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Review

# Kinetics of carbonyl sulfide reaction with alkanolamines: A review

Prakash D. Vaidya [a], Eugeny Y. Kenig [b,*]

[a] *Department of Chemical Engineering, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India*
[b] *Faculty of Mechanical Engineering, Chair of Fluid Process Engineering, University of Paderborn, D-33098 Paderborn, Germany*

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ABSTRACT

Carbonyl sulfide represents an undesirable impurity in a variety of industrial gases and it has to be removed down to very low concentrations to meet the required specifications. This can be achieved by chemisorption with alkanolamines. In this article, the kinetics of the reaction of carbonyl sulfide with alkanolamines is reviewed. Different reaction mechanisms used to interpret experimental kinetic data, *viz.* zwitterion, termolecular and base-catalysed hydration are described in detail. The kinetic behaviour of several conventional, sterically hindered, cyclic amines and diamines proposed in the literature is analysed. Generally, the reaction of carbonyl sulfide with primary, secondary and sterically hindered amines is described by the zwitterion mechanism, whereas the reaction with tertiary amines is described by the base-catalysed hydration of carbonyl sulfide. The same reaction pathways are followed by carbon dioxide which is similar in structure to carbonyl sulfide. While the carbon dioxide reaction with alkanolamines has been comprehensively reviewed, e.g., in our recent paper (P.D. Vaidya, E.Y. Kenig, $CO_2$–alkanolamine reaction kinetics: a review on recent studies, Chem. Eng. Technol. 30 (2007) 1467), an overview on the kinetic behaviour of carbonyl sulfide is still missing. In this paper, an evaluation of the published results is given to close this gap.

## 1. Introduction

Various gaseous streams, either to be recycled to chemical processes, or discharged into the atmosphere or used as fuels, have to be cleaned of carbon dioxide ($CO_2$), hydrogen sulfide ($H_2S$) and carbonyl sulfide (COS). For instance, the removal of these acid gases from process gas streams in methane reforming and oil refining is essential, as they are detrimental to processes either by poisoning the catalyst or/and by causing equipment damage due to corrosion. Similarly, the capture of these compounds, down to very low concentrations, is of considerable importance in coal gasification, in the petrochemical industry, and in chemical fertilizer plants. $CO_2$ is a Greenhouse gas responsible for global warming, whereas the sulfur-containing gases $H_2S$ and COS are toxic. Therefore, their discharge limits in the refinery off-gas are becoming increasingly stringent. Furthermore, $CO_2$, $H_2S$ and COS must be removed from natural gas before it is directed to transmission lines, as $CO_2$ reduces the heating value of the gas whereas $H_2S$ and COS are corrosive to pipelines. Reactive absorption is the preferred technology used in the gas processing industry for acid gas removal, where aqueous solutions of alkanolamines, mainly monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) promoted with piperazine (PZ) represent the most popular absorbents [2].

The selective absorption of sulfur compounds from gaseous streams containing large amounts of $CO_2$ has received considerable attention by both academia and industry. $H_2S$ reacts extremely fast with amines (primary, secondary and tertiary) in aqueous solutions and hence the reaction rates are considered to be infinitely fast as compared to those of mass transfer (instantaneous reactions) [3]. On the other hand, COS and $CO_2$ react with alkanolamines much slower. Sharma [4] investigated the kinetics of the reactions of COS and $CO_2$ with several primary and secondary amines and found that the reactions with COS are approximately 100 times slower than those with $CO_2$. The $CO_2$ reactions with amines have been extensively studied and there are several comprehensive reviews on the kinetic behaviour of such systems available [1,5–7].

A detailed knowledge on the reaction kinetics with COS is essential to meet the desired sulfur specifications. This work provides an overview on the COS reactions with conventional, sterically hindered and cyclic amines. The reaction mechanisms used to interpret kinetics – zwitterion, termolecular and base-catalysed

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*Abbreviations:* AEEA, 2-((2-aminoethyl)amino)ethanol; AMP, 2-amino-2-methyl-1-propanol; AMPD, 2-amino-2-methyl-1,3-propanediol; BHEEU, *N,N'*bis (hydroxyethoxyethyl) urea; DEA, diethanolamine; DEMEA, diethylmonoethanolamine; DGA, diglycolamine; DIPA, diisopropanolamine; DMMEA, dimethylmonoethanolamine; MDEA, methyldiethanolamine; MEA, monoethanolamine; MMEA, methylmonoethanolamine; MOR, morpholine; TEA, triethanolamine; PZ, piperazine.

