

## Kinetic Study on Absorption of Carbonyl Sulfide in Aqueous Monoethanolamine

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The kinetics of the reaction between carbonyl sulfide and aqueous monoethanolamine were studied over a range of temperature (298-348 K) and amine concentrations using a wetted-sphere absorber. The key physicochemical properties used to interpret the data included the solubility and diffusivity of the COS in the aqueous amine solution. The experimental data were interpreted using a zwitterion mechanism, which produced an Arrhenius plot with third-order kinetic rate constants. The fit of these data was

$$k_3 = 1.32 \times 10^{10} \exp\left(\frac{-6136}{T}\right)$$

Key words : Carbonyl sulfide, Monoethanolamine, Zwitterion mechanism, Chemical kinetics

### 1. Introduction

The removal of acid gas impurities like H<sub>2</sub>S and COS are important processes in the treatment of natural gas, synthesis gas, and petrochemicals. Depending on where it is produced, natural gas contains varying amounts of CO<sub>2</sub>, H<sub>2</sub>S, and COS. H<sub>2</sub>S is the most common sulfur species in natural gas, however, it is usually accompanied by COS and other sulfur compounds like CS<sub>2</sub>. These sulfur species are corrosive to pipelines and other processing equipment, plus toxic. Therefore, there are usually stringent pipeline specifications regulating the concentrations of these sulfur species, for example, a content below 4 ppm is often required.

The most common way of removing acid gas compounds, is by absorption in alkanolamines. In industry, the amines most commonly used for acid gas removal include the primary amine monoethanolamine(MEA), the secondary amine diethanolamine(DEA), and the tertiary amine methyldiethanolamine(MDEA).

Even though the chemical and physical properties of CO<sub>2</sub> and H<sub>2</sub>S in alkanolamines have been

studied for years by various researchers, very little attention has been paid to COS and CS<sub>2</sub>. Sharma<sup>1)</sup> conducted a brief study on the kinetics of COS absorption in various amines, however, this data is limited to one temperature and concentration. Littel et al<sup>2)</sup> also studied the physical properties and chemical kinetics of COS in various amines, while Al-Ghawas<sup>3)</sup> investigated the absorption of COS in MDEA.

A lot of effort has been focused on identifying a process that can selectively absorb sulfur compounds excluding CO<sub>2</sub>, as the removal of CO<sub>2</sub> is often disadvantageous from a technical or economic point of view. The reaction between H<sub>2</sub>S and alkanolamines is virtually instantaneous, whereas the reaction rate of CO<sub>2</sub> is finite. In primary and secondary amines, CO<sub>2</sub> reacts directly and forms carbamates. However, in tertiary amines, CO<sub>2</sub> does not react directly due to lack of vacant N-H bonds in the amine. Consequently, the reaction between tertiary amines and CO<sub>2</sub> is relatively slow. Moreover, the reaction of COS and CS<sub>2</sub> with all alkanolamines is much slower than that of CO<sub>2</sub>, hence the efficiency of COS and CS<sub>2</sub> removal in H<sub>2</sub>S selective absorption processes is always far

too low. Accordingly, the purpose of the current research was to measure the chemical kinetics of the reaction between COS and MEA in an aqueous solution and determine the physical solubility and diffusion coefficient for COS in aqueous MEA over a range of temperatures and concentrations. The nitrous oxide analogy method was used to determine the COS solubility and diffusivity in the aqueous MEA solutions.

## 2. Experimental

The apparatus and experimental procedure are described in detail by Rinker and Sandall<sup>4)</sup>. The chemical kinetics of the aqueous reaction between COS and MEA were measured over an MEA concentration range of 5-20 wt% and temperature range of 298-348 K. Absorption data were also obtained using a wetted-sphere absorber. A diagram of the apparatus is shown in Figure 1. A wetted-sphere reactor was selected to determine the kinetics because the residence time of the liquid is longer and the surface area is larger than in a laminar liquid jet apparatus. The experimental procedure is described by Rinker et al<sup>5)</sup>. The absorption chamber consisted of a 31cm-long, 7.6cm inner-diameter glass cylinder enclosed by a temperature control jacket consisting of a 31cm-long 16.5cm-inner-diameter glass cylinder. Both cylinders were kept together by two stainless steel flanges the ends of which were sealed with a GoreTex sealant. The sphere itself was made of a 3.76cm-diameter ball mounted on a 0.4cm-diameter rod of the same material. The rod hung from the top of the chamber and was attached to a liquid distributor with eight holes. The liquid entered through the distributor and, after flowing over the sphere, it passed down a short length of the rod before entering a 0.9 cm-diameter, 10cm-long glass receiver tube, which was fitted into a funnel-shaped teflon base. The base was tightly fitted to the lower part of the absorption chamber, and had two holes in the bottom. One hole was for feeding the gas, whereas the other was connected to a suction flask, which was used for draining any overflow liquid from the receiver tube during the start-up of the experiment.

