

Physical Solubility and Diffusivity of Carbonyl Sulfide in Aqueous Diethanolamine

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This paper reports on an experimental study of the absorption of COS in a secondary amine diethanolamine. The primary objectives were to investigate an analogy between N₂O and COS, thereby allowing an estimation of the physical solubility and diffusivity of the sulfur gases in the reacting amine solutions. The solubilities and diffusivities of N₂O and COS in 5~25% aqueous polyethylene glycol at 25°C were measured. The results appeared to verify the use of an N₂O-COS analogy for estimating the solubility and diffusivity of COS in aqueous solutions of alkanolamines up to an approximate 25 weight % concentration. The mean deviation of the N₂O analogy relative to the measured solubilities was 3.7%, and the mean deviation between the analogy and the measured diffusion coefficients using the experimental values for H_{COS}/PEG was 14.6%.

Key words : solubility, diffusivity, N₂O analogy method, alkanolamines

1. Introduction

The removal of acid gas impurities like H₂S, COS, and CS₂ is an important process in the treatment of natural gas, synthesized gas, and petrochemicals. Depending on where it is produced, natural gas contains varying amounts of CO₂, H₂S, COS, and CS₂. H₂S is the most common sulfur species in natural gas, however, it is usually accompanied by COS and other sulfur compounds like CS₂. These sulfur species are toxic plus corrosive to pipelines and other processing equipment. As such, there are usually stringent pipeline specifications regulating the concentrations of these sulfur species; a content of below 4 ppm is often required.

The most common way of removing acid gas compounds is by absorption in alkanolamines. Industrially, the most common amines for acid gas removal are primary amine monoethanolamine (MEA), secondary amine diethanolamine (DEA), and tertiary amine methyldiethanolamine (MDEA). These alkanolamines are normally used in aqueous solutions, however, other solvents, like sulfinol in

the Shell Sulfinol process, are also used.

Although the chemical and physical properties of CO₂ and H₂S in alkanolamines have been studied for years by various researchers, very little attention has been paid to COS. Sharma¹⁾ conducted a brief study on the kinetics of COS absorption in different amines, however, this data is limited to one temperature and concentration. Littel et al.²⁾ also studied the physical properties and chemical kinetics of COS in various amines, while Al-Ghawas³⁾ investigated the absorption of COS in MDEA.

Much effort has been focused on identifying a process which can selectively absorb sulfur compounds, yet not CO₂, as the removal of CO₂ is often disadvantageous from a technical and economic point of view. The reaction between H₂S and alkanolamines is virtually instantaneous, whereas the reaction rate of CO₂ is finite. In primary and secondary amines, CO₂ reacts directly and forms carbamates. However, in tertiary amines, CO₂ does not react directly due to a lack of vacant N-H bonds in the amine. As a result, the reaction between tertiary amines and CO₂ is relatively slow.

For this reason, tertiary amines, such as MDEA, have been successfully utilized for achieving the selective removal of H₂S from gases containing CO₂. However, since COS reacts much more slowly with all alkanolamines than CO₂, the efficiency of COS removal in the H₂S selective absorption processes is far too low.

Accordingly, to properly model and design gas purification equipment, fundamental physical properties, including physical solubility and diffusivity, are required. In addition, the chemical reaction rates between the acid gas and the absorbing liquid are of crucial importance, and these properties differ relative to the amine species and temperature. As such, the purpose of the current research presented was to obtain kinetic data for the absorption of carbonyl sulfide in aqueous solutions of DEA over a temperature range of 25-75°C.

2. Materials and Methods

2.1. Solubility experiments

Solubility measurements were carried out in a modified Zipperclave reactor. The apparatus of the reactor, as shown in Figure 1, consisted of a 1-liter stainless steel cylindrical tank with an air-driven magnetically coupled stirrer on the top. There were also inlet gas and liquid valves plus a connection to a vacuum pump. A type J thermocouple inserted in the cell measured the temperature to an accuracy of $\pm 0.1^\circ\text{C}$. The pressure was measured by an Omega pressure transducer, with an accuracy of ± 0.02 psi. Initially, a weighed sample of approximately 500 g liquid was sucked into the cylinder. The cell was then closed and the temperature adjusted and maintained at the desired temperature using two external heating jackets. Next, a vacuum was applied to the cell and the stirrer turned on. After 2-3 minutes, the vacuum and stirrer were turned off and the system was allowed to reach a vapor-liquid equilibrium. The pressure was then measured using the pressure transducer, and recorded as the vapor pressure of the liquid in the cell, P_v . The gas inlet was opened and the gas injected slowly in order to avoid any rippling of the liquid surface. Before entering the Zipperclave reactor, the gas line was run through

