

ABSORPTION OF CARBONYL SULPHIDE IN AQUEOUS PIPERAZINE

P.J.G. Huttenhuis^{1,3}, A. Mohan¹, S. van Loo¹, G.F. Versteeg²

¹Procede Group B.V. P.O. Box 328, 7500 AH, Enschede, The Netherlands

(E-mail: Patrick.huttenhuis@procede.nl)

²University of Twente, Department of Chemical Engineering P.O. Box 217, 7500 AE, Enschede, The Netherlands

³The corresponding author is ir. P.J.G. Huttenhuis, Tel: (+31) 53 489 5340; Fax: (+31) 53 489 5399, E-mail: patrick.huttenhuis@procede.nl

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INTRODUCTION

Acid gas treating has gained a wide importance over the last few decades. With the implementation of more stringent environmental regulations, the need for efficient removal of acid gases like CO₂ (carbon dioxide), H₂S (hydrogen sulphide) has increased significantly. Therefore additional effort for research in this field is inevitable. Since most of the current research activities are focused on CO₂ and H₂S removal, less attention has been paid to the removal of the substantially lesser reactive sulphur species like e.g. COS (carbonyl sulphide), CS₂ (carbon disulphide) and RSH (mercaptans), which are also present in (industrial) gas streams. As the pipeline and environmental specifications are normally given as total amount of sulphur instead of H₂S, the removal of the latter sulphuric species becomes more and more important.

One of the most used processes in the gas treating industry is the absorption of acid (gaseous) components with aqueous alkanolamine solutions. An extensive overview of these different treating processes is given by Kohl and Nielsen (1997). For the design of gas treating equipment the gas absorption rate should be determined. This absorption rate is determined by:

- Mass transfer coefficient k_g , k_l and interfacial area a
- The physical and chemical solubility of the gaseous component
- The enhancement factor, which is determined by the reaction rate of the gaseous component with the absorption liquid

The current work is focused on the absorption kinetics of COS in aqueous piperazine solutions. This study was carried out as part of a research program which focuses on the removal of acid gases using activated aqueous amine solutions. An activated solvent basically consists of a tertiary amine in combination with a small amount of a secondary or primary amine (activator). A blend of MDEA (methyl diethanol amine)

and piperazine (a cyclic secondary amine) was found to be effective for efficient removal of CO₂ (Bishnoi 2000, Derks 2005). With this blend the advantages of a tertiary amine (high capacity, cheap, stable) are combined with the advantages of primary/secondary amines (high reaction rates). Because of the similarities between CO₂ and COS, it is expected that these activated amine solutions would be effective for COS removal. It must be stated, however that the reaction rate of COS with alkanolamines is about two orders of magnitude lower compared to CO₂. The reaction mechanism between COS and an aqueous solution of MDEA and piperazine is very complex. Before this mechanism can be studied in detail the reaction rate expressions for the reaction between COS and the individual amines (MDEA and PZ) must be determined independently. The reaction between MDEA and COS has been studied before (ref Littell; Al Ghawas). In this work the reaction of COS in a aqueous solution of piperazine has been studied quantitatively. Data used in this work can be used for improving the quality of rate based absorption models used in the gas treating industry.

THEORETICAL

The chemical structure of MDEA and piperazine are given in Figure 1.

From this structure it can be seen that piperazine contains two secondary nitrogen atoms and MDEA contains one tertiary nitrogen atom. For CO₂ it is known that tertiary amines do not react directly with an amine, but a catalyzed acid-base reaction occurs.

The reaction of COS with primary and secondary amines proceeds similarly to CO₂, via a zwitterion mechanism:



To determine the reaction rate of the COS-PZ system directly from absorption experiments, the reaction should be carried out in the so-called pseudo-first order regime. In this regime the following condition should be satisfied:

$$2 < Ha \ll E_{\text{COS},\infty}$$

$$\text{with, } Ha = \frac{\sqrt{k_{1,1}D_{\text{COS}}}}{K_I} \text{ and } E_{\text{COS},\infty} = 1 + \frac{D_{\text{PZ}}[\text{PZ}]_i}{\gamma_{\text{PZ}}D_{\text{COS}}[\text{COS}]_i}$$

The above relation for $E_{\text{COS},\infty}$ is only applicable for irreversible reactions. It is known that the reaction between amines and acid gases are reversible reactions, which has a decreasing effect on $E_{\text{COS},\infty}$ (Versteeg et al., 1988). This can be taken into account by applying a more severe condition on $Ha \ll E_{\text{COS},\infty}$ (usually a factor 10).