The 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%. The carbonyl sulfide was obtained from the Aldrich Chemical Company with a minimum purity of 96%.

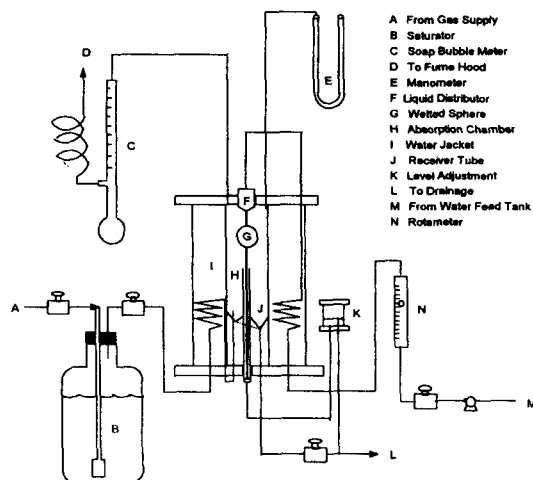
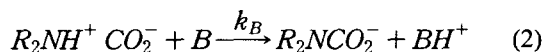
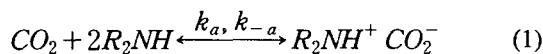


Fig. 1. Wetted-sphere apparatus.

## 3. Results and Discussion

### 3.1. Reaction mechanism

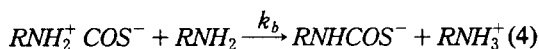
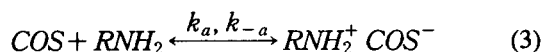
The reaction between  $\text{CO}_2$  and primary and secondary alkanolamines in aqueous solutions has been previously studied by many researchers. The earliest reports disagree over whether the reaction is of the first or second order. A mechanism first proposed by Caplow<sup>6)</sup> and reintroduced by Dankwerts<sup>7)</sup> has been used to explain the differences in the reaction order. The reaction involves the formation of an intermediate zwitterion and the subsequent removal of a proton by a base:



This deprotonation can be principally caused by any base in the system, depending on its strength and concentration. However, in aqueous solutions of a single amine, it has been shown by Rinker that the main contribution to the deprotonation of

a zwitterion comes from the amine itself, and the effect of  $H_2O$  and  $OH^-$  is usually negligible.

Sharma<sup>1)</sup> 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 a primary amine can thus be given by :



Littel et al<sup>2)</sup> also found that the reaction between COS and primary or secondary amines can be described by the above zwitterion mechanism. As such, the rate of consumption of COS per unit volume can be derived as

$$r_{COS} = \frac{k_a [COS][RNH_2]}{1 + \frac{1}{\left(\frac{k_b}{k_{-a}}\right)[RNH_2]}} \quad (5)$$

Equation (5) assumes that the zwitterion is a

reactive intermediate that rapidly establishes its steady-state composition.

### 3.2. Chemical kinetics of COS/MEA reaction

The chemical kinetics of the aqueous phase reaction between COS and MEA were measured over an MEA concentration range of 5-20 wt% and temperature range of 298-348K. The absorption data were interpreted using the theoretical results of Ashour and Sandall<sup>8)</sup> for absorption into a liquid flowing over a sphere with a second-order reversible chemical reaction. The apparent second-order rate constant,  $k_{2,app}$ , as determined from the COS absorption rates, is related to the kinetic rate constants of the zwitterion mechanism

$$k_{2,app} = \frac{1}{\frac{1}{k_a} + \frac{1}{\left(\frac{k_a k_b}{k_{-a}}\right)[MEA]}} \quad (6)$$

Table 1 gives the values of  $k_{2,app}$  and figure 2 shows the absorption rate relative to the aqueous MEA solutions. Figures 3, 4, 5, and 6 shows the