a metal coil immersed in an external waterbath maintaining the same temperature as in the cell. The gas flow was stopped when the total pressure in the cell reached an arbitrary value within a range of 5-10 psi above atmospheric pressure. The new pressure was recorded as the initial pressure, P_i . The system was then stirred for 5-10 minutes until the pressure reached a constant value and a gas-liquid equilibrium was assumed. The new pressure reading was then recorded as the final pressure, P_f . Thereafter, Henry's constant was calculated using the following equation:

$$H = \frac{(P_f - P_v)V_l}{(P_i - P_f)V_g} RT \quad (1)$$

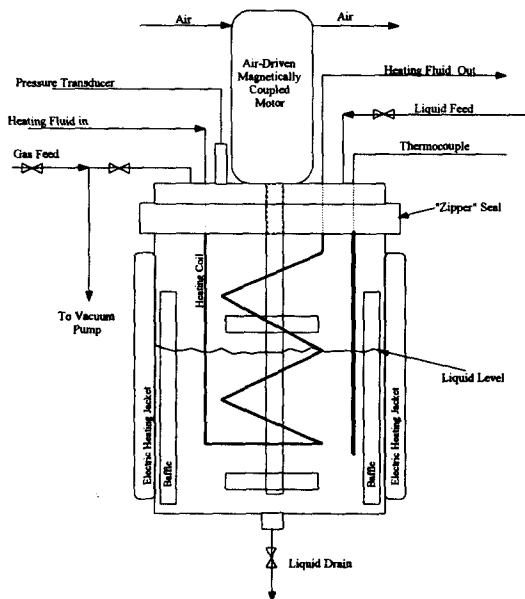


Fig. 1. Zipperclave reactor.

The pressures were determined as explained above. For the COS and N₂O solubility measurements, the gas was injected from pressurized gas cylinders. At temperatures higher than 25°C, the Zipperclave reactor was kept inside a constant temperature box, equipped with heatguns connected to a thermostat. The temperature in the box was maintained at the same level as in the cell. This enhanced the temperature control inside the cell and stabilized the pressure transducer

reading, which is sensitive to external temperature changes. Each data point was the result of at least two parallel runs.

2.2. Diffusivity experiments

The wetted sphere absorber used in this work was the same as previously described by Al-Ghawas³. The absorption chamber consisted of a 31 cm-long, 7.6 cm-inner-diameter glass cylinder and was enclosed by a temperature control jacket consisting of a 31 cm-long, 16.5 cm-inner-diameter glass cylinder. These two cylinders were connected by two stainless steel flanges, the ends of which were sealed with a GoreTex sealant. The sphere itself was made of a 3.76 cm-diameter hastelloy ball, which was mounted on a 0.4 cm-diameter rod of the same material. The rod hung from the top of the chamber, 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, 10 cm-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 used for the entry of the gas feed, whereas the other was connected to a suction flask and was used for draining the liquid flowing over the receiver tube during the start-up of the experiment.

The waterjacket surrounding the absorption chamber was connected to a circulating constant temperature waterbath, and both the liquid and the gas feed passed through the coils inside this jacket. The temperature inside the reaction chamber was measured using an electronic thermocouple, and the temperature inside the absorption chamber was maintained within $\pm 0.3^\circ\text{C}$ of the desired temperature. The setup used for the diffusion experiments with N_2O and COS is shown in Figure 2. The COS and N_2O gas was supplied from pressurized gas cylinders. The gas flowed from the cylinder through a water saturation bottle before entering the cell through a coil immersed in the water jacket. A soap bubble meter was connected to the top of the reaction chamber, which then led to a 1.2 cm-diameter, 12 meter-long PVC coil.

All experiments were carried out at atmospheric pressure. De-ionized water was used for all

experiments. The PEG was obtained from Fischer chemicals, and was of laboratory grade. The nitrous oxide was purchased from Puritan-Bennet and was of 99.99% purity. The COS was obtained from Aldrich Chemicals and had a minimum purity of 96%.

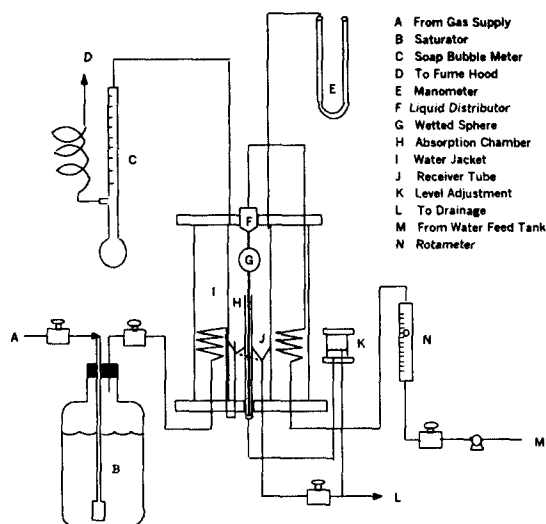


Fig. 2. Wetted sphere absorber as used for COS and N_2O experiments.