* Corresponding author. Tel.: +49 5251 60 2408; fax: +49 5251 60 3207.
*E-mail address:* eugeny.kenig@upb.de (E.Y. Kenig).

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### Nomenclature

| | |
|---|---|
| AmH | alkanolamine |
| (AmH) | concentration of alkanolamine (kmol/$m^3$) |
| B | base |
| (B) | concentration of base B (kmol/$m^3$) |
| (COS) | concentration of COS (kmol/$m^3$) |
| (DEA) | concentration of DEA (kmol/$m^3$) |
| ($H_2O$) | concentration of $H_2O$ (kmol/$m^3$) |
| $k_1$ | forward reaction rate constant in Eq. (1) ($m^3$/(kmol s)) |
| $k_{-1}$ | backward reaction rate constant in Eq. (1) ($s^{-1}$) |
| $k_3$ | third-order rate constant |
| $k_{AmH}$ | rate constant in Eq. (6) |
| $k_B$ | rate constant in Eq. (2) ($m^3$/(kmol s)) |
| $k_{H_2O}$ | rate constant in Eq. (6) |
| $k_{obs}$ | observed reaction rate constant ($s^{-1}$) |
| (MEA) | concentration of MEA (kmol/$m^3$) |
| $r$ | rate of reaction (kmol/($m^3$ s)) |
| $R_3N$ | tertiary alkanolamine |
| $T$ | temperature (K) |

hydration – are described in detail. The published data on reaction kinetics of several specific amine systems is considered.

## 2. Reaction mechanism

The COS reactions with primary and secondary amines (denoted here as AmH) are analogous to those of $CO_2$ and can be represented by the zwitterion mechanism [4]:

$$\mathrm{COS} + \mathrm{AmH} \overset{k_1, k_{-1}}{\longleftrightarrow} \mathrm{AmH^+COS^-} \tag{1}$$

$$\mathrm{AmH^+COS^-} + B \xrightarrow{k_B} \mathrm{AmCOS^-} + \mathrm{BH^+} \tag{2}$$

Eq. (1) represents the formation of the intermediate zwitterion whereas Eq. (2) describes the zwitterion deprotonation reaction. Any base (or bases) B present in solution deprotonates the zwitterion, which results in thiocarbamate formation. Some subsequent works are in agreement with this mechanism [8–11]. Assuming that the zwitterion is a reactive intermediate whose concentration is small and quickly reaches a steady state value, the rate of reaction of COS is given by

$$r = \frac{k_1(\mathrm{COS})(\mathrm{AmH})}{1 + k_{-1}/k_B(B)} \tag{3}$$

or

$$r = k_{obs}(\mathrm{COS}) \tag{4}$$

where $k_B(B)$ represents deprotonation of zwitterion by any base, such as $H_2O$, $OH^-$ or AmH, as well as by a combination of them. The observed pseudo first-order rate constant ($k_{obs}$) is related to the kinetic rate constants of the zwitterion mechanism as follows:

$$k_{obs} = \left[\frac{k_1(\mathrm{AmH})}{1 + k_{-1}/k_B(B)}\right] \tag{5}$$

When the contribution of $OH^-$ to zwitterion deprotonation is negligible due to its low concentration, $k_{obs}$ is given by

$$k_{obs} = \left[\frac{k_1(\mathrm{AmH})}{1 + k_{-1}/(k_{AmH}(\mathrm{AmH}) + k_{H_2O}(\mathrm{H_2O}))}\right] \tag{6}$$

When deprotonation is almost instantaneous as compared to the reverse reaction in Eq. (1) ($k_{-1} \ll k_B(B)$) and zwitterion formation is rate-determining, Eq. (3) takes the form:

$$r = k_1(\mathrm{COS})(\mathrm{AmH}) \tag{7}$$

thereby suggesting that the reaction is of the first order with respect to both COS and amine. When zwitterion deprotonation is rate-determining ($k_{-1} \gg k_B(B)$), Eq. (3) takes the form

$$r = \frac{k_1 k_B(B)}{k_{-1}}(\mathrm{COS})(\mathrm{AmH}) \tag{8}$$

Eq. (8) suggests a fractional reaction order between one and two with respect to amine concentration. The overall reaction is of the second order with respect to amine if other bases such as $H_2O$ and $OH^-$ do not contribute to zwitterion deprotonation, whereas the contribution of amine is significant. If the terms $k_{-1}$ and $k_B(B)$ in Eq. (3) are comparable, reaction order with respect to amine is between one and two.