Table 1. COS/MEA Experimental Kinetic Data

Temp (K)	wt% MEA (%)	[MEA] (mol/l)	P <sub>COS</sub> (atm)	Liquid Rate (cm <sup>3</sup> /s)	R <sub>COS</sub> x 10 <sup>5</sup> (mol/s)	k <sub>2,app</sub> (l mol/s)
25	5	0.187	0.967	1.23	1.330	28.06
	10	1.638	0.969	1.22	1.627	24.92
	15	2.462	0.969	1.11	2.115	33.53
	20	3.293	0.966	1.40	2.822	54.00
40	5	0.814	0.926	0.58	1.335	43.13
	10	1.631	0.928	0.43	2.301	77.75
	15	2.451	0.931	0.80	3.089	96.01
	20	3.277	0.933	0.60	3.809	122.98
60	5	0.807	0.804	0.88	1.635	171.18
	10	1.615	0.808	1.66	2.336	180.97
	15	2.428	0.806	0.83	3.426	289.31
	20	3.261	0.815	0.95	4.495	396.54
75	5	0.800	0.624	1.07	1.449	383.35
	10	1.601	0.630	0.97	2.053	358.53
	15	2.405	0.639	0.35	4.044	845.21
	20	3.200	0.645	0.43	5.016	967.18

$k_{2,app}$  plots as a function of the MEA concentration for temperatures of 298, 313, 333, and 348 K. Since the plots show that the  $k_{2,app}$  data could be represented by a straight line through the origin, this indicated that the term,  $1/k_a$ , was small compared to the other term in the denominator of Equation (6) and the rate-limiting step was the deprotonation of the zwitterion, Equation (4). The kinetics for the reaction between COS and aqueous MEA can thus be expressed by

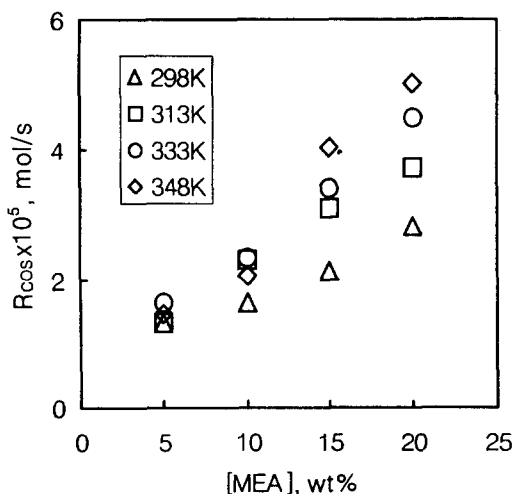


Fig. 2. Absorption rate of COS into MEA solutions at different temperatures.

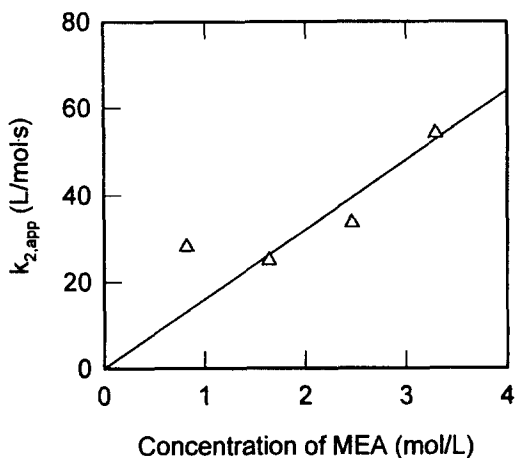


Fig. 3. Second-order rate constant for COS/MEA reaction at 298K.

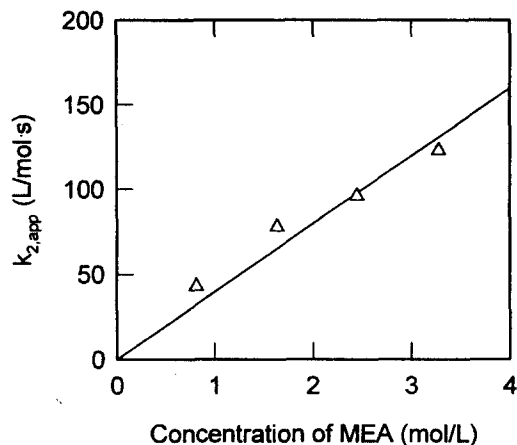


Fig. 4. Second-order rate constant for COS/MEA reaction at 333K.

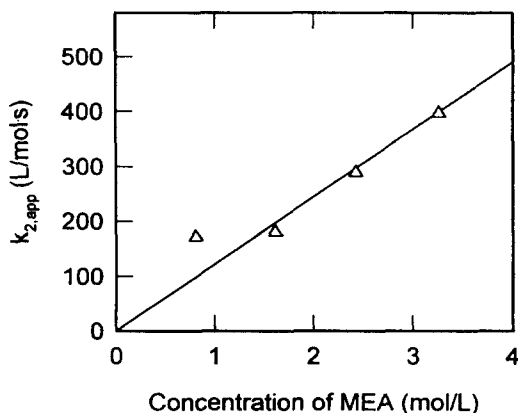


Fig. 5. Second-order rate constant for COS/MEA reaction at 313K.

