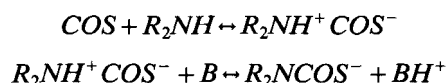


Kinetics of COS with Primary and Secondary Amines in Aqueous Solutions

R. J. Littel, G. F. Versteeg, and W. P. M. van Swaaij

Dept. of Chemical Engineering, University of Twente, 7500 AE Enschede, The Netherlands

The reaction between COS and aqueous solutions of primary and secondary amines has been studied by means of the stirred cell technique. Kinetic experiments at temperatures 283 to 333 K were carried out with MEA, DGA, DEA, DIPA, MMEA, AMP, and MOR. All kinetic experiments could be described by a zwitterion reaction mechanism similar to the mechanism proposed by Caplow (1968) for the reaction between CO₂ and secondary amines:



Analysis of concentrated amine solutions at high COS concentrations by various analytical techniques confirmed the conclusions from the kinetic experiments. For all amines except for MEA, the overall reaction rate was found to be determined entirely by the zwitterion deprotonation rate.

Introduction

In process industry, basic alkanolamine solutions are used frequently to remove acidic components such as H₂S, COS, and CO₂, from natural and refinery gases. Industrially important alkanolamines for this operation are the primary amines monoethanolamine (MEA) and diglycolamine (DGA), the secondary amines diethanolamine (DEA) and diisopropanolamine (DIPA), and the tertiary amine N-methyldiethanolamine (MDEA). Usually these alkanolamines are applied in aqueous solutions, but combined solvents like water and sulfolane in the Shell Sulfinol process are used also (Kohl and Riesenfeld, 1985). Much research has been focused on the selective absorption of sulfur compounds, particularly H₂S, because simultaneous removal of CO₂ often is not preferred both from technical and economical points of view.

The reaction between H₂S and alkanolamines can be considered instantaneous with respect to mass transfer, whereas the reaction between CO₂ and alkanolamines is a finite rate reaction. Consequently, improvement of H₂S selectivity can, among others, be achieved by applying an alkanolamine which reacts relatively slow with CO₂. This explains the increasing

popularity of tertiary and sterically hindered (secondary) alkanolamines for selective H₂S absorption. However, COS reacts much slower with alkanolamines than CO₂. As a result, an increase in H₂S selectivity is usually accompanied by a decrease in COS absorption capacity. Eventually, the attainable sulfur selectivity is limited by this decrease in COS removal because the treating target is a total sulfur specification. Obviously, thorough knowledge of reaction mechanism and kinetics for the reaction between COS and alkanolamines is necessary for an adequate design of gas treating plants.

Data for the reaction of COS with primary and secondary alkanolamines are very scarce in literature. Sharma (1965) presented some kinetic data for CO₂ and COS with various amines and concluded that CO₂ and COS follow similar reaction mechanisms, with COS reacting about a factor 100 slower. He, however, carried out kinetic experiments at only one amine concentration. Recently, Singh and Bullin (1988) reported some data for the reaction between COS and DGA over a temperature range of 307 to 322 K. From their experiments they concluded that the overall reaction rate was first order in the COS concentration and first order in the DGA concentration.

In the present work, the reaction of COS with primary and secondary amines has been studied extensively by means of

Present address of R. J. Littel: Koninklijke/Shell Laboratorium Amsterdam, P.O. Box 3003, 1003 AA Amsterdam, The Netherlands.

the stirred cell reactor technique. Kinetic experiments at temperatures ranging from 283 to 333 K were carried out with aqueous solutions of MEA, DGA, DEA, DIPA, methylmonoethanolamine (MMEA), 2-amino-2-methyl-1-propanol (AMP), and morpholine (MOR). Amine solutions at high COS loadings were analyzed with various analytical techniques to provide additional confirmation for the findings from the kinetic experiments.

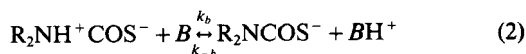
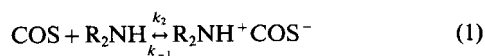
Literature

The reaction of COS with primary and secondary amines in aqueous solutions has received very little attention in literature. Sharma (1965) carried out absorption experiments of CO₂ and COS into aqueous solutions of various amines at 298 K and concluded from his experiments that CO₂ and COS react similarly with amines. He observed a reaction rate for COS which was about a factor 100 lower than that for CO₂. Although the experiments of Sharma (1965) seem valid, it should be noted that for each amine experiments were carried out at only one concentration (1,000 mol·m⁻³).