If the base B in the reaction described by Eq. (2) is the amine itself, the thiocarbamate formation can be represented as follows:

$$\mathrm{AmH^+COS^-} + \mathrm{AmH} \rightarrow \mathrm{AmCOS^-} + \mathrm{AmH_2}^+ \tag{9}$$

In this case, the overall reaction, which accounts for thiocarbamate formation in a solution, is given by the sum of reactions expressed by Eqs. (1) and (9):

$$\mathrm{COS} + 2\mathrm{AmH} \leftrightarrow \mathrm{AmCOS^-} + \mathrm{AmH_2}^+ \tag{10}$$

If zwitterion reacts more easily with water than with AmH, the following reaction takes place:

$$\mathrm{AmHCOS^-} + \mathrm{H_2O} \rightarrow \mathrm{AmH_2}^+ + \mathrm{HCO_2S^-} \tag{11}$$

In this case, the overall reaction is given by the sum of reactions represented by Eqs. (1) and (11):

$$\mathrm{COS} + \mathrm{AmH} + \mathrm{H_2O} \leftrightarrow \mathrm{HCO_2S^-} + \mathrm{AmH_2}^+ \tag{12}$$

The following reactions may also take place simultaneously in an aqueous amine solution:

$$\mathrm{AmH} + \mathrm{H_2O} \leftrightarrow \mathrm{AmH_2}^+ + \mathrm{OH^-} \quad \text{(instantaneous)} \tag{13}$$

$$\mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{OH^-} \tag{14}$$

$$\mathrm{COS} + 4\mathrm{OH^-} \leftrightarrow \mathrm{CO_3}^{2-} + \mathrm{S}^{2-} + 2\mathrm{H_2O} \tag{15}$$

The hydrolysis of COS is represented by

$$\mathrm{COS} + \mathrm{H_2O} \overset{k_{H_2O}}{\longleftrightarrow} \mathrm{CO_2} + \mathrm{H_2S} \tag{16}$$

The reaction given by Eq. (16) is very slow compared to other COS reactions in an aqueous solution [12,13].

The termolecular mechanism, originally proposed by Crooks and Donnellan [14] for the reactions of $CO_2$ with aqueous amines, can also be adopted for thiocarbamate formation [15]. This mechanism assumes that an amine reacts simultaneously with one molecule of COS and one molecule of a base. The reaction proceeds in a single step via a loosely bound encounter complex as the intermediate. This can be represented as

$$\mathrm{COS} + \mathrm{AmH} \cdots \mathrm{B} \leftrightarrow \mathrm{AmCOS^-} \cdots \mathrm{BH^+} \tag{17}$$

This complex breaks up to form reactant molecules, while its small fraction reacts with a second molecule of the amine or a water molecule to give ionic products. The value of $k_{obs}$ is given by

$$k_{obs} = [k_{H_2O}(\mathrm{H_2O}) + k_{AmH}(\mathrm{AmH})](\mathrm{AmH}) \tag{18}$$

Eq. (18), whose form is similar to that of the limiting case of the zwitterion mechanism represented by Eq. (8), can explain fractional and higher-order kinetics in primary and secondary alkanolamines.

The base-catalysed hydration mechanism is used to describe the kinetics of the reaction of COS with tertiary amines [16]. This mechanism suggests that tertiary amines have a base-catalytic effect on the hydration of COS. This can be represented as follows (here tertiary amines are denoted as $R_3N$):

$$R_3N + H_2O + COS \leftrightarrow R_3N^+H + HCO_2S^- \tag{19}$$

Eq. (19) is similar to the mechanism earlier proposed by Donaldson and Nguyen [17] for the reaction between $CO_2$ and tertiary amines. Besides, as observed by Littel et al. [18], the following reaction may also occur:

$$HCO_2S^- + R_3N + H_2O \leftrightarrow R_3N^+H + HCO_3{}^- + HS^- \tag{20}$$

Eqs. (19) and (20) are the base-catalysed analogues of the reaction mechanism for COS hydrolysis, earlier proposed by Philipp and Dautzenberg [19]:

$$COS + OH^- \leftrightarrow HCO_2S^- \tag{21}$$

$$HCO_2S^- + H_2O \rightarrow HCO_3{}^- + H_2S \tag{22}$$

## 3. Reaction kinetics

In this section, the published data on kinetics of the reactions of COS with aqueous solutions containing amines is discussed. The experimental kinetic parameters are analysed in terms of the mechanisms described in the previous section.