3. Results and Discussion

3.1. N_2O analogy

Since COS reacts chemically with amine solutions, the purely physical solubility and the diffusivity of such gases in amines can not be determined directly. Clarke⁴ showed that due to the similarity in the molecular shape and weight of CO_2 and N_2O , the relative change in solubility and diffusivity in water and alkanolamines remains fairly constant with the same temperature. This can be expressed as:

$$\left(\frac{H_{\text{N}_2\text{O}}}{H_{\text{CO}_2}} \right)_{\text{amine}} = \left(\frac{H_{\text{N}_2\text{O}}}{H_{\text{CO}_2}} \right)_{\text{water}} \quad (2)$$

$$\left(\frac{D_{\text{N}_2\text{O}}}{D_{\text{CO}_2}} \right)_{\text{amine}} = \left(\frac{D_{\text{N}_2\text{O}}}{D_{\text{CO}_2}} \right)_{\text{water}} \quad (3)$$

Solubility measurements of CO_2 and N_2O in aqueous solutions of non-reacting organic solvents

were performed by Laddha et al.⁵⁾, and they found that the ratio of the gas solubilities remained constant with varying concentrations. Haimor and Sandall⁶⁾ absorbed CO₂ in MDEA using very short contact times in a laminar jet apparatus to eliminate any chemical reaction. As a result, they were able to measure the group \sqrt{D}/H , and the results agreed well with the predicted values from the N₂O analogy. This analogy is now widely used for the estimation of the Henry's constants and diffusion coefficients of CO₂ in alkanolamines, plus various researchers have reported data on the solubility and diffusivity of N₂O in water and amine solutions.

Al-Ghawas³⁾ suggested that a similar N₂O analogy is applicable to COS absorption in aqueous solutions of MDEA. This COS-N₂O analogy can be expressed as:

$$\left(\frac{H_{N_2O}}{H_{COS}}\right)_{amine} = \left(\frac{H_{N_2O}}{H_{COS}}\right)_{water} \quad (4)$$

$$\left(\frac{D_{N_2O}}{D_{COS}}\right)_{amine} = \left(\frac{D_{N_2O}}{D_{COS}}\right)_{water} \quad (5)$$

The validity of this analogy has been supported by measuring the diffusivity constants and Henry's constants of N₂O and COS in water and in 15.5% aqueous ethylene glycol. The difference between the H_{N_2O}/H_{COS} ratios measured in the glycol solution and in water was found to be lower than the experimental error. Furthermore, the use of the N₂O-COS analogy in MDEA solutions was verified by the direct absorption of COS in MDEA, utilizing very short contact times in a liquid jet absorber to eliminate any chemical reaction. The group \sqrt{D}/H compared well to the values predicted from the N₂O analogy. Littel et al.²⁾ further investigated the analogy between COS and N₂O. As a result, solubility data have been presented for COS in aqueous ethylene glycol, sulfolane, and water, and for N₂O in solutions of MDEA, ethylene glycol, and sulfolane, demonstrating that the N₂O analogy can correctly predict the solubilities of COS in aqueous solutions of ethylene glycol and sulfolane up to concentrations of about a 25 weight %. According to Littel et al, this justifies the use of this analogy for predicting COS solubilities in diluted aqueous amine solutions. Direct verification of the COS-N₂O analogy was provided by ab-

sorbing COS and N₂O in aqueous MDEA solutions without any chemical reaction, using short contact times in a laminar film reactor. The COS absorption in solutions of 0-1 mol/L MDEA gave \sqrt{D}/H values that matched well with those obtained from the N₂O analogy.

3.2. Solubility

3.2.1. Henry's law

Henry's law predicts that the partial pressure of a gas in equilibrium with a solution is proportional to the concentration of that gas in the solution:

$$P_A = H_A C_A^* \quad (6)$$

Hence, a higher solubility gives a lower Henry's constant. If the liquid is perfectly mixed, the concentration of A is uniform; $C_A^* = C_A$.

Henry's law constant is strongly dependent on temperature, and follows the correlation

$$\log H_A = a \frac{1}{T} \quad (7)$$

where a is the constant.