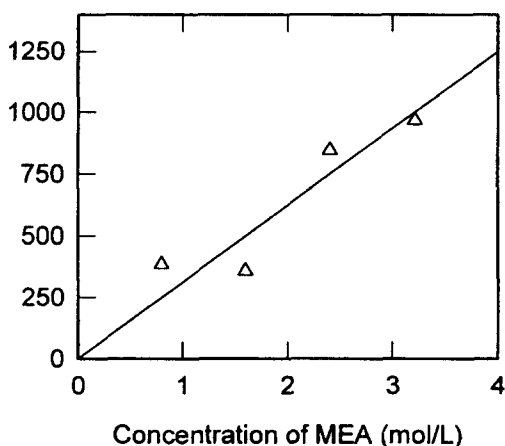


Fig. 6. Second-order rate constant for COS/MEA reaction at 348K.

$$r_{\text{COS}} = k_3 [\text{COS}] [\text{MEA}]^2 \quad (7)$$

where the third-order rate constant is given by

$$k_3 = \frac{k_a k_b}{k_{-a}} \quad (8)$$

Figure 7 shows an Arrhenius plot of the third-order kinetic rate constants. A fit of these data gives

$$k_3 = 1.32 \times 10^{10} \exp\left(\frac{-6136}{T}\right) \quad (9)$$

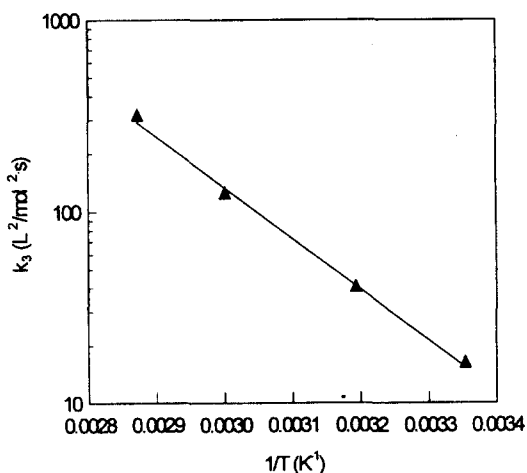


Fig. 7. Arrhenius plot of third-order rate constants for COS/MEA reaction.

Sharma<sup>1)</sup> presented kinetic data in the form of a pseudo first-order rate constant at 298 K and at a single MEA concentration of 1 mol/L and reported a value of 16 s<sup>-1</sup>. Equation (9) gave 15.1 s<sup>-1</sup> as the apparent pseudo-first order rate constant at [MEA]=1 mol/L and 298 K. As such, the kinetic data determined in the current study matched quite closely with the single measurement of Sharma. Little et al. reported on a pseudo-first order rate constant of 18.2 s<sup>-1</sup> for the COS/MEA reaction at a temperature of 303 K and [MEA]=1 mol/L. Equation (9) gave a pseudo first-order rate constant of 21.2 s<sup>-1</sup> for these conditions. This was also a fairly close agreement. However, Little et al.<sup>9)</sup> found that although the term representing the zwitterion formation, 1/k<sub>a</sub> in Equation (6), was small, it was not negligible for MEA. Therefore, when studying other primary and secondary amines, namely diethanolamine, diglycolamine and

diisopropanolamine, they found (in agreement with the current study for MEA) a third-order overall reaction rate, which was solely determined by the deprotonation of the zwitterion.

#### 4. Conclusions

The kinetic data obtained in this study can be interpreted using the zwitterion mechanism with the deprotonation of the zwitterion as the rate limiting step. Data were obtained over a temperature range of 298 to 348 K, which should essentially cover most absorber conditions. The kinetic data identified in this study were relatively close in agreement with the single measurements of other workers. Plus third-order kinetic rate constants were found for the reaction between carbonyl sulfide and aqueous monoethanolamine.

#### Nomenclature

[COS]	Concentration of carbonyl sulfide, mol/L
k <sub>2,app</sub>	Apparent second-order rate constant, L/mol s
k <sub>3</sub>	Third-order rate constant, L <sup>2</sup> /mol <sup>2</sup> s
k <sub>a</sub>	Rate constant for zwitterion formation, L/mol s
k <sub>-a</sub>	Rate constant for zwitterion reversion, s <sup>-1</sup>
k <sub>b</sub>	Rate constant for zwitterion deprotonation, L/mol s
[MEA]	Concentration of monoethanolamine, mol/L
r <sub>COS</sub>	Rate of reaction per unit volume, mol/L s
[RNH <sub>2</sub> ]	Concentration of primary amine, mol/L
T	Temperature, K

#### References

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