MEA has high effectiveness for COS removal [20]. However, MEA reacts irreversibly with COS to form degradation products [2]. A comprehensive study of the COS reaction with MEA was reported in [21]. Littel et al. [11] studied the kinetics of COS removal by MEA and used the zwitterion mechanism to describe reaction kinetics. The reaction order with respect to MEA was found to be between one and two. The overall reaction rate was not entirely determined by the deprotonation reaction, whereas the contribution of water as well as MEA to zwitterion deprotonation was significant. The dependence of the deprotonation rate constants of MEA and $H_2O$ on temperature ($283 < T < 333$ K) was given by

$$k_{MEA} = 1.31 \times 10^{-2} \exp\left(-\frac{1771}{T}\right) \tag{23}$$

$$k_{H_2O} = 1.35 \times 10^{5} \exp\left(-\frac{8320}{T}\right) \tag{24}$$

Lee et al. [22] more recently studied the kinetics of the COS–MEA system. The overall reaction was found to be of first order with respect to COS concentration and second order with respect to MEA concentration, thereby suggesting that zwitterion deprotonation is the rate-limiting step and the contribution of $H_2O$ and $OH^-$ to deprotonation is insignificant. The reaction rate for this mechanism was represented by

$$r = k_3(COS)(MEA)^2 \tag{25}$$

where the third-order rate constant $k_3$ is given by

$$k_3 = \frac{k_1 k_B}{k_{-1}} \tag{26}$$

The dependence of $k_3$ on temperature ($298 < T < 348$ K) was given by

$$k_3 = 1.32 \times 10^{10} \exp\left(-\frac{6136}{T}\right) \tag{27}$$

The pseudo first-order rate constant ($16\,s^{-1}$), reported by Sharma [4] at a MEA concentration of 1 kmol/$m^3$ and at 298 K, is in agreement with the value of $15.1\,s^{-1}$ reported by Lee et al. [22]. The above-mentioned main characteristics of the kinetic studies on the COS–MEA system are listed in Table 1. It is worthy of note that the reaction order with respect to MEA varies depending on whether zwitterion formation or deprotonation is rate-determining.

**Table 1**
Kinetic studies of the reaction system COS–aqueous MEA

| Temperature (K) | MEA (kmol/$m^3$) | Order with respect to MEA | Pseudo first-order rate constant ($s^{-1}$) | Reference |
|---|---|---|---|---|
| 298 | 1 | 1 | 16 | [4] |
| 303 | 1 | 1.3 | 18.2 | [11] |
| 298 | 1 | 2 | 15.1 | [22] |
| 303 | 1 | 2 | 21.2 | |

Another primary amine – diglycolamine (DGA) – is potentially attractive for COS capture from gaseous streams [23]. Its low vapor pressure permits its use in relatively high concentrations (30–60 wt%), thereby resulting in lower circulation rates and steam consumption when compared to MEA. The kinetics of the COS reaction with DGA was investigated by Singh and Bullin [24]. The reaction was found to be of the first order with respect to DGA, and hence, of the second order totally. At 300 K, the second-order rate constant attained a value of 2.3 $m^3$/(kmol s). Sharma [4] and Rahman [25] earlier proposed a similar second-order rate expression for the COS–DGA system. However, the reaction rate constant (166 $m^3$/(kmol s)) reported by Rahman [25] is much larger. These studies are summarised in Table 2. In our opinion, it is probable that the value of the rate constant reported in [25] is overestimated.

Contrary to the previously published values, Littel et al. [11] reported a fractional order between 1 and 2 with respect to DGA. Zwitterion deprotonation was found to be the rate-controlling step. The dependence of the deprotonation rate constants of DGA and $H_2O$ on temperature ($283 < T < 333$ K) was given by

$$k_{DGA} = 5.34 \times 10^{5} \exp\left(-\frac{7346}{T}\right) \tag{28}$$

$$k_{H_2O} = 4.93 \times 10^{6} \exp\left(-\frac{9409}{T}\right) \tag{29}$$

Other studies on the COS–DGA system were reported in [26–28]. Rahman et al. [26] studied the formation of thiocarbamate salt of DGA in aqueous solutions. Moore et al. [27] suggested that the COS reaction with DGA could be represented by

$$2DGA + COS \leftrightarrow BHEEU + H_2S \tag{30}$$

where BHEEU denotes *N*,*N*′bis(hydroxyethoxyethyl) urea. BHEEU may readily undergo hydrolysis, thereby resulting in DGA regeneration [28]. This can be represented as follows:

$$BHEEU + H_2O \leftrightarrow 2DGA + CO_2 \tag{31}$$

Diisopropanolamine (DIPA) and DEA are secondary alkanolamines commonly used in sour gas purification. DIPA is used as a solvent for COS removal along with sulfolane in Shell's Sulfinol process [2]. Due to the steric hindrance caused by the 2-propanol groups in DIPA, the transport of COS to the N atom is hampered. However, it has low steam regeneration requirement and is