Recently, Singh and Bullin (1988) reported kinetic data for the reaction of COS with aqueous solutions of diglycolamine over a temperature range of 307 to 322 K. They carried out absorption experiments in a continuously operated gas-liquid contactor which was designed to simulate a single tray in an absorption column. COS and other components in the amine solutions were analyzed by means of a GC technique. From their experiments, Singh and Bullin (1988) concluded that the overall reaction was single order in both the COS and amine concentrations. Their interpretation method, however, did not allow for broken reaction orders.

Rahman et al. (1989) analyzed anhydrous amines loaded with COS by means of ¹H and ¹³C NMR. From their spectra they concluded that thiocarbamates were formed in the case of MEA, DEA and DGA, whereas the thiocarbamate salt of DIPA could not be positively ascertained. However, some remarks must be presented with respect to the work of Rahman et al. (1989). It is probably not completely correct to compare spectra for pure amine and loaded amine to each other if these spectra have been obtained with different solvents: in general, the place of a peak and even the occurrence of a peak may differ considerably for different solvents. Moreover, the large difference in noise level between ¹³C NMR spectra for pure amines and those for loaded amines seems peculiar and may even lead to artificial peaks.

Experimental work on the cleavage of monothiocarbamates (Ewing et al., 1980; Millican et al., 1983) suggests a zwitterion mechanism for the reaction between COS and primary and secondary amines. For the reaction of CO₂ with these amines, the zwitterion mechanism is widely accepted (see, for example, Caplow, 1968; Danckwerts, 1979; Blauwhoff et al., 1984; Versteeg and van Swaaij, 1988a; Versteeg and Oyeveaar, 1989; Littel et al., 1992a,b). In the case of COS, a zwitterion reaction mechanism would be given by Eqs. 1 and 2.



This mechanism comprises two steps: formation of the COS-

amine zwitterion (reaction 1), followed by base-catalyzed deprotonation of this zwitterion (reaction 2). In principle, any base present in solution will contribute to the deprotonation of the zwitterion.

Considering the very limited information in open literature, additional experimental information is necessary to determine the validity of the zwitterion mechanism for the reaction between COS and primary and secondary amines. Therefore, in the present work kinetic experiments at various temperatures were carried out with aqueous solutions of various primary and secondary amines.

Experimental Studies

All kinetic experiments were carried out in a thermostatted stirred cell reactor with a flat, horizontal gas-liquid interface. The stirred-cell reactor was operated batchwise with respect to both gas and liquid phase. The pressure decrease, measured by a pressure transducer which was connected to an Apple IIe computer, was recorded as a function of time. Experimental setup and procedure have been described in more detail by, for example, Blauwhoff et al. (1984).

Based on mass balances for both gas and liquid phase, the following expression for the carbonyl sulfide flux can be derived:

$$J_{\text{COS}} = m_{\text{COS}} k_{L,\text{COS}} E \frac{P_{\text{COS}}}{RT} \quad (3)$$

The enhancement factor E is equal to Ha if pseudo-first-order conditions are fulfilled:

$$3 < Ha \ll E^\infty \quad (4)$$

with:

$$Ha = \frac{\sqrt{k_{ov} D_{\text{COS}}}}{k_{L,\text{COS}}} \quad (5)$$

$$E^\infty = \sqrt{\frac{D_{\text{COS}}}{D_{\text{R}_2\text{NH}}}} + \sqrt{\frac{D_{\text{R}_2\text{NH}}}{D_{\text{COS}}} \frac{[\text{R}_2\text{NH}]RT}{\gamma m_{\text{COS}} P_{\text{COS}}}} \quad (6)$$

The reaction between COS and amines is reversible and, strictly speaking, Eq. 6 is valid only for irreversible reactions. However, low amine conversions in combination with high equilibrium constants as encountered in the present work validate sufficiently the application of Eq. 6. The observed reaction rates and the applied COS pressures were low and, consequently, condition 4 could be fulfilled easily. From the work of Thompson et al. (1935) and Philipp and Dautzenberg (1965), it could be concluded that the contribution of the reaction between COS and OH⁻ to the overall reaction rate was negligible.