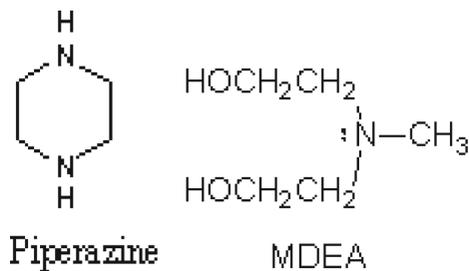


Figure 1. Chemical structure of piperazine and MDEA

EXPERIMENTAL SETUP AND PROCEDURES

Both the vapour liquid equilibrium and the absorption rate experiments have been carried out in a 1 liter stirred cell. A schematic sketch of the experimental set-up is given in Figure 2. The set-up contains the following parts:

- Büchi reactor with water bath heater and stirrer
- gas (N_2O and COS) supply vessels

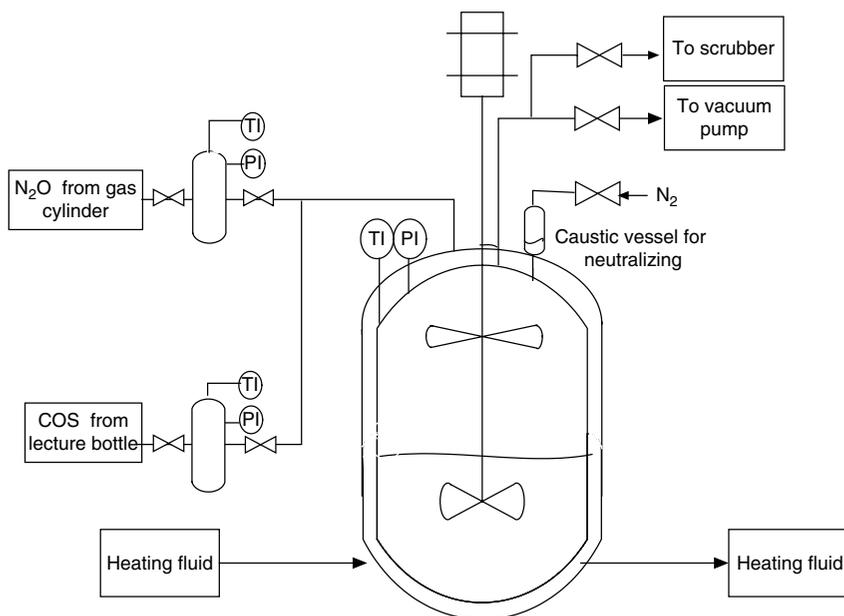


Figure 2. Sketch of the experimental set-up

- Vacuum system to remove inert gases
- Gas disposal system (Scrubber with caustic solution)

Before each experiment approximately 0.5 liter aqueous solution is fed to the reactor. The reactor is kept at the desired temperature with a water bath.

The absorption experiments of COS in aqueous piperazine solutions were carried out in the batch stirred cell reactor using a flat interface. The experiments were conducted in a temperature range of 293–313 K and piperazine concentrations between 0.1 and 1.5 M.

The gases used in this work were N₂O (purity 99+%) and COS (99.9%) and were delivered by Hoekloos and Scott respectively. Piperazine (anhydrous; purity 99+%) was delivered by Across and an aqueous alkanolamine solution was prepared by using demineralised water. A more detailed description of experimental setup and procedure can be found in Blauwhoff et al. (1984).

Knowing the total gas and liquid volume in the reactor the dimensionless gas solubility can be derived from Henry's relation.

$$m = \frac{H^E}{RT} = \frac{(P_{\text{int}} - P_{\text{eq}})}{P_{\text{eq}} - P_{\text{vap}}} \cdot \frac{V_g}{V_l}$$

Where:

m = dimensionless solubility, defined as the ratio of the liquid-phase concentration to the gas-phase concentration of the solute at equilibrium conditions.