Henry's constant also varies slightly relative to concentration, and the law is only valid for sparingly soluble gases at low partial pressures. Since COS and N₂O are both sparingly soluble in water, plus N₂O is the same in DEA-solutions, it is assumed that these solubilities can be effectively described using Henry's law under atmospheric or lower pressures. In order to use the N₂O analogy for calculating Henry's constant, the H for N₂O and for the acid gas in the water are both needed.

The solubility of N₂O in water at 25°C has been previously reported by a variety of researchers. Young⁷⁾ edited an IUPAC evaluation of Henry's constants for N₂O in water available in current literature, and the recommended value from this work, 41.38 atm L/mol, was used in the present study.

The solubilities of N₂O in polyethylene glycol 400(PEG) at 25°C are shown in Figure 3 and compared to the H_{N_2O/H_2O} from Young. An increase in the Henry's constant was observed relative to the concentration of PEG. The measured solubilities of COS in 0-25 weight % PEG solutions at 25°C are given in Figure 4 and compared to

the values predicted from the N₂O analogy. The solubility of N₂O in aqueous PEG solutions showed a close to linear increase in the Henry's constant relative to the PEG concentration, thereby indicating a slightly lower solubility of N₂O in the organic solvent than in water.

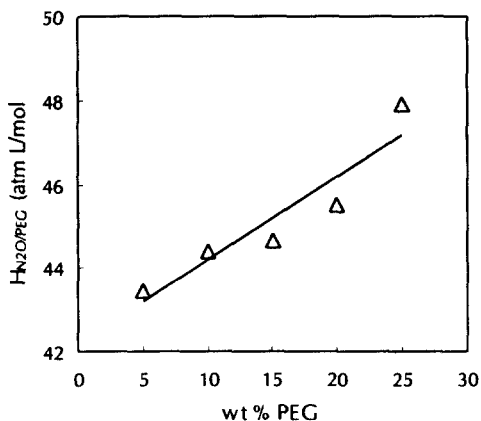


Fig. 3. Solubility of N₂O in PEG solutions at 25°C.

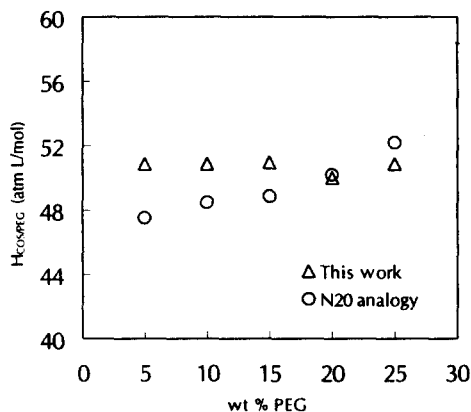


Fig. 4. Solubility of COS in aqueous solutions of PEG at 25°C.

3.3. Diffusivity

The Wilke-Chang equation is commonly used for estimating diffusivities of gases in liquids. This correlation is written as:

$$D_A = 7.4 \times 10^{-8} \left(\frac{(\psi M)^{1/2} T}{\mu V_m^{0.6}} \right) \quad (9)$$

Wilke-Chang recommend a value of 2.6 for water. To calculate diffusivities using the N₂O

analogy, the diffusivity of the current gas in water is required, plus the following references were used for all the N₂O analogy diffusion calculations.

Al-Ghawas³⁾ gives the value of $D_{\text{COS/water}}$ as $1.727 \times 10^{-5} \text{ cm}^2/\text{s}$, and presents a modified Stokes-Einstein correlation for estimating water diffusivities as a function of temperature and viscosity.

The diffusivities of gases absorbed in a solution flowing in a laminar film over a wetted sphere can be calculated using the following equation developed by Olbrich and Wild⁸⁾:

$$R_A = \left(\frac{p_i}{H} \right) m_L \left[1 - \sum_i b_i \exp(\lambda_i^2 \epsilon) \right] \quad (10)$$

$$\text{where, } \epsilon = 13.5 \left(\frac{g \cdot r_s^7}{v \cdot m_L^4} \right)^{1/3} D_A \quad (11)$$

The viscosity and density values for the DEA solutions were taken from Rinker et al⁹⁾, while the viscosities for the PEG solutions were obtained from unpublished results from Davis et al¹⁰⁾.

The partial pressures of COS and N₂O were established using Raoult's law, assuming that water was the only liquid contributing any vapor pressure in the system:

$$P_i = P_{\text{tot}} - x_{\text{H}_2\text{O}} \cdot P_{\text{H}_2\text{O}}^v \quad (12)$$

where, P_{tot} is the total pressure, $x_{\text{H}_2\text{O}}$ the mole fraction of water, and $P_{\text{H}_2\text{O}}^v$ the vapor pressure of water taken from Perry¹¹⁾.