Since COS reacts with amine solutions, it is not possible in general to determine its solubility and diffusivity directly. The COS solubility was determined based on a COS-N₂O analogy (Littel et al., 1992c). The diffusivity of COS in amine solutions can be obtained from the COS diffusivity in water using the modified Stokes-Einstein relationship reported by Versteeg and van Swaaij (1988b). Since no reliable data on the temperature

Table 1. Viscosity and N₂O Solubility Data for Aqueous Amine Solutions at 283 K

| MEA | | | DGA | | | DEA | | |
|---------------------------------|----------------------------------|------------|---------------------------------|----------------------------------|------------|---------------------------------|----------------------------------|------------|
| [MEA] [mol·m ⁻³] | η [10 ³ Pa·s] | m_{N_2O} | [DGA] [mol·m ⁻³] | η [10 ³ Pa·s] | m_{N_2O} | [DEA] [mol·m ⁻³] | η [10 ³ Pa·s] | m_{N_2O} |
| 194 | 1.36 | | 218 | 1.41 | | 187 | 1.41 | |
| 204 | | 0.877 | 199 | | 0.900 | 210 | | 0.886 |
| 206 | | 0.891 | 200 | | 0.897 | 212 | | 0.868 |
| 393 | 1.41 | | 408 | 1.51 | | 372 | 1.55 | |
| 391 | | 0.892 | 435 | | 0.860 | 387 | | 0.879 |
| 392 | | 0.882 | 437 | | 0.890 | 389 | | 0.882 |
| 789 | 1.53 | | 795 | 1.76 | | 760 | 1.79 | |
| 782 | | 0.881 | 847 | | 0.849 | 761 | | 0.874 |
| 782 | | 0.864 | 847 | | 0.855 | 767 | | 0.859 |
| 1,588 | 1.81 | | 1,555 | 2.39 | | 1,532 | 2.52 | |
| 1,619 | | 0.864 | 1,667 | | 0.800 | 1,536 | | 0.834 |
| 1,621 | | 0.869 | 1,676 | | 0.771 | 1,541 | | 0.840 |
| 2,414 | 2.17 | | 2,463 | 3.57 | | 2,393 | 3.84 | |
| 2,422 | | 0.844 | 2,527 | | 0.719 | 2,367 | | 0.778 |
| 2,425 | | 0.832 | 2,553 | | 0.715 | 2,373 | | 0.778 |
| 3,243 | 2.63 | | 3,332 | 4.99 | | 3,265 | 6.17 | |
| 3,162 | | 0.819 | 3,112 | | 0.671 | 3,161 | | 0.717 |
| 3,163 | | 0.811 | 3,147 | | 0.663 | 3,169 | | 0.705 |

dependence are available in literature, the COS diffusivity in water at various temperatures was estimated from the COS diffusivity at 298 K reported by Littel et al. (1992c), assuming the same activation energy as reported by Versteeg and Swaaij (1988b) for CO₂. Viscosity and N₂O solubility data for amine solutions used in the present work are presented in Table 1 or were reported by Littel et al. (1992c).

For all kinetic experiments, COS pressures and amine loadings were typically 0.001–0.010 MPa and 1–10%, respectively.

MEA, DEA, MMEA, AMP, and MOR were obtained from Janssen Chimica, DIPA was obtained from Riedel-de Haën, and DGA was provided by Texaco Chemical Company. All amines were at least 99% pure and used as received. COS with a minimum purity of 97.5% was obtained from UCAR.

Results

Kinetic Experiments

The reaction between COS and the primary alkanolamines

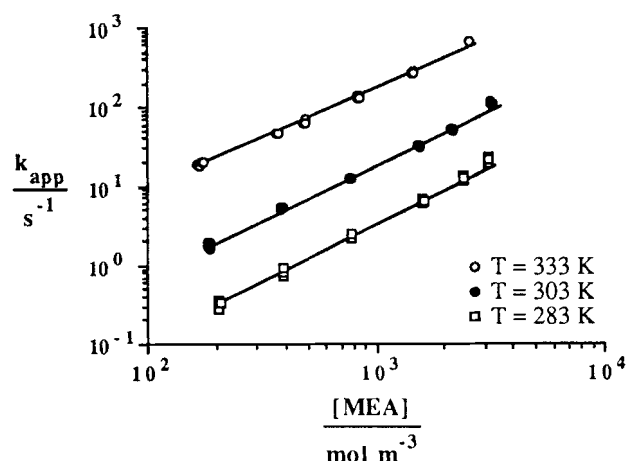


Figure 1. Experimental results for aqueous MEA solutions.

MEA and DGA has been studied in aqueous solutions as a function of temperature. For MEA, kinetic experiments were carried out at 283, 303 and 333 K; the reaction of COS with DGA was studied at 283, 303 and 318 K. The experimental data are presented in Figures 1 and 2 for MEA and DGA, respectively. These figures show that a broken reaction order in amine was observed for all temperatures investigated. This reaction order in amine was found to be unaffected by temperature within experimental accuracy. For MEA the reaction order in amine was about 1.4, whereas for DGA is was about 1.6. The experimental data in Figures 1 and 2 show a definite influence of temperature on the overall reaction rate.