**Table 2**
Kinetic studies of the reaction system COS–aqueous DGA

| Temperature (K) | DGA (kmol/$m^3$) | Order with respect to DGA | Second-order rate constant ($m^3$/(kmol s)) | Reference |
|---|---|---|---|---|
| 303 | 0.2–3.1 | 1.5 | – | [11] |
| 300 | 5.7 | 1 | 2.3 | [24] |
| 300 | Not available | 1 | 166 | [25] |

non-corrosive. Littel et al. [11] studied the kinetics of the COS–DIPA and COS–DEA systems in the temperature range of 283–333 K. These reactions were found to be of the second order with respect to the amine concentrations, and hence, of the third order totally. The temperature dependence of deprotonation rate constants of DEA and $H_2O$ was given by

$$k_{\mathrm{DEA}} = 1.16 \times 10^3 \exp\left(-\frac{5714}{T}\right) \quad (32)$$

$$k_{\mathrm{H_2O}} = 2.45 \times 10^5 \exp\left(-\frac{9199}{T}\right) \quad (33)$$

The pseudo first-order rate constants for DIPA and DEA at 303 K and 1 $\mathrm{kmol/m^3}$ amine concentration were found to be 3.5 and 7.6 $\mathrm{s^{-1}}$ respectively. Rahman et al. [26] found that the second-order rate constants for MEA, DEA and DIPA at 298 K were equal to 16, 11 and 6 $\mathrm{m^3/(kmol\,s)}$ respectively.

Hinderaker and Sandall [29] studied the absorption of COS in aqueous DEA solutions (5–25 wt%) and interpreted the kinetic data with the help of the zwitterion mechanism. Zwitterion deprotonation was found to be the rate-controlling step. Furthermore, the reaction was of the second-order with respect to DEA. The reaction rate constants were approximately two orders of magnitude smaller than those found for the $CO_2$–DEA system. The reaction rate was represented by

$$r = k_3(\mathrm{COS})(\mathrm{DEA})^2 \quad (34)$$

whereas the dependence of $k_3$ on temperature ($298 < T < 348$ K) was given by

$$k_3 = 1.604 \times 10^{10} \exp\left(-\frac{6297}{T}\right) \quad (35)$$

Amararene and Bouallou [30] investigated COS–DEA reaction kinetics in the temperature range of 313–353 K and DEA concentration range of 5–40 wt%. The $k_3$ dependence on temperature was given by the following expression:

$$k_3 = \{2121 - 0.4(\mathrm{DEA})\} \exp\left(-\frac{5785}{T}\right) \quad (36)$$

The activation energy obtained in [30] (48.1 kJ/mol) was in agreement with that reported by Hinderaker and Sandall [29] (52.35 kJ/mol). The temperature dependence of the deprotonation rate constants of DEA and $H_2O$ was given by

$$k_{\mathrm{DEA}} = 9.63 \times 10^2 \exp\left(-\frac{5772}{T}\right) \quad (37)$$

$$k_{\mathrm{H_2O}} = 4.55 \times 10^2 \exp\left(-\frac{6333}{T}\right) \quad (38)$$

The contribution of $H_2O$ to zwitterion deprotonation was found to be insignificant. All the above-mentioned kinetic studies on the COS–DEA system are summarised in Table 3. Contrary to the case for the $CO_2$–DEA system, there is a general agreement among various researchers that the COS–DEA reaction is of the third order totally.

Methylmonoethanolamine (MMEA) is a secondary alkanolamine linked to a methyl group, which may possibly be used for COS removal. Littel et al. [11] reported a fractional reaction order with respect to MMEA concentration (1.8). Due to its high basicity, the overall reaction rate in aqueous MMEA solutions was higher than that in MEA, DGA, DEA and DIPA solutions.

Morpholine (MOR) – a cyclic amine – displayed a much faster reaction rate with COS than conventional primary and secondary amines [11]. An aqueous MOR sample loaded with COS was chemically analysed in [11] and, in accordance with the zwitterion mechanism, a complex of thiocarbamate and protonated amine was identified. At 303 K and 1 $\mathrm{kmol/m^3}$ amine concentration, the pseudo first-order rate constant attained a value of 176 $\mathrm{s^{-1}}$. Sharma [4] reported a value of 220 $\mathrm{s^{-1}}$ at 298 K.

