Absorption of Carbonyl Sulfide in Aqueous Monoethanolamine

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1. INTRODUCTION

The most common means of removal of acid gas compounds such as H\textsubscript{2}S, CO\textsubscript{2}, and COS in waste gas is absorption using aqueous solutions of various alkanolamines. Some typical alkanolamines used are the primary amine, monoethanolamine (MEA), the secondary amine, diethanolamine (DEA), and the tertiary amine, methyldiethanolamine (MDEA). Sharma measured the chemical kinetics for the liquid phase reaction between CO\textsubscript{2} and COS with several primary and secondary amines and found that the reactions with COS are approximately 100 times slower than for CO\textsubscript{2}.

In order to properly design and develop an acid gas treating system, it is necessary to know the kinetics of the reaction and the key physicochemical properties which include the gas solubility and diffusivity in the aqueous amine solution. The purpose of the research described here was to measure the chemical kinetics of the reaction between COS and MEA in aqueous solution and to determine the physical solubility and diffusion coefficient for COS in aqueous MEA over a range in temperature and concentration. The nitrous oxide analogy method was used to determine COS solubility and diffusivity in the aqueous MEA solutions. This method, originally proposed by Clark to estimate properties for CO\textsubscript{2} in aqueous amine solutions, was shown by Al-Ghawas et al. and Littel et al. to be also valid for COS.

The density and viscosity of aqueous MEA solutions were also measured in this work since these properties were needed to interpret the absorption data. These are useful physical properties for the design of industrial absorbers.

2. REACTION MECHANISM

Sharma studied the kinetics of COS in primary and secondary amines at 298 K and proposed a reaction mechanism involving the formation of an intermediate zwitterion. The zwitterion mechanism for the reaction of COS with the primary amine is given by:

\[
\text{COS} + \text{RNH}_2 \rightleftharpoons k_1 \text{RNH}_2^+\text{COS}^- \]
\[ RNH_2^+COS^- + RNH_2 \xrightarrow{k} RNHCOS^- + RNH_3^+ \]

Littel et al. also found that the reaction between COS and primary or secondary amines could be described by the above zwitterion mechanism. The rate of consumption of COS per unit volume can be derived as

\[ r_{\text{COS}} = \frac{k_a[COS][RNH_2]}{1 + \left( \frac{k_b}{k_{-a}} \right)[RNH_2]} \]

3. EXPERIMENTAL

MEA was supplied by Fisher Scientific with a minimum purity of 99% and was used without further purification. The aqueous MEA solutions were prepared by weight with deionized water. The nitrous oxide was medical grade with a stated purity of 99.99%. Carbonyl sulfide was obtained from Aldrich Chemical Company with a minimum purity of 96%.

The densities of aqueous MEA solutions were measured over the concentration range 10–40 wt% and over the temperature range 298 to 348 K. The density measurements were performed by using a 25-ml Gay–Lussac pycnometer which was submerged in a thermostated water bath. Viscosity measurements were made using a Cannon–Fenske type viscometer (B58, size 100) for 10–40 wt% MEA solutions over the temperature range 298 to 348 K. In this work, we used a modified Zipperclave Reactor to measure the solubility of \( \text{N}_2\text{O} \) in aqueous MEA solutions. The apparatus and experimental procedure are described in detail by Rinker and Sandall. The diffusivity experiments were carried out in a wetted–sphere absorber. The experimental setup and procedure is described by Tamimi et al. The chemical kinetics of the aqueous reaction between COS and MEA were measured over the MEA concentration range 5–20 wt% and over the temperature range 298–348 K. Absorption data were also obtained using the wetted–sphere absorber. The experimental procedure is described by Rinker et al.

4. RESULTS AND DISCUSSION

4.1. Solubility of \( \text{N}_2\text{O} \) in aqueous MEA

A key property needed in the evaluation of the chemical kinetics is the physical solubility of COS in aqueous amine solution. As explained in the introduction we used the \( \text{N}_2\text{O} \) analogy method to estimate the COS solubility according to
\[
\left( \frac{H_{\text{COS}}}{H_{\text{SE}_{i}} } \right)_{\text{MEA}} = \left( \frac{H_{\text{COS}}}{H_{\text{SE}_{i}} } \right)_{H_{2}O}
\]

where \( H_{i} \) is the Henry constant in Henry’s law for the physical solubility:

\[
p_{i} = H_{i} x_{i} = H_{i} C_{i}
\]

4.2. Chemical kinetics of the COS/MEA reaction

Absorption data were interpreted using the theoretical results of Ashour and Sandall for absorption into a liquid flowing over a sphere with a second-order reversible chemical reaction. The apparent second order rate constant, \( k_{2,\text{app}} \), as determined from the COS absorption rates is related to the kinetic rate constants of the zwitterion mechanism

\[
k_{2,\text{app}} = \frac{1}{\frac{1}{k_{a}} + \frac{1}{k_{a}} \left( \frac{k_{b} k_{\text{SE}_{i}}}{k_{-a}} \right) \text{[MEA]} }
\]

The kinetics for the reaction between COS and aqueous MEA is thus expressed by data may be represented by a straight line through the origin. This indicates that the term, plots as a function of MEA concentration for the temperature 298, 313, 333 and 348 K. It is seen in these plots that the shows the

\[
r_{\text{COS}} = k_{3} \text{[COS]} \text{[MEA]}^2
\]

where the third-order rate constant is given by

\[
k_{3} = \frac{k_{a} k_{b}}{k_{-a}}
\]

5. CONCLUSIONS

We have measured and correlated the key physicochemical properties needed for the design of absorbers using MEA to remove COS. The kinetics data obtained in this study can be interpreted according to the zwitterion mechanism with the rate limiting step being the deprotonation of the zwitterion. Data were obtained over the temperature range 298 to 348 K. This temperature range should essentially cover most absorber conditions.
REFERENCES

Figure 5. Apparent second-order rate constant for COS/MEA reaction as function of temperature.