REACTION KINETICS OF CARBONYL SULFIDE IN AQUEOUS DIETHANOLAMINE

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Abstract: The primary objectives were measurement of kinetic rate data for the absorption of carbonyl sulfide(COS) in the secondary amine, diethanolamine(DEA), important for future modeling and design purposes. The reaction rate between COS and 5~25 wt% solutions of DEA at 25, 40, 60 and 75°C has been measured using a wetted sphere absorber. All the obtained rate measurements can be described by a zwitterion mechanism analogous to the mechanism widely accepted for the reaction between CO₂ and primary and secondary amines. It was found that the overall reaction rate was entirely determined by the zwitterion deprotonation rate.

Key Words: COS, diethanolamine, wetted sphere absorber, zwitterion mechanism

INTRODUCTION

The most common way of removing acid gas compounds, is by absorption in alkanolamines. The industrially most common amines for acid gas removal are the primary amine, monoethanolamine(MEA), the secondary amine, diethanolamine(DEA), and the tertiary amine, methyldiethanolamine(MDEA). Usually these alkanolamines are used in aqueous solutions, but other solvents like sulfinol in the Shell Sulfinol process are also used. Removal of acid gas impurities like H₂S, carbonyl sulfide(COS) are important processes in treatment of natural gas, synthesis gas and petrochemicals. Depending on where it is produced, natural gas contains varying amounts of CO₂, H₂S and COS. H₂S is the most common sulfur species in natural gas, but it is usually accompanied by COS and often other sulfur compounds like CS₂. These sulfur species are corrosive to pipelines and other processing equipment, and are also toxic.

The chemical and physical properties of CO₂ and H₂S in alkanolamines have been studied for years by a variety of researchers. However, very little attention has been paid to COS. Sharma¹ did a brief study of kinetics of COS absorption in various amines, but this data is limited to one temperature and concentration. Littel et al.² studied physical properties and chemical kinetics of COS in various amines, while Al-Ghawas et al.³ investigated absorption of COS in MDEA. COS reacts much slower with all alkanolamines than does CO₂, hence the efficiency of COS removal in H₂S selective absorption processes will be far too low.
The experimental study of the absorption of COS in DEA was performed in this work. The objectives were measurement of kinetic rate data for the absorption of COS in DEA, important for future modeling and design purposes.

THEORY

Reaction Mechanism

Sharma$^1$ studied the kinetics of COS absorption in primary and secondary amines. Due to the similarities in molecular structure, Sharma suggested that the reaction mechanism of COS and CO$_2$ are the same. Therefore, the proposed mechanism of COS in a secondary amine like DEA is

$$COS + 2R_2NH \rightleftharpoons k_2, k_{-1} \rightarrow R_2NH^+ COS^-$$  \hspace{1cm} (1)

$$R_2NH^+ COS^- + R_2NH \rightarrow k_{R_2NH} R_2NCOS^- + R_2NH_2^+$$  \hspace{1cm} (2)

The reactions between COS and the primary and secondary amines monoethanolamine, diisopropylamine, methylthiolactamine, 2-amino-2-methyl-1-propanol, morpholine, and diethanolamine were studied by Littel et al.$^9$ They found that the kinetics of COS reacting with all these amines could be described by the mechanism in Equations (1) and (2). The case of COS will be used for further description of the zwitterion mechanism.

Danckwerts$^3$ proposed that the zwitterion is in pseudo-steady state, which means that the concentration of the intermediate is small and does not change during the course of the reaction. Therefore, the net reaction rate of the zwitterion is zero:

$$r_z = 0 = k_2[COS][R_2NH] - k_{-1}[R_2NH^+ COS^-] - k_{R_2NH}[R_2NH^+ COS^-][R_2NH]$$  \hspace{1cm} (3)

The reaction rate for the consumption of COS according to Equation (3) is:

$$r_{COS} = k_2[COS][R_2NH] - k_{-1}[R_2NH^+ COS^-]$$  \hspace{1cm} (4)