The COS reaction with sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-amino-2-methyl-1,3-propanediol (AMPD) was studied in [11,15]. AMP, which is potentially attractive for selective $H_2S$ removal, has a high $\mathrm{p}K_\mathrm{a}$ value of 9.52 at 303 K. However, the COS reaction rates in aqueous AMP solutions were found to be lower than in the non-hindered amines and they were much lower than those for the $CO_2$–AMP system. The COS reaction with AMPD was slower than that with AMP [15]. At 303 K and 1 $\mathrm{kmol/m^3}$ AMPD concentration, $k_{\mathrm{obs}}$ attained a value of 0.09 $\mathrm{s^{-1}}$. The kinetics of the COS reaction with AMPD was described by both the zwitterion and the termolecular mechanism.

A diamine, 2-((2-aminoethyl)amino)ethanol (AEEA), was recently investigated by Bouhamra and Alper [31]. At 298 K and 1 $\mathrm{kmol/m^3}$ AEEA concentration, $k_{\mathrm{obs}}$ attained a value of 19.2 $\mathrm{s^{-1}}$. The reaction order with respect to AEEA was reported as 1.31. It was found that Eq. (6) satisfactorily fitted data for the amine concentration range studied (0.25–1.75 $\mathrm{kmol/m^3}$).

Al-Ghawas et al. [16] studied the kinetics of COS reaction with MDEA—a tertiary amine. The absorption of COS in aqueous MDEA solutions was found to be slower than that of $CO_2$. In [16], a base-catalysis reaction (Eq. (19)) was proposed with a second-order rate constant of 0.90 $\mathrm{m^3/(mol\,s)}$ at 298 K. The rate constant was expressed as a function of temperature ($293 < T < 313$ K) in the MDEA concentration range of 1.26 to 2.6 $\mathrm{kmol/m^3}$. This expression is as follows:

$$k_{\mathrm{MDEA}} = 4198.74 \exp\left(-\frac{4575.8}{T}\right) \quad (39)$$

However, Alper [32] later found that the values of $k_{\mathrm{obs}}$ were about ten times smaller than those reported by Al-Ghawas et al. [16].

Littel et al. [18] found that the reaction rate constant for the COS–MDEA system (cf. Eq. (19)) was about a factor of 30 smaller than that reported by Al-Ghawas et al. [16]. At the moment, the reasons for this wide variation in the rate constant cannot be explained. In [18], the dependence of $k_{\mathrm{MDEA}}$ on temperature ($298 < T < 348$ K) was given by

$$k_{\mathrm{MDEA}} = 2.35 \times 10^6 \exp\left(-\frac{7624}{T}\right) \quad (40)$$

Eqs. (19) and (20) were used to describe the reaction kinetics.

Amararene and Bouallou [30] studied kinetics of the COS–MDEA system in the temperature range of 313–353 K and MDEA concentration range of 5–50 wt %. They also found that the rate constants reported by Al-Ghawas et al. [16] were overestimated. The energy of activation obtained in their study was in agreement with that reported by Littel et al. [18]. Recently, Rivera-Tinoco and Bouallou [33] presented a kinetic model for COS absorption into aqueous MDEA, based on the two-step mechanism represented by Eqs. (19) and (20). The reaction rate constants estimated in their study were compared with those reported by Littel et al. [18] and it was found that they agreed well. These studies are summarised in Table 4.

**Table 3**
Kinetic studies of the reaction system COS–aqueous DEA

| Temperature (K) | DEA ($\mathrm{kmol/m^3}$) | Order with respect to DEA | Pseudo first-order rate constant ($\mathrm{s^{-1}}$) | Reference |
|---|---|---|---|---|
| 298 | 1 | Not available | 11 | [4] |
| 303 | 1 | 2 | 7.6 | [11] |
| 298–348 | 0.47–2.4 | 2 | Not available | [29] |
| 313 | 0.47 | 2 | 4.6 | [30] |

**Table 4**
Kinetic studies of the reaction system COS–aqueous MDEA

| Temperature (K) | MDEA ($kmol/m^3$) | Order with respect to MDEA | Second-order rate constant ($m^3/(kmol\,s)$) | Reference |
|---|---|---|---|---|
| 298 | 1.26–2.6 | 1 | 0.9 | [16] |
| 313 | 0.15–0.8 | 1 | 0.058 | [18] |
| 313 | 2.4 | 1 | 0.45 | [30] |
| 313 | 0.41–4.25 | 1 | 0.048 | [33] |

The base-catalysed reaction was also used to describe the COS reaction with further tertiary amines such as triethanolamine (TEA), dimethylmonoethanolamine (DMMEA) and diethylmonoethanolamine (DEMEA) [18,34]. Lammers et al. [35] suggested that the rate of COS absorption into aqueous MDEA solutions could be increased by the addition of polyhydroxyalcohols.

