

## Solubility and Diffusivity of CS<sub>2</sub> in DEA Solution

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An experimental study of the absorption of CS<sub>2</sub> in the secondary amine diethanolamine(DEA) was performed in this work. The primary objectives were to investigate an analogy between N<sub>2</sub>O and CS<sub>2</sub>, permitting estimation of the physical solubility and diffusivity of the sulfur gases in the reacting amine solutions. The solubilities of CS<sub>2</sub> in water at 25, 40 and 60°C has been measured. The data show fair agreement with previous literature values. The solubility of CS<sub>2</sub> in 5-25 weight % polyethylene glycol has been measured in order to investigate a possible analogy between CS<sub>2</sub> and N<sub>2</sub>O.

The diffusivities of CS<sub>2</sub> in water and the reaction rate between CS<sub>2</sub> and DEA has been measured at 25 and 40°C, using a wetted sphere apparatus operated at approximately 1/3 atmospheres pressure, which is a previously untried method.

Key words: CS<sub>2</sub>, Solubility, Diffusivity, N<sub>2</sub>O analogy method, Diethanolamine(DEA)

### 1. Introduction

The removal of acid gas impurities like H<sub>2</sub>S, COS, and CS<sub>2</sub> 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 CO<sub>2</sub>, H<sub>2</sub>S, COS, and CS<sub>2</sub>. H<sub>2</sub>S is the most common sulfur species in natural gas, however, it is usually accompanied by COS and other sulfur compounds like CS<sub>2</sub>. These sulfur species are toxic and 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.

Park<sup>1,2)</sup> studied solubility of CO<sub>2</sub> and N<sub>2</sub>O with MDEA. Park et al.<sup>3)</sup> also have studied on the kinetics of the reaction of aqueous MEA with COS. Sharma<sup>4)</sup> conducted a brief study on the kinetics of carbonyl sulfide absorption in different amines, however, this data is limited to one temperature and concentration. Littel et al.<sup>5)</sup> studied the physical properties and chemical kinetics of carbonyl sulfide in various amines, while Al-Ghawas<sup>6)</sup> investigated the absorption of carbonyl sulfide in MDEA. No literature has been found on the physical or chemical properties of CS<sub>2</sub> in alkanolamines.

The reaction between H<sub>2</sub>S and alkanolamines is virtually instantaneous, whereas the reaction rate of CO<sub>2</sub> is finite. In primary and secondary amines, CO<sub>2</sub> reacts directly and forms carbamates. In tertiary amines, however, CO<sub>2</sub> does not react directly due to lack of vacant N-H bonds in the amine. Therefore the reaction between tertiary amines and CO<sub>2</sub> is relatively slow. For this reason, tertiary amines like MDEA have successfully been utilized for achieving selective removal of H<sub>2</sub>S from gases containing CO<sub>2</sub>. However, carbonyl sulfide and CS<sub>2</sub> react much

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slower with all alkanolamines than  $\text{CO}_2$ , hence the efficiency of carbonyl sulfide and  $\text{CS}_2$  removal in  $\text{H}_2\text{S}$  selective absorption processes will be far too low.

In order to properly model and design gas purification equipment, fundamental physical properties like physical solubility and diffusivity are needed. Also of crucial importance are the chemical reaction rates between the acid gas and the absorbing liquid. These properties differ with amine species and temperature. The purpose of the research presented in this thesis is to obtain kinetic and thermodynamic data for the absorption of carbonyl sulfide and  $\text{CS}_2$  in DEA over the temperature range of 25-75°C.

## 2. Materials and Methods

### 2.1. Solubility Measurements

Solubility measurements were carried out in a modified Zipperclave reactor. The apparatus of the reactor, as shown in Fig. 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  $\pm 0.02$  psi. Initially, a weighed sample of approximately 500g 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:

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

The  $\text{CS}_2$  vapor was supplied from a round flask with stirrer and thermometer, immersed in a constant temperature water bath. A vacuum pump was connected to the  $\text{CS}_2$  line, and this connection was close to the cell inlet in order to remove all air from the vapor inlet line.

At temperatures higher than 25°C, the Zipperclave reactor was kept inside a constant temperature box, equipped with heat guns connected to a thermostat. The temperature in the box was held at the same level as in the cell. This enhanced temperature control inside the cell, and stabilized the pressure transducer reading, which is sensitive to external temperature changes. When doing solubility measurements with  $\text{CS}_2$ , the higher temperature in the box prevented condensation of  $\text{CS}_2$  in the gas feed line, and thus permitted higher temperature and pressure

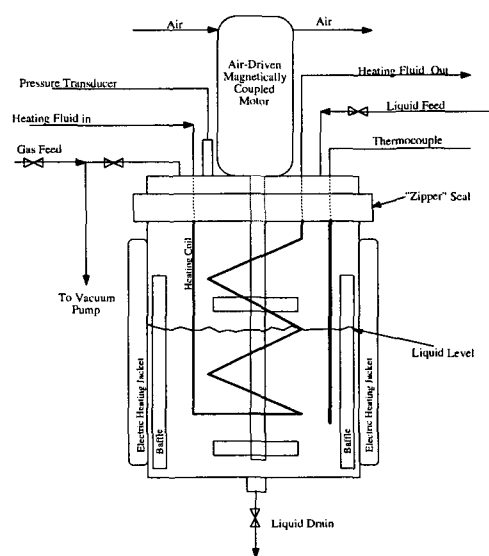


Fig. 1. Zipperclave reactor.

of the CS<sub>2</sub> vapor.