The liquid mass transfer coefficient, k_l , was calculated using the decrease in pressure as a function of time using the following formula

$$\ln\left(\frac{P(t) - P_{\text{eq}}}{P_{\text{int}} - P_{\text{eq}}}\right) = k_l \cdot a \cdot \left(\frac{mV_l + V_g}{V_l V_g}\right) t$$

The data pressure decrease experiments of COS for both the solubility and the kinetics respectively were monitored and recorded. The physical solubility of COS in aqueous piperazine solutions were derived via the so-called COS-N₂O analogy. The solubility of COS and N₂O in pure water were taken from Al Ghawas (1988) and Versteeg (1988) respectively.

For the absorption experiments, the flux equation was used as presented below:

$$J_{\text{COS}} = m_{\text{COS}} k_l E \frac{P_{\text{COS}}}{RT}$$

The enhancement factor is equal to Hatta number if pseudo first order conditions are fulfilled.

$$Ha = \frac{\sqrt{K_{\text{app}} D_{\text{COS}}}}{k_l}$$

For pseudo first order reaction $2 < M_H \ll E_{COS,\infty}$

$$E_{COS,\infty} = 1 + \frac{D_a \min e^{RT}}{D_{COS} \gamma m_{COS} P_{COS}}$$

The diffusivity of COS in aqueous piperazine was estimated from the modified Stokes Einstein relationship given by Versteeg (1988). The diffusivity of COS in water was found using the diffusivity value in 298 K and using the same activation energy as used for diffusivity of CO₂ in water. Similarly the diffusivity of piperazine in aqueous piperazine solution was found using another modified stokes Einstein's relationship developed by Versteeg et al. (1988). The diffusivity of amine in water was estimated using the method given by Wilke-Chang (1955). The viscosities of aqueous piperazine were obtained from the experimental measurements of Derks et al. (2005).

RESULTS

In order to evaluate the experimental setup and procedures used in this work some calibration experiments were carried out. Therefore the kinetics of the reaction between COS and aqueous DEA were determined and compared with the data measured by Little et al. (1992). These experiments were also carried out in the pseudo first order regime ($2 < Ha \ll E_{COS,\infty}$). It appeared that pseudo first order constant determined by Little (1992) could be reproduced in this work within 10%. So it was concluded that the experimental set-up and procedures are suitable to measure absorption of COS in aqueous piperazine system.

After the validation experiments of COS with aqueous DEA, absorption studies for COS in aqueous piperazine were conducted at various concentrations (0.1, 0.3, 0.6 & 1.5 M) at temperatures of 293, 303 and 313 K. The experiments were conducted at a COS initial partial pressures of approximately 0.5 bar. Figure 3 shows the experimental measurements of apparent pseudo first order rate constants. The reaction order was found to be unaffected by temperature within the experimental accuracy. The reaction order in amine was about 1.6 which confirms that the reaction undergoes a proceeds via a zwitterion type of mechanism. This supports the findings of Little (1991) who observed that the reaction order of COS with secondary alkanolamines with respect to amine concentration was also between 1–2 and the reaction order with respect to COS was 1.

DISCUSSION AND CONCLUSION

During the kinetic experiments of COS in aqueous piperazine it appeared that the order of the reaction was about 1.6 in piperazine concentration. This strongly suggests that the reaction between COS and piperazine can be described by the zwitterions mechanism as given in 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

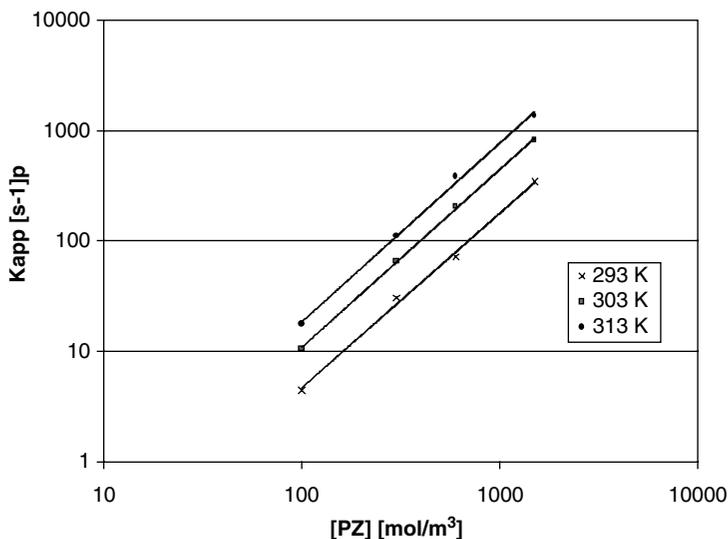


Figure 3. Pseudo first order constant for the reaction of COS in aqueous piperazine