## 4. Some general remarks

By now, the reaction of COS with several amine-based solvents has been investigated. Primary amines such as MEA and DGA, which have high reactivity, may undergo severe degradation in presence of COS. Although DEA and DIPA are able to offer only moderate COS removal, they are less susceptible to degradation by COS [20]. MDEA has low reactivity towards COS. For the case of conventional primary and secondary amines, the selectivity towards COS removal could possibly be improved by using higher amine concentrations and higher temperatures [11]. Among the other alkanolamines studied, MMEA and AEEA may be potentially attractive for selective COS removal. However, MMEA may form degradation compounds with COS. Therefore, more experimental work needs to be conducted to provide a comprehensive insight into the performance of these absorbents for COS capture.

The use of amine blends, *viz.* (tertiary + primary) or (tertiary + secondary) may be advantageous in COS removal and it would be interesting to study their performance. By now, the information on the kinetics of the reaction of COS with amine blends is missing in the open literature.

## 5. Conclusions

In this work, kinetics of the COS reaction with alkanolamines in aqueous solutions is reviewed. COS capture using amines has been extensively studied and the reaction pathways are well described. COS, which is very similar in structure to $CO_2$, follows the same reaction mechanism. However, its reaction rates with amines are much lower. The COS reaction with primary, secondary and sterically hindered amines is usually described by the zwitterion mechanism, whereas the reaction with tertiary amines is governed by the base-catalysed hydration of COS. It would be desirable to investigate absorption into novel amine-based solvents. For instance, MMEA and AEEA, which have higher reactivity than MEA, DGA, DEA and DIPA, may be potentially attractive for COS removal. A further study of the performance of these absorbents in COS capture is essential. MDEA – a tertiary amine – has low reactivity towards COS. The COS reaction with tertiary amines may be accelerated by the addition of primary or secondary amines. Therefore, further experimental work on the absorption of COS into aqueous amine blends is required.

## References

[1] P.D. Vaidya, E.Y. Kenig, $CO_2$–alkanolamine reaction kinetics: a review on recent studies, Chem. Eng. Technol. 30 (2007) 1467.

[2] A. Kohl, R. Nielsen, Gas Purification, fifth ed., Gulf Publishing Company, Houston, 1997.

[3] P.V. Danckwerts, Gas–liquid Reactions, McGraw-Hill, New York, 1970.

[4] M.M. Sharma, Kinetics of reactions of carbonyl sulphide and carbon dioxide with amines and catalysis by bronsted bases of the hydrolysis of COS, Trans. Faraday Soc. 61 (1965) 681.

[5] P.M.M. Blauwhoff, G.F. Versteeg, W.P.M. van Swaaij, A study on the reaction between $CO_2$ and alkanolamines in aqueous solutions, Chem. Eng. Sci. 39 (1984) 207.

[6] V.V. Mahajani, J.B. Joshi, Kinetics of reactions between carbon dioxide and alkanolamines, Gas Sep. Purif. 2 (1988) 50.

[7] G.F. Versteeg, L.A.J. van Dijck, W.P.M. van Swaaij, On the kinetics between $CO_2$ and alkanolamines both in aqueous and non-aqueous solutions. An overview, Chem. Eng. Commun. 144 (1996) 113.

[8] S.P. Ewing, D. Lockshon, W.P. Jencks, Mechanism of cleavage of carbamate anions, J. Am. Chem. Soc. 102 (1980) 3072.

[9] R.J. Millican, M. Angelopoulos, A. Bose, B. Riegel, D. Robinson, C.K. Wagner, Uncatalyzed and general acid catalyzed decomposition of alkyl xanthates and monothiocarbonates in aqueous solutions, J. Am. Chem. Soc. 105 (1983) 3622.

[10] E. Alper, Reaction kinetics of carbonyl sulfide with aqueous diglycolamine by the stopped flow technique, in: Gas Processing Fundamentals I, AIChE Spring National Meeting, Houston, 1989, Paper No. 56F.

[11] R.J. Littel, G.F. Versteeg, W.P.M. van Swaaij, Kinetics of COS with primary and secondary amines in aqueous solutions, AIChE J. 38 (1992) 244.

[12] H.W. Thompson, C.F. Kearton, S.A. Lamb, The kinetics of the reaction between carbonyl sulfide and water, J. Chem. Soc. 31 (1935) 1033.

