.

D.4 Detailed description of invention

A method for enhancing the performance of processes for the removal of acid gas, in accordance with the invention, includes the step of adjusting the dielectric constant of a solvent associated with a process for removing acid gas.

Important and inevitable information for the design and operation of both absorber and desorber is the vapour-liquid equilibrium (VLE); i.e. the relation between the concentration acid gas in the absorption liquid and the partial pressure acid gas in the gas phase at equilibrium conditions.
The solvents used exhibit a substantial thermodynamically non-ideal behavior, because the acid component reacts chemically to ionic species with the alkaline solvent. For this reason an accurate prediction of the thermodynamic equilibrium can only be obtained with rigorous thermodynamic models. In these models the non-ideality of all molecular and ionic species present in the liquid phase is incorporated, because the chemical activities of these components are calculated.

An important physical input parameter in these rigorous thermodynamic models is the dielectric constant of the solvent. During simulations with one of the rigorous thermodynamic models it has been noted that adjustment of this parameter influences the thermodynamic equilibrium significantly. It has been noted that when the dielectric constant is changed with 10% a change in acid gas solubility of more than 30% could be realized. This change in solubility can be used to manipulate and improve on the performance of these kind of acid gas treating systems. If for example the acid gas solubility is increased in the absorber system, the capacity of the solvent will increase, resulting in smaller equipment and/or a lower solvent circulation rate. If the acid gas solubility is decreased in the desorber the amount of energy required to strip the acid gas, the size of the desorber and/or the desorber temperature will be affected positively.

Experiments were illustrated using model calculations on the absorption of CO$_2$ using a 40 wt% aqueous MDEA solution at 40$^\circ$C. It is anticipated that this principle of adjusting the dielectric constant works for all acid gases and all solvents used in the treating of sour gas streams. Accordingly the performance of acid gas absorption processes can be improved by changing the dielectric constant of the solvent in the absorber, desorber or somewhere else in the process. The dielectric constant of a solvent can be adjusted via several routes, including the following:

1. By adding additional components to the solvent prior to entering the absorber or desorber column. The component should however be removed downstream the absorber or respective desorber.
   
   (a) Lowering the solvent dielectric constant can be attained by adding a component which has a dielectric constant lower than water.
   
   (b) Increasing the solvent dielectric constant can be achieved generally by adding a component with a high dielectric constant.

2. By applying an electric field to change the dielectric constant. For example Basu & Sharma (Effect of dielectric saturation on disjoining pressure in thin films of aqueous electrolytes, J. Colloid Interface Sci. 1994, 165, 355) have reported a change in the dielectric constant of water above a field intensity of 107 V/m: At very high electric field strengths, the water molecules develop specific orientations and the effective dielectric constant decreases.

3. By applying electromagnetic waves which influences the dielectric constant of a solvent, as this property is a strong function of the frequency of electromagnetic waves (above a certain frequency). In the case of water, e.g., it is known that its dielectric constant decreases strongly at a frequency above 8 GHz.

D.5 Patent claims

1. A method for enhancing the performance of processes for the removal of acid gas, which includes the step of adjusting the dielectric constant of a solvent associated with a process for removing acid gas.
2. A method as claimed in claim 1, in which the dielectric constant of the solvent is changed in the absorber, desorber and/or somewhere else in the process.

3. A method as claimed in claim 1 or claim 2, in which the adjustment of the dielectric constant of the solvent influences the thermodynamic equilibrium of the process.

4. A method as claimed in any one of the preceding claims, in which a change of the dielectric constant of 10% changes the solubility of the acid gas by more than 30%.

5. A method as claimed in any one of the preceding claims, in which acid gas solubility is increased in the absorber system, in order to increase the capacity of the solvent, resulting in smaller equipment and/or a lower solvent circulation rate.

6. A method as claimed in any one of the preceding claims, in which acid gas solubility is decreased in the desorber system, in order to decrease the amount of energy required to strip the acid gas, decrease the size of the desorber and/or decrease the desorber temperature.