The reaction between COS and various secondary amines has been investigated in aqueous solutions. The reaction of COS and DEA was studied at 283, 303 and 333 K, whereas kinetic experiments of COS with DIPA, MMEA, AMP, and MOR were carried out at 303 K. The measured overall reaction rate constants are plotted against the amine concentration in Figures 3 to 5. For all secondary amines investigated, a reaction order in amine of almost 2 was observed. The overall reaction

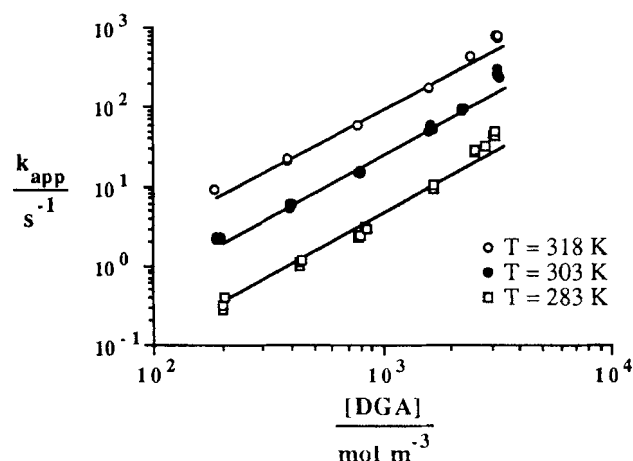


Figure 2. Experimental results for DGA solutions.

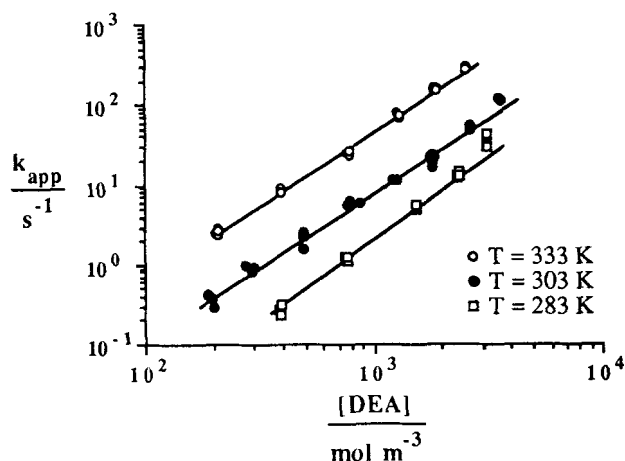


Figure 3. Experimental results for aqueous DEA solutions.

rate of COS with DEA showed a significant dependence on temperature.

Close inspection of Figures 1 to 5 shows that the observed first-order apparent reaction rate constants deviate systematically at the highest amine concentrations. This must probably be attributed to a tendency of the COS-N₂O analogy to underestimate the COS solubility at higher amine concentrations. Littel et al. (1992c) showed for aqueous ethyleneglycol and aqueous sulfolane solutions that this COS-N₂O analogy is valid only for dilute aqueous solutions up to about 20 wt. %. For the present kinetic experiments, this limit appears to have been violated at the highest amine concentrations for the bulkier amines. Therefore, these experiments were not taken into account in the calculation of kinetic rate constants from the observed overall rate constants.

For all amines investigated, a reaction order in amine between 1 and 2 has been observed. From the COS pressure decrease as a function of time, it could be concluded that the reaction order in COS was 1. These observed reaction orders can be described by the zwitterion reaction mechanism (reactions 1 and 2), and apparently the overall reaction rate is, at least partially, determined by the zwitterion deprotonation

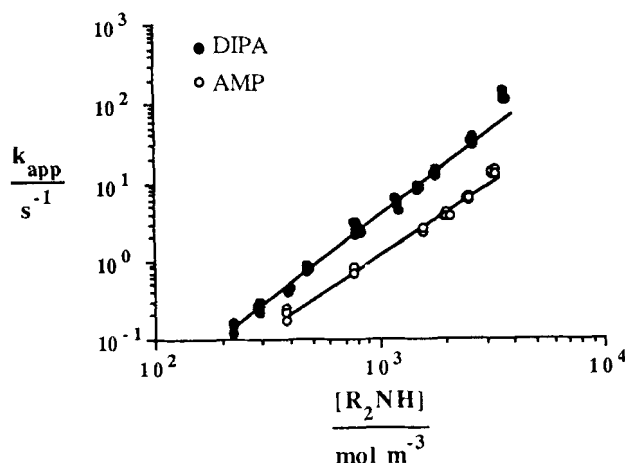


Figure 4. Experimental results for aqueous DIPA and AMP solutions at 303 K.