overall forward reaction rate:

$$R_{\text{COS}} = \frac{[\text{Pz}][\text{COS}]}{\frac{1}{K_2} + \frac{1}{K_{\text{H}_2\text{O}}[\text{H}_2\text{O}] + K_{\text{R}_2\text{NH}}[\text{Pz}]}} = K_{\text{app}}[\text{COS}]$$

with

$$K_{\text{H}_2\text{O}} = \frac{K_2 K_{\text{b,H}_2\text{O}}}{K_{-1}}; K_{\text{Pz}} = \frac{K_2 K_{\text{b,Pz}}}{K_{-1}}$$

All the bases in the solution contribute to the zwitterion de-protonation rate. The contribution of bases other than H_2O and the amine itself were found to be negligible. The observed reaction rate equations were fitted using a levenberg-marquardt fitting procedure. It appeared that the overall reaction rate was a function of zwitterion de-protonation rate. This means that the zwitterion formation rate K_2 can be neglected. Figure 2 was fitted simultaneously using 2 independent variables (piperazine and water concentration). The best fit was obtained and Arrhenius plots for the de-protonation rate constants were obtained.

From these best fits the following Arrhenius equations were developed:

$$\text{Piperazine: } K_{\text{PZ}} = 9.33 \times 10^3 \exp\left(\frac{-5304}{T}\right);$$

$$K_{\text{H}_2\text{O, PZ}} = 2.0 \times 10^7 \exp\left(\frac{-8989}{T}\right) \quad \text{this work}$$

$$\text{DEA: } K_{\text{DEA}} = 1.16 \times 10^3 \exp\left(\frac{-5714}{T}\right);$$

$$K_{\text{H}_2\text{O, DEA}} = 2.45 \times 10^5 \exp\left(\frac{-9199}{T}\right) \quad \text{Littel (1992)}$$

$$\text{DGA: } K_{\text{DEA}} = 5.34 \times 10^5 \exp\left(\frac{-7346}{T}\right);$$

$$K_{\text{H}_2\text{O, DGA}} = 4.9 \times 10^6 \exp\left(\frac{-9409}{T}\right) \quad \text{Littel (1992)}$$

From the expressions described above, it can be observed that the measured activation energies for piperazine are of the same order of magnitude as DEA and DGA, being slightly higher for DGA. For $K_{\text{H}_2\text{O}}$, it can be seen that the activation energies are almost identical for all the three amines. Table 1 represents the values of the pseudo first order constants for 1 M amine solutions piperazine (this work), DEA and DGA (Littel 1992) at 293 K.

From the table above, it can be concluded that the pseudo first order constant of piperazine is significantly higher, than the ones measured for DEA and DGA. So it seems that piperazine is an interesting accelerator for the removal of COS from industrial gas streams as currently used for CO_2 removal. Further kinetic research is required to study the reaction mechanism of blended amine systems like MDEA-piperazine. Data used in this work can be used for improving the quality of rate based absorption models used in the gas treating industry.

Table 1. Pseudo first order reaction rate for 1 M amine at 293 K

1M amine	$K_{\text{app}} [\text{s}^{-1}]$	ref.
Piperazine	1.8 E-4	This work
DEA	4.3 E-6	Littel (1992)
DGA	1.0 E-5	Littel (1992)

NOTATIONS

C	Concentration [mole/m ³]
P	Pressure [bara]
D	Diffusion coefficient [m ² /s]
E	Enhancement factor [–]
E _{a,∞}	Infinity Enhancement factor of component a [–]
Ha	Hatta Number [–]
H ^E	Henry's constant [bar·m ³ /mol.Kelvin]
J _A	Molar flux of component A from gas to liquid phase [mole/m ² /s]
k _{app}	Apparent reaction constant for a Pseudo- first order reaction. [s ⁻¹]
k	Mass transfer coefficient [m/s]
m	Distribution coefficient (C _l /C _g) [–]
A	Area of interface [m ²]
N	Stirrer speed [rpm]
V	Volume [m ³]
T	Temperature [Kelvin]
R	Gas constant [8.314e-05 bar·m ³ /mol·K]
B	Base [–]

SUBSCRIPTS

Int	Initial
L	Liquid
G	Gas
Eq	At equilibrium conditions
App	Apparent

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