7. A method as claimed in any one of the preceding claims, in which the dielectric constant of the solvent is adjusted by at least one of the steps selected from the group consisting of:
   (a) adding additional component(s) to the solvent prior to entering the absorber or desorber column;
   (b) applying an electric field to change the dielectric constant of the solvent; and
   (c) applying electromagnetic waves adapted to influence the dielectric constant of a solvent.

8. A method as claimed in any one of the preceding claims, in which the dielectric constant of the solvent is adjusted by adding additional component(s) to the solvent prior to entering the absorber or desorber column and in which the added additional component(s) are removed downstream the absorber or respective desorber.

9. A method as claimed in any one of the preceding claims, in which the dielectric constant of the solvent is decreased by adding a component which has a dielectric constant lower than water.

10. A method as claimed in any one of the preceding claims, in which the dielectric constant of the solvent is increased by adding a component with a high dielectric constant.

11. A process for the removal of acid gas, which includes the steps
   (a) of passing a feed-stream through an absorber/desorber system;
   (b) of adding a solvent to the system; and
   (c) of adjusting the dielectric constant of the solvent in order to enhance the performance of the system.

12. A process as claimed in claim 11, in which the dielectric constant of the solvent is changed in the absorber, desorber and/or somewhere else in the process.

13. A process as claimed in claim 11 or claim 12, in which the adjustment of the dielectric constant of the solvent influences the thermodynamic equilibrium of the process.

14. A process as claimed in any one of claims 11 to 13, in which the dielectric constant of the solvent is adjusted by at least one of the steps selected from the group consisting of:
(a) adding additional component(s) to the solvent prior to entering the absorber or desorber column;
(b) applying an electric field to change the dielectric constant of the solvent; and
(c) applying electromagnetic waves adapted to influence the dielectric constant of a solvent.

15. A process as claimed in any one of claims 11 to 14, in which the dielectric constant of the solvent is adjusted by adding additional component(s) to the solvent prior to entering the absorber or desorber column and in which the added additional component(s) are removed downstream the absorber or respective desorber.

16. A process as claimed in any one of claims 11 to 15, in which the dielectric constant of the solvent is decreased by adding a component which has a dielectric constant lower than water.

17. A process as claimed in any one of claims 11 to 16, in which the dielectric constant of the solvent is increased by adding a component with a high dielectric constant.

18. An arrangement for the removal of acid gas in an acid gas removal process, which includes
   (a) an absorber;
   (b) a desorber; and
   (c) adjustment means adapted to adjust the dielectric constant of a solvent added to the process in order to enhance the performance of the system.

19. An arrangement as claimed in claim 18, in which the dielectric constant of the solvent is changed in the absorber, desorber and/or somewhere else in the process.

20. An arrangement as claimed in claim 18 or claim 19, in which the adjustment of the dielectric constant of the solvent influences the thermodynamic equilibrium of the process.

21. An arrangement as claimed in any one of claims 18 to 20, in which the dielectric constant of the solvent is adjusted by at least one of the steps selected from the group consisting of:
   (a) adding additional component(s) to the solvent prior to entering the absorber or desorber column;
   (b) applying an electric field to change the dielectric constant of the solvent; and
   (c) applying electromagnetic waves adapted to influence the dielectric constant of a solvent.

22. An arrangement as claimed in any one of claims 18 to 21, in which the dielectric constant of the solvent is adjusted by adding additional component(s) to the solvent prior to entering the absorber or desorber column and in which the added additional component(s) are removed downstream the absorber or respective desorber.

23. An arrangement as claimed in any one of claims 18 to 22, in which the dielectric constant of the solvent is decreased by adding a component which has a dielectric constant lower than water.

24. An arrangement as claimed in any one of claims 18 to 23, in which the dielectric constant of the solvent is increased by adding a component with a high dielectric constant.

25. A method for enhancing the performance of processes for the removal of acid gas substantially as hereinbefore described.
26. A process for the removal of acid gas substantially as hereinbefore described.

27. An arrangement for the removal of acid gas in an acid gas removal process substantially as hereinbefore described.