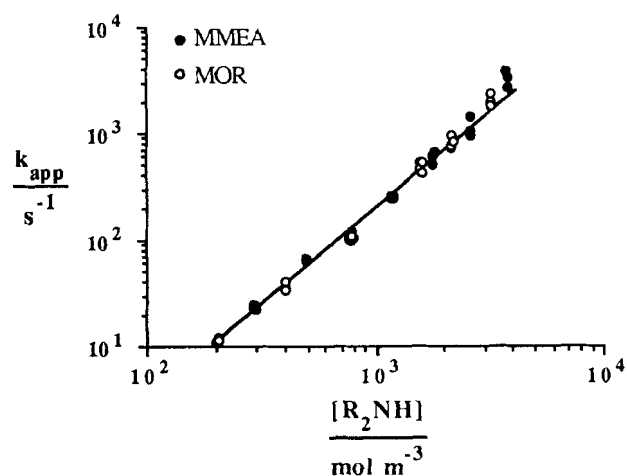


Figure 5. Experimental results for aqueous MMEA and MOR solutions at 303 K.

rate. The overall reaction rate was found to increase with increasing basic strength of the alkanolamine for the amines with similar compositions (MEA, DGA, DEA, DIPA, and MMEA). Compared to these amines, the sterically hindered amine AMP reacts much slower than expected from its basic strength whereas the cyclic amine MOR reacts much faster.

Chemical analyses

To obtain additional confirmation for the findings of the kinetic experiments, amine samples with about 10 wt. % water were heavily loaded with COS (2–10 wt. % S) and analyzed by means of chemical analysis techniques. Techniques used were: ¹H and ¹³C NMR, GLC, MS and element analysis.

GLC and NMR analysis of the loaded MEA and MMEA samples showed significant amounts of degradation products. For MEA, the observed degradation products were well in line with the degradation mechanism suggested by Pearce et al. (1961) and Berlie et al. (1965). In the case of MMEA, the degradation products could not be identified. For DEA and AMP, no significant differences between NMR spectra for loaded and unloaded samples were observed. All these observations seem to agree with the proposed zwitterion reaction mechanism, because the NMR technique is rather insensitive to differences between reactants and products postulated by this mechanism.

In loading the MOR sample with COS, a white salt crystallized, which was well soluble in water. The MS spectrum of this salt showed a peak with a brutto molecular weight of 147, which corresponded to a brutto molecule formula of C₅H₉NSO₂. Element analysis of the water-free salt yielded a brutto molecule formula of C_{8.7}H_{16.1}N_{1.9}SO_{2.9}. The NMR spectra of this salt solved in D₂O showed the presence of a loosely bound complex, which could not be identified unambiguously. The analysis by means of GLC showed only MOR, probably as a result of disintegration of the salt due to the conditions applied in GLC. Considering all chemical analyses, the most likely composition of the obtained salt is presented in Figure 6, which shows a complex of thiocarbamate and protonated amine. In loading a MOR sample with CO₂ also a white salt crystallized, and analysis of this salt indicated a similar composition as that given in Figure 6.

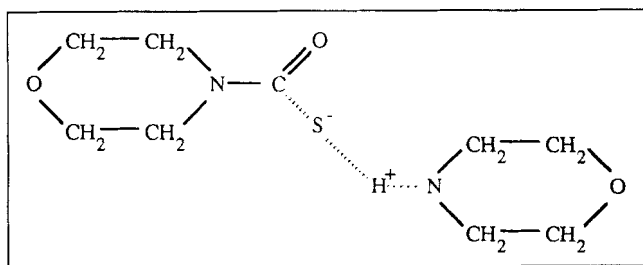


Figure 6. Composition of crystallization product from concentrated MOR solution at high COS concentrations.

In summarizing the results from the analysis of amine samples heavily loaded with COS, it can be concluded that no evidence was obtained which contradicts the zwitterion mechanism, whereas the observations for MOR clearly support this mechanism. Since MEA and MMEA were shown to be strongly susceptible to degradation by COS, they seem to be unsuitable for COS removal. This susceptibility to degradation by COS did not hamper the kinetic experiments with MEA and MMEA, as only low amine conversions were applied and fresh amine solutions were used in those experiments.