Rearranging Equation (3) to give an expression for the concentration of the zwitterion, and substituting it in Equation (4) gives the following expression for the reaction rate of the gas according to the zwitterion mechanism:

$$r_{COS} = \frac{k_2[COS][R_2NH]}{1 + \frac{1}{k_{R_2NH}}[R_2NH]}$$  \hspace{1cm} (5)

$$= k_{app}[COS][R_2NH]$$

If the reaction can be considered to be pseudo-first order, the relation between the apparent rate constants of first and second order is:

$$k_{app} = k_{app}[R_2NH]$$  \hspace{1cm} (6)

Hence the expression for the pseudo-first order apparent rate constant according to the zwitterion mechanism is written:

$$k_{app} = \frac{k_2[R_2NH]}{1 + \frac{1}{k_{R_2NH}}[R_2NH]}$$  \hspace{1cm} (7)

Reaction Rate Constant

Physical absorption in a liquid laminar film flowing over a sphere was studied by Davidson and Cullen.$^6$ They assumed a semi-infinite film model, and developed an approximate solution for small depths of penetration. In the case of a chemical reaction, the penetration depth is less due to the consumption of the gas species by the reaction. Hence, the same assumptions can be applied here.

The time of exposure for a element of liquid flowing over a wetted sphere is given by:

$$t = \int_0^l \frac{x}{u} d\theta$$  \hspace{1cm} (8)

where
\[ u = \frac{3L (\sin \theta)}{4\pi \nu \delta_t} \frac{1}{1/3} \]  
\[ \delta_t = \left[ \frac{3\nu L}{2\pi \nu g} \right]^{1/3} \]  
Equation (9)  
Equation (10)  

Numerical integration gives
\[ \int_0^\pi \left( \sin \pi \right)^{1/3} = 2.58 \]  
Equation (11)  

Substituting Equations (11), (10) and (9) into Equation (8) gives the following expression for the residence time of liquid flowing over a sphere:
\[ t = 4\pi \nu \left( \frac{2.58}{3} \right) \left( \frac{3\nu}{2\pi \nu g} \right)^{1/3} L^{-2/3} \]  
Equation (12)  

Wild and Potter solved numerically the continuity equation for absorption accompanied by an irreversible pseudo-first order chemical reaction in the liquid phase. The solution was approximated to analytical expressions by dividing the curve in sections. The pseudo-first order rate constant \( k_1 \) for absorption in a wetted sphere apparatus can be calculated using the appropriate of the following equations:

For \( X<1.0 \), \( Y = 1.6393 + 0.455X \)  
Equation (13)  

For \( 1.0<X<5.0 \), \( Y = 1.428X^{1/2} + 0.698X^{-1/2} \)  
Equation (14)  

For \( 5.0<X<25.0 \), \( Y = 1.428X^{1/2} + 0.54X^{-1/2} \)  
Equation (15)  

For \( X>25.0 \), \( Y = 1.428X^{1/2} \)  
Equation (16)  

where
\[ X = k_1 t \]  
Equation (17)  
\[ Y = \frac{R_A}{L C_A \Psi^{1/2}} \]  
Equation (18)  
\[ \Psi = \frac{2.24\pi \nu D_A}{L \delta_t} \]  
Equation (19)  
\[ C_A^* = \frac{P_A}{H_A} \]  
Equation (20)  

The error in the above expressions is reported by Wild and Potter to be less than 1% if the value of \( \Psi \) is lower than 0.05, and less than 5% for \( \Psi < 0.2 \).

The method given by Wild and Potter is only valid if the reaction can be treated as of pseudo-first order. Ashour and Sandall performed a theoretical study of the absorption of a gas into a liquid in laminar flow over a sphere with a second-order chemical reaction between the gas and a reagent in the liquid solution. If the reaction is of the form
\[ A_{(aq)} + nB_{(aq)} \xrightarrow{k_2} \text{products} \]  
Equation (21)  

and if the rate of reaction is described by \( R_A = -k_2 C_A C_B \), Ashour and Sandall give the following inequality to test if the reaction can be considered as pseudo-first order:
\[ 2.37 \sqrt{\alpha} \leq \left( \frac{1}{D} + \frac{\sqrt{D}}{\beta} \right) \]  
Equation (22)  

where
\[ D = \frac{D_B}{D_A} \]  
Equation (23)  
\[ \alpha = k_2 C_B \left( \frac{4\pi^2 \nu^2}{L^2 g} \right)^{1/3} \]  
Equation (24)  
\[ \beta = \frac{nP_A}{H_A C_B} \]  
Equation (25)  