The diffusivity of N₂O in 5-25 weight % PEG solutions at 25°C was measured. The results are shown in Figure 5 and were compared to the diffusivity of N₂O in water at 25°C as measured by Rinker. The diffusivities of COS in 0-25 weight % PEG solutions at 25°C were measured in the current study. When calculating the diffusion coefficient from the experimental raw data, a Henry's constant is required. As such, the diffusivity was calculated using the solubilities of COS in PEG obtained from the N₂O analogy. These values were then compared to the diffusivities predicted directly from the N₂O analogy. The measured diffusivities of N₂O in aqueous solutions of 5-25 weight % PEG at 25°C showed a close to hyperbolic decrease relative to the PEG concentration, as shown in Figure 6. This signifies a lower diffusivity in the organic solvent than in water. These results match well with the diffusivity

of N_2O in pure water, as previously measured by Rinker⁹.

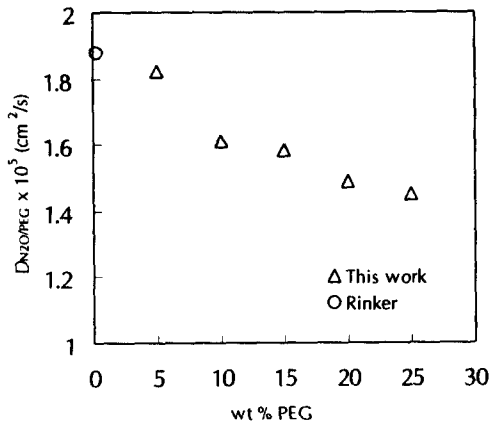


Fig. 5. Diffusion coefficients of N_2O in aqueous PEG solutions at 25°C.

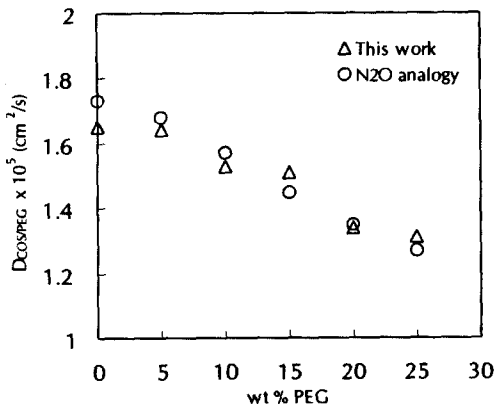


Fig. 6. Diffusion coefficients of COS in aqueous PEG solutions at 25°C.

4. Conclusion

Based on the data from the current study, the N_2O analogy predicted an increase of 15% in the Henry's constant from pure water to a 25 weight % PEG solution. The solubilities of COS in PEG solutions as measured in this work appeared to be close to constant with an increasing PEG concentration up to 25 weight %. The mean deviation of the N_2O analogy relative to the measured solubilities was 3.7%, which was lower than the predicted maximum error of 5% for the solubilities

predicted using the N_2O analogy.

The diffusivities of COS in 0-25% solutions of PEG at 25°C were calculated using the Henry's constant from both the experimental results of COS in PEG solutions and the N_2O analogy, based on the diffusivity of COS in water as given by Al-Ghawas. With the exception of the data point for 20% PEG, the resulting diffusion coefficients matched well with the values predicted directly using the N_2O -COS diffusivity analogy. The maximum experimental error for the diffusion measurements was previously estimated by Rinker at 14%. Accordingly, since the mean deviation between the analogy and the measured diffusion coefficients using the experimental values for $H_{COS/PEG}$ was 14.6%, this was less than the sum of the two above maximum errors.

Nomenclature

b_i, λ_i constants

C_A^* concentration of gas at surface of solution, mol/l

D diffusion coefficient, cm²/s

g acceleration of gravity, cm/s²

H = Henry's constant, atm cm³/mol

H_A = Henry's law constant for considered gas and liquid, atm L/mol

M = molecular weight of liquid

m_L = liquid flow rate, cm³/s

n = kinematic viscosity, cm²/s

P_A = partial pressure of gas species i , atm

p_i = partial pressure of gas, atm

R = ideal gas constant, 0.08205 atm L/mol K

R_A = rate of absorption, mol/s

r_s = radius of sphere, cm

T = absolute temperature, K

V_l = liquid volume, L

V_g = vapor volume, L

V_m = molal volume of gas, cm³/mol

μ = liquid viscosity, cP

ψ = association parameter

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