Discussion

The kinetic experiments and the analysis of aqueous amine samples loaded with COS suggest strongly that the reaction between COS and primary or secondary amines can be described by the zwitterion reaction mechanism given by reactions 1 and 2. If pseudo-steady-state conditions are assumed for the COS-amine zwitterion concentration, the following expression can be derived for the overall forward reaction rate:

$$R_{\text{COS}} = \frac{[R_2\text{NH}][\text{COS}]}{\frac{1}{k_2} + \frac{1}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + k_{R_2\text{NH}}[R_2\text{NH}]} = k_{\text{app}}[\text{COS}] \quad (7)$$

with:

$$k_{\text{H}_2\text{O}} = \frac{k_2 k_{b,\text{H}_2\text{O}}}{k_{-1}} \quad k_{R_2\text{NH}} = \frac{k_2 k_{b,R_2\text{NH}}}{k_{-1}}$$

Strictly speaking, all bases present in solution will contribute to the deprotonation of the zwitterion (including OH^-). However, the contribution of bases other than H_2O and the amine itself was found to be negligible without loss of accuracy. The observed apparent reaction rate constants were fitted to reaction rate expression 7 by means of a Levenberg-Marquardt fitting procedure. The fitted reaction rate constants are summarized in Table 2.

The zwitterion formation rate constant could be determined only for MEA; for all other amines, the overall reaction rate was determined entirely by the zwitterion deprotonation rate. This zwitterion deprotonation rate was found to be determined primarily by the contribution of amine as can also be concluded from the observed reaction order in amine which was almost 2 for most amines. For DEA at 283 K and DIPA at 303 K, the contribution of H_2O to the zwitterion deprotonation rate was too small to determine values for the zwitterion deprotonation rate constants by H_2O .

Both zwitterion deprotonation rate constants were observed to increase with temperature. This temperature influence is given by Eqs. 8 to 10 and by Figures 7 and 8 which show Arrhenius plots for the deprotonation rate constants by amine and water, respectively.

MEA:

$$k_{R_2\text{NH}} = 1.31 \times 10^{-2} \exp\left(\frac{-1,771}{T}\right)$$

$$k_{\text{H}_2\text{O}} = 1.35 \times 10^5 \exp\left(\frac{-8,320}{T}\right) \quad (8)$$

DGA:

$$k_{R_2\text{NH}} = 5.34 \times 10^5 \exp\left(\frac{-7,346}{T}\right)$$

$$k_{\text{H}_2\text{O}} = 4.93 \times 10^6 \exp\left(\frac{-9,409}{T}\right) \quad (9)$$

Table 2. Fitted Reaction Rate Constants

| Amine | <i>T</i> [K] | <i>pKa</i> | Apparent Reaction Order in Amine* | <i>k</i> ₂ [m ³ ·mol ⁻¹ ·s ⁻¹] | 10 ⁵ <i>k</i> _{R₂NH} [m ⁶ ·mol ⁻² ·s ⁻¹] | 10 ⁷ <i>k</i> _{H₂O} [m ⁶ ·mol ⁻² ·s ⁻¹] |
|-------|-----------------|------------|--------------------------------------|--|--|---|
| MEA | 283 | 9.98 | 1.5 | 0.021 | 2.5 | 0.23 |
| MEA | 303 | 9.36 | 1.3 | 0.030 | 3.8 | 1.6 |
| MEA | 333 | 8.56 | 1.3 | — | 6.4 | 19 |
| DGA | 283 | 9.90 | 1.7 | — | 0.29 | 0.18 |
| DGA | 303 | 9.31 | 1.5 | — | 1.5 | 1.6 |
| DGA | 318 | 8.98 | 1.4 | — | 5.1 | 7.0 |
| DEA | 283 | 9.27 | 2.0 | — | 0.21 | — |
| DEA | 303 | 8.75 | 1.8 | — | 0.68 | 0.16 |
| DEA | 333 | 8.10 | 1.9 | — | 4.3 | 0.67 |
| DIPA | 303 | 8.76 | 2.0 | — | 0.35 | — |
| MMEA | 303 | 9.64 | 1.8 | — | 15 | 6.2 |
| AMP | 303 | 9.52 | 1.8 | — | 0.089 | 0.050 |
| MOR | 303 | 8.24** | 1.8 | — | 15 | 5.1 |

* Approximate error bounds: ±0.1.