**EXPERIMENTAL**

The wetted sphere absorber used in this work is the same as previously described by Al-Ghawas et al. The absorption chamber consists of a 31 cm long, 7.6 cm inner diameter glass cylinder, and is enclosed by a temperature control jacket consisting of a 31 cm long, 16.5 cm inner diameter glass cylinder. Both cylinders are kept together by two stainless steel flanges, and the ends are sealed with GoreTect sealant. The sphere itself is made of a 3.76 cm diameter ball, and is mounted on a 0.4 cm diameter rod of the same material. The rod hangs from the top of the
chamber, attached to a liquid distributor with eight holes. The liquid enters through the distributor, and after flowing over the sphere, it passes down a short length of the rod before entering a 0.9 cm diameter, 10 cm long glass receiver tube which is fitted into a funnel shaped teflon base. The base is tightly fitted to the lower part of the absorption chamber, and has two holes in the bottom. One hole is for the entering gas feed, the other is connected to a suction flask, and is used for draining liquid flowing over the receiver tube during start-up of the experiment.

The water jacket surrounding the absorption chamber is connected to a circulating constant temperature water bath, and both the liquid and the gas feed passes through coils inside the jacket. The temperature inside the reaction chamber is measured using an electronic thermocouple, and the temperature inside the absorption chamber was maintained within $\pm 0.3^\circ C$ of the desired temperature. The setup used for diffusion experiments with $N_2O$ and COS is shown in Figure 1. The COS and $N_2O$ gas is supplied from pressurized gas cylinders. The gas flows from the cylinder through a water saturation bottle before entering the cell through a coil immersed in the water jacket. Connected to the top of the reaction chamber is the soap bubble meter, which leads to a 1.2 cm diameter, 12 m long PVC coil.

All experiments were carried out at atmo-
spheric pressure. De-ionized water was used for all experiments. The nitrous oxide was delivered from Puritan-Bennet and was of 99.99% purity. COS was delivered from Aldrich Chemicals, and had a minimum purity of 96%.

**RESULTS AND DISCUSSION**

**COS Kinetics**

The program solves the equations which describe the diffusion-reaction processes for the second order reaction, as presented by Ashour and Sandall. The differential equations are transformed to ordinary differential equations by the method of lines, and are solved using implicit backward differential formulas. Shown in Table 1 are the rate constants calculated from the equations of Wild and Potter, compared to those performed by Ashour and Sandall. Both methods of calculations use the same experimental data.

Table 1. Rate constants for COS in aqueous DEA solutions

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>DEA (wt%)</th>
<th>$C_{DEA}$ (mol/L)</th>
<th>$k_{app}$ (s$^{-1}$)</th>
<th>$k_{app}$ (L/mol·s)</th>
<th>$k_{app}$ (L/mol·s)</th>
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<tr>
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<td>3.56</td>
<td>7.49</td>
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<tr>
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<td>2.383</td>
<td>2302</td>
<td>966.2</td>
<td>1023.5</td>
<td></td>
</tr>
</tbody>
</table>

* calculated using the analytical method by Wild and Potter, ** calculated by Ashour and Sandall
Figures 2, 3, 4 and 5 present the obtained rate constants as a functions of DEA concentration, and compare the results from this work with the values of Sharma\(^1\) and Littel et al.\(^4\) The values obtained for 60°C agree well with the values of Littel et al. Littel's rate constants for 30°C are lower than the ones for 25°C from this work, but Littel's data look more scattered. It shall be noted, however, that Littel did not report the numerical values, and his data presented here are read off a double logarithmic graph, giving some inaccuracy.

The kinetic experiments in this study suggest that the reaction between COS and aqueous solutions of DEA can be described by the zwitterion mechanism as given in Equations (1) and (2). Equation (7) can be rewritten as:

\[
\frac{1}{k_\text{obs}} = \frac{1}{k_2} \cdot \frac{1}{[R_2NH]} + \frac{k_{-1} k_{R,NH}}{k_2 [R_2NH]^2}
\]  

(26)

The obtained rate data for COS have been fitted to Equation (26) using a linear least squares method. It was found that \(1/k_2\) was so close to zero that \(k_2\) could not be determined. This probably signifies that the formation of the zwitterion is so fast that it has no effect on the overall reaction rate. Hence, the rate of reaction is entirely determined by the zwitterion deprotonation rate, which also was found by Littel et al.\(^6\) The values for \(k_2 k_{R,NH} / k_{-1}\) are given in Table 2 and presented as an Arrhenius plot in Figure 6.