[13] P.V. Danckwerts, M.M. Sharma, The absorption of carbon dioxide into solutions of alkalis and amines (with some notes on hydrogen sulphide and carbonyl sulphide), Chem. Eng. (1966) CE244.

[14] J.E. Crooks, J.P. Donnellan, Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution, J. Chem. Soc., Perkin Trans. 2 (4) (1989) 331.

[15] E. Alper, Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1,3-propanediol and carbonyl sulphide, Turk. J. Chem. 25 (2001) 209.

[16] H.A. Al-Ghawas, G. Ruiz-Ibanez, O.C. Sandall, Absorption of carbonyl sulfide in aqueous methyldiethanolamine, Chem. Eng. Sci. 44 (1989) 631.

[17] T.L. Donaldson, Y.N. Nguyen, Carbon dioxide reaction kinetics and transport in aqueous amine membranes, Ind. Eng. Chem. Fundam. 19 (1980) 260.

[18] R.J. Littel, G.F. Versteeg, W.P.M. van Swaaij, Kinetic study of COS with tertiary alkanolamine solutions. 1. Experiments in an intensely stirred batch reactor, Ind. Eng. Chem. Res. 31 (1992) 1262.

[19] B. Philipp, H. Dautzenberg, Kinetische Untersuchungen zur Bildung und Zersetzung von Monothiocarbonat in wassrige Losung, Z. Phys. Chem. 229 (1965) 210.

[20] J. Seagraves, Sulfur removal in amine plants, Hydrocarbon Eng. 12 (2001) 47.

[21] R.L. Pearce, J.L. Arnold, C.K. Hall, Studies show carbonyl sulphide problem, Hydrocarbon Process. Petroleum Refiner. 40 (1961) 121.

[22] S.C. Lee, M.J. Snodgrass, M.K. Park, O.C. Sandall, Kinetics of removal of carbonyl sulfide by aqueous monoethanolamine, Environ. Sci. Technol. 35 (2001) 2352.

[23] R.W. Bucklin, DGA—a workhouse for gas sweetening, Oil Gas J. 80 (1982) 204.

[24] M. Singh, J.A. Bullin, Determination of rate constants for the reaction between diglycolamine and carbonyl sulphide, Gas Sep. Purif. 2 (1988) 131.

[25] M.A. Rahman, Study of reactions of carbon dioxide and sulphur containing compounds with ethanolamines, PhD thesis, Oklahoma State University, USA, 1984.

[26] M.A. Rahman, R.N. Maddox, G.J. Mains, Reactions of carbonyl sulfide and methyl mercaptan with ethanolamines, Ind. Eng. Chem. Res. 28 (1989) 470.

[27] T.F. Moore, J.C. Dingman, F.L. Johnson Jr., in: S.A. Newman (Ed.), A review of Current Diglycolamine Agent Gas Treating Applications—Acid and Sour Gas Treating Processes, Gulf Publishing Company, Houston, 1985.

[28] G.P. McClure, D.C. Morrow, Amine process for removal of COS from propane economically, Oil Gas J. 77 (1979) 106.

[29] G. Hinderaker, O.C. Sandall, Absorption of carbonyl sulfide in aqueous diethanolamine, Chem. Eng. Sci. 55 (2000) 5813.

[30] F. Amararene, C. Bouallou, Kinetics of carbonyl sulfide (COS) absorption with aqueous solutions of diethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res. 43 (2004) 6136.

[31] W. Bouhamra, E. Alper, Reaction kinetics of carbon dioxide, carbonyl sulfide and carbon disulfide with aqueous 2-(2 aminoethylamino) ethanol, Chem. Eng. Technol. 23 (2000) 421.

[32] E. Alper, Comments on kinetics of reaction of carbonyl sulphide with aqueous MDEA, Chem. Eng. Sci. 48 (1993) 1179.

[33] R. Rivera-Tinoco, C. Bouallou, Kinetic study of carbonyl sulfide (COS) absorption by methyldiethanolamine aqueous solutions from 415 $mol/m^3$ to 4250 $mol/m^3$ and 313 K to 353 K, Ind. Eng. Chem. Res. 46 (2007) 6430.

[34] R.J. Littel, G.F. Versteeg, W.P.M. van Swaaij, Kinetic study of COS with tertiary alkanolamine solutions. 2. Modeling and experiments in a stirred cell reactor, Ind. Eng. Chem. Res. 31 (1992) 1269.

[35] J.N.J.J. Lammers, J. Haringa, R.J. Littel, Effect of polyhydroxyalcohols on COS absorption in aqueous methyldiethanolamine, Chem. Eng. J. 60 (1995) 123.