** Estimated from *pKa* value at 298 K.

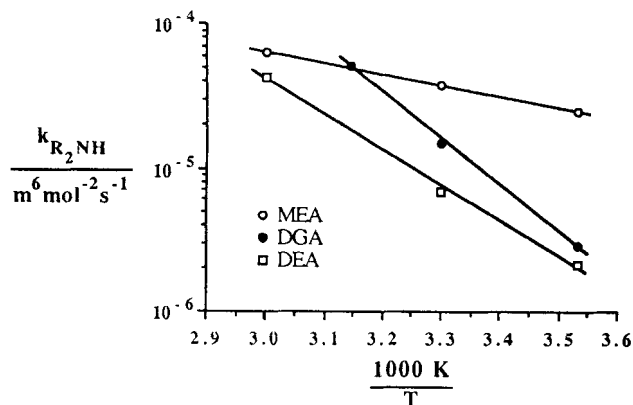


Figure 7. Arrhenius plot for the zwitterion deprotonation rate constants by amine.

DEA:

$$k_{R_2NH} = 1.16 \times 10^3 \exp\left(\frac{-5,714}{T}\right)$$

$$k_{H_2O} = 2.45 \times 10^5 \exp\left(\frac{-9,199}{T}\right) \quad (10)$$

It is remarkable that the activation temperature for the k_{R_2NH} shows a large variation for the different amines, whereas the activation temperature for the k_{H_2O} is almost identical for all three amines. It should be realized, however, that the deprotonation rate constants are a combination of three elementary rate constant (see expression 7) and that therefore no *a priori* statements can be made concerning the activation temperature for the combined reaction rate constants. For the reaction between CO_2 and secondary amines, the deprotonation rate constants were even found to be almost independent of temperature (Littel et al., 1992b).

Sharma (1965) presented kinetic data, obtained in a stirred cell reactor, for various amines at 298 K. However, he carried out experiments only at one amine concentration ($1,000 \text{ mol} \cdot \text{m}^{-3}$) and assumed that the physical data needed for the interpretation of the kinetic experiments were equal to those in water. Nevertheless, a comparison has been made between the kinetic data reported by Sharma (1965) at 298 K and the

Table 3. Comparison Between Work of Sharma (1965) and Present Work

| Amine | Sharma (1965)* $k_{app} [\text{s}^{-1}]$ | Present Work** $k_{app} [\text{s}^{-1}]$ |
|-------|---|---|
| MEA | 16 | 18.2 |
| DEA | 11 | 7.6 |
| DIPA | 5.6 | 3.5 |
| MMEA | 220 | 182 |
| AMP | 4.5 | 1.1 |
| MOR | 220 | 176 |

* $T = 298 \text{ K}$, $[Am] = 1,000 \text{ mol} \cdot \text{m}^{-3}$

** $T = 303 \text{ K}$, $[Am] = 1,000 \text{ mol} \cdot \text{m}^{-3}$

present data at 303 K. Table 3 shows that the agreement between the apparent reaction rate constants at $1,000 \text{ mol} \cdot \text{m}^{-3}$ amine obtained in both works is very acceptable.

Singh and Bullin (1988) carried out kinetic experiments in a continuously operated gas-liquid contactor for aqueous solutions of DGA at temperatures ranging from 307 to 322 K. The progression of the reaction was followed by means of GC analysis of the composition of the amine solutions. They reported a single-order behavior in both COS and amine concentrations, although it should be noted that their interpretation method did not allow for broken reaction orders. This first-order behavior in amine is in contradiction with the present work. Also the overall reaction rates presented by Singh and Bullin (1988) are substantially lower than those observed for DGA in the present work. The reasons for these discrepancies are hard to clarify because the work of Singh and Bullin (1988) lacks information on the actually measured reaction rates as a function of amine concentration. Moreover, Singh and Bullin (1988) report that the brutto CO_2 concentrations present in solution were found to be negligible, whereas significant brutto concentrations of H_2S were observed. Since H_2S and CO_2 are produced in equal amounts by the disintegration of COS, this discrepancy possibly indicates significant desorption of CO_2 which might have obscured the kinetic experiments of Singh and Bullin (1988).

The present kinetic data obtained for the reaction between COS and primary or secondary amines can be compared to the kinetic data for CO_2 as reported by Versteeg and van Swaaij (1988a), Bosch et al. (1990), and Littel et al. (1991b). For the nonhindered alkanolamines (MEA, DGA, DEA, DIPA, and MMEA), the observed reaction rates for COS are in general roughly a factor 100 lower than the reaction rates for CO_2 . The reaction order in amine for COS, however, is usually higher than that for CO_2 , indicating that the overall reaction rate for COS is much more limited by the zwitterion deprotonation rate. The zwitterion deprotonation rate for the COS-amine zwitterion was observed to increase considerably with increasing temperature, whereas the deprotonation rate of the CO_2 -amine zwitterion appears to be almost independent of temperature (Littel et al., 1991b). Since all bases present in solution will contribute to the zwitterion deprotonation, the application of blends of tertiary and secondary or primary amines might be beneficial for selective COS removal. Also relatively high amine concentrations, which lead to higher ratios of COS and CO_2 solubilities, seem to promote COS removal.