![Figure 2](image1.png)  
**Figure 2.** Apparent second order rate constants for COS absorption in aqueous DEA solutions at 25°C.

![Figure 4](image2.png)  
**Figure 4.** Apparent second order rate constants for COS absorption in aqueous DEA solutions at 60°C.

![Figure 3](image3.png)  
**Figure 3.** Apparent second order rate constants for COS absorption in aqueous DEA solutions at 40°C.

![Figure 5](image4.png)  
**Figure 5.** Apparent second order rate constants for COS absorption in aqueous DEA solutions at 75°C.
Table 2. Zwitterion deprotonation constants

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \frac{k_{2k} k_{2NH}}{k_{-1}} \times 10^5 (\text{m}^6 \text{mol}^{-6} \text{mol}^2 \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.21</td>
</tr>
<tr>
<td>25</td>
<td>1.57</td>
</tr>
<tr>
<td>30</td>
<td>0.68</td>
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<td>40</td>
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</tr>
<tr>
<td>60</td>
<td>4.3</td>
</tr>
<tr>
<td>75</td>
<td>38.43</td>
</tr>
<tr>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Littel et al. (1992)</td>
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</tbody>
</table>

Figure 6. Zwitterion deprotonation constants in the reaction of COS with DEA.

CONCLUSION

The experimental study of the absorption of carbonyl sulfide in the secondary amine, diethanolamine was performed in this work. The reaction rate between carbonyl sulfide and 5–25 wt% solutions of diethanolamine at 25, 40, 60 and 75 °C has been measured using a wetted sphere absorber. All the obtained rate measurements can be described by a zwitterion mechanism analogy to the mechanism widely accepted for the reaction between CO₂ and primary and secondary amines. It was found that the overall reaction rate was entirely determined by the zwitterion deprotonation rate. The results are in good agreement with previously presented literature data.

NOMENCLATURES

\( H_A \)  
Henry’s law constant of gas, atm · L/mol

\( C_A \)  
concentration of gas A, mol/L

\( C_A^o \)  
concentration of gas A at gas-liquid interface, mol/L

\( C_B^o \)  
bulk concentration of B, mol/L

\( D_A \)  
diffusivity coefficient of gas A, cm²/s

\( D_B \)  
diffusion coefficient of liquid B in solution, cm²/s

\( D \)  
ratio between liquid and gas diffusivity

\( g \)  
acceleration of gravity, 981 cm/s²

\( k_{1app} \)  
apparent first order rate constant, 1/s

\( k_{2app} \)  
apparent second order rate constant, L/mol·s

\( k_j \)  
forward rate constant, 1/s for first order reactions, L/mol·s for second order reactions

\( k_{rj} \)  
reverse rate constant, 1/s for first order reactions, L/mol·s for second order reactions

\( L \)  
volumetric liquid flowrate, cm³/s

\( n \)  
stoichiometric coefficient

\( P_A \)  
partial pressure of gas A, atm

\( R_A \)  
rate of absorption of gas A, mol/s

\( r_{cos} \)  
rate of reaction per unit volume, mol/L·s

\( r_s \)  
radius of sphere, cm

\( r_z \)  
reaction rate, mol/L·s

\( T \)  
temperature, K

\( t \)  
time, s

\( u \)  
velocity in \( \theta \) -direction over a wetted sphere, cm/s

\( X \)  
parameter defined in equation (17)

\( Y \)  
parameter defined in equation (18)

\( \alpha \)  
dimensionless parameter defined in equation (24)

\( \beta \)  
dimensionless parameter defined in equation (25)

\( \nu \)  
kinematic viscosity, cm²/s

\( \psi \)  
dimensionless parameter defined in equation (19)

\( \delta_1 \)  
film thickness over equator of wetted sphere, cm

\( [\text{COS}] \)  
concentration of carbonyl sulfide,
mol/L
[R₂NH] concentration of secondary amine, mol/L

REFERENCES