Sterically hindered secondary amines like AMP appear to be suitable for selective H_2S removal (Sartori et al., 1987).

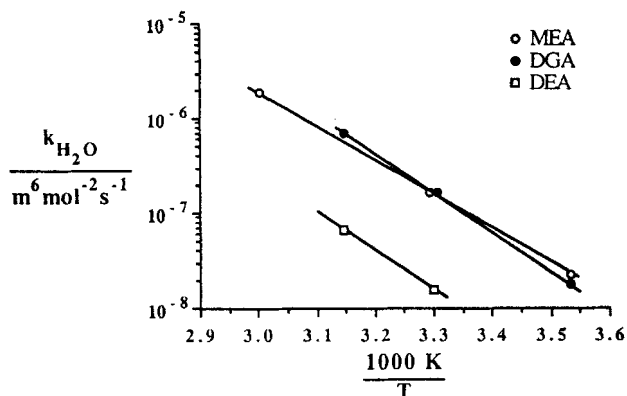


Figure 8. Arrhenius plot for the zwitterion deprotonation rate constants by H_2O .

However, the difference between the reaction rates of COS and of CO₂ with aqueous AMP solutions (Bosch et al., 1990) is substantially larger than for the nonhindered amines, indicating that sterically hindered secondary amines are probably not suitable for selective COS removal. The cyclic amine MOR reacts relatively fast with COS in relation to its basic strength, but it was found to react fast also with CO₂ (Littel et al., 1991b).

Conclusions

The reaction between COS and aqueous solutions of primary and secondary amines has been studied by means of the stirred cell technique. Kinetic experiments at temperatures ranging from 283 to 333 K were carried out with MEA, DGA, DEA, DIPA, MMEA, AMP, and MOR.

All kinetic experiments could be described by a zwitterion mechanism similar to the zwitterion mechanism proposed by Caplow (1968) for the reaction between CO₂ and secondary amines. Analysis of concentrated amine solutions at high COS concentrations by means of various analytical techniques confirmed the conclusions from the kinetic experiments. For all amines except for MEA, the overall reaction rate was found to be entirely determined by the zwitterion deprotonation rate.

Solutions of MEA and MMEA were found to be susceptible to amine degradation and seem therefore not suitable for COS removal. Also solutions of sterically hindered secondary amines like AMP seem to be unsuited to selective COS removal due to the very low reaction rates of AMP with COS in comparison to the reaction rates between CO₂ and AMP. For nonhindered amines, the COS reaction rate with respect to the CO₂ reaction rate is promoted by higher amine concentrations and higher temperatures.

Acknowledgment

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Notation

| | |
|-------------|--|
| D | = diffusivity, m ² ·s ⁻¹ |
| E | = enhancement factor |
| E^∞ | = maximum enhancement factor (Eq. 6) |
| Ha | = Hatta number (Eq. 5) |
| J | = molar flux, mol·m ⁻² ·s ⁻¹ |
| k_{app} | = apparent psuedo-first-order reaction rate constant, s ⁻¹ |
| k_{ov} | = overall psuedo-first-order reaction rate constant, s ⁻¹ |
| k_2 | = zwitterion formation rate constant, m ³ ·mol ⁻¹ ·s ⁻¹ |
| k_{R_2NH} | = zwitterion deprotonation constant by amine, m ⁶ ·mol ⁻² ·s ⁻¹ |
| k_{H_2O} | = zwitterion deprotonation constant by water, m ⁶ ·mol ⁻² ·s ⁻¹ |
| k_L | = liquid phase mass transfer coefficient, m·s ⁻¹ |
| m | = dimensionless solubility, mol·mol ⁻¹ |
| P | = pressure, Pa |
| R | = ideal gas constant, 8.314 J·mol ⁻¹ ·K ⁻¹ |
| T | = temperature, T |

Greek letters

η = viscosity, Pa·s

Amine abbreviations

| | |
|-------------------|---|
| AMP | = 2-amino-2-methyl-1-propanol |
| DEA | = diethanolamine |
| DGA | = diglycolamine, 2-(2-aminoethoxy)ethanol |
| DIPA | = diisopropanolamine |
| MEA | = monoethanolamine |
| MMEA | = methylmonoethanolamine |
| MOR | = morpholine |
| R ₂ NH | = primary or secondary amine |

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