Each data point is the result of at least two parallel runs. De-ionized water was used for all experiments. The Polyethylene glycol was obtained from Fischer chemicals, and was of laboratory grade. The nitrous oxide was of 99.9 % purity. The CS<sub>2</sub> was a minimum purity of 96% and 99.8 %, respectively.

## 2.2. Diffusivity Measurements

The diffusivity measurements for CS<sub>2</sub> were carried out in the same wetted sphere absorber as the experiments for COS and N<sub>2</sub>O, but the setup and operation was slightly different, as detailed below. A schematic of the experimental setup for the CS<sub>2</sub> experiments is shown in Fig. 2.

CS<sub>2</sub> is a liquid at atmospheric pressure and ambient temperature, so in order to determine gas absorption kinetics, the wetted sphere apparatus assembly was modified for operation under vacuum. CS<sub>2</sub> vapor was supplied from a round flask immersed in a water bath at 19°C containing liquid CS<sub>2</sub>. The CS<sub>2</sub> was impelled by a stirrer, in order to improve the heat transfer from the waterbath and such keeping the temperature as constant as possible. A mercury thermometer immersed in the round flask measured the temperature in the solution. The CS<sub>2</sub> container was connected to a soap bubble meter, which led directly to an inlet at the top of the absorption chamber. A pressure transducer was connected to the top of the cell.

The solution running out of the absorption chamber, through the leveling device, entered a 20 liter bottle with a tight rubber stopper. The large volume flask was chosen to minimize the pressure change as the liquid level in the bottle increases. Connected to the liquid collecting bottle was a line to a vacuum pump, and a line connecting it to the leveling device in order to maintain equal pressure in these two vessels, giving a steady liquid flow.

Initially, the surge tank was filled 5/6 full with liquid, and the pump valve was closed. The vacuum pump was turned on and ran for approximately 10 minutes to remove air and fill the cell with CS<sub>2</sub> vapor. When vacuum was applied, liquid from the surge tank was sucked into the chamber until the pressure in the tank equaled the pressure in the cell. The liquid

level in the surge tank was now approximately 3/4 of maximum, which gave a good damping of oscillations from the pump, but at the same time allowed reasonably fast adjustment of the liquid flow rate.

The vapor pressure of CS<sub>2</sub> in the cell was monitored by a pressure transducer. When pressure was constant, and the soap bubble meter showed no gas flow between the cell and the CS<sub>2</sub> container, the liquid flow was started. The liquid flow rate was controlled by the pump and the valve on the liquid inlet line. In order to get the sphere completely wet, the liquid flow rate was kept high in the beginning, but once even liquid distribution over the sphere was achieved, the flow rate was turned down to the desired value, usually around 0.7 ml/s. As CS<sub>2</sub> gas was being absorbed in the liquid flowing over the sphere, vapor flowed from the CS<sub>2</sub> liquid container because of the pressure difference. Because the temperature in the container was constant, the vapor pressure over the CS<sub>2</sub> liquid remains the same. The absorption rate was measured by the soap bubble meter on the CS<sub>2</sub> vapor line.

The rotameter reading was registered, and the actual liquid flow rate was determined by running the same solution through the cell at atmospheric pressure with the same rotameter value. The flow rate was then measured by filling a container and recording the weight and

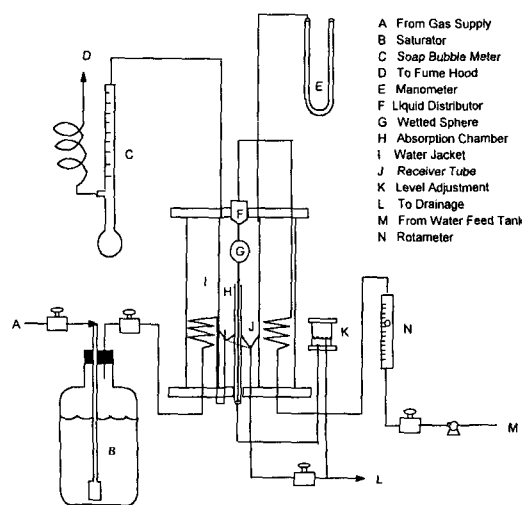


Fig. 2. Wetted sphere absorber as used for CS<sub>2</sub> experiments.

time. The liquid was degassed by stirring under vacuum for at least 15 minutes before use, which prevented formation of small gas bubbles when flowing over the sphere under vacuum, and such breaking of the laminar flow. De-ionized water was used for all experiments.

### 3. Results and Discussion

#### 3.1. Solubility

The physical solubility of a gas in aqueous solutions is essential in the modeling of gas absorption towers, and also in the analysis of kinetic rate. 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

$$P_A = H_A C_A^* \quad (2)$$

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

$$\log H_A = a \frac{1}{T} \quad (3)$$

where,  $a$  is the constant.

Henry's constant is slightly variable with concentration, and the law is only valid for sparingly soluble gases at low partial pressures. Since  $\text{CS}_2$  and  $\text{N}_2\text{O}$  are sparingly soluble in water, and  $\text{N}_2\text{O}$  the same in DEA-solutions, it is assumed that these solubilities can be validly described by Henry's law.

The solubility of  $\text{CS}_2$  in water has been measured at temperatures of 25, 40 and 60°C.

Table 1. Solubility data for  $\text{CS}_2$  in water

T(°C)	$H_{\text{CS}_2/\text{water}}$ (atm · L/mol)		
	This work	Elliot(1989)	Mc Kee(1941)
0.5		4.9	
8		7.6	
16		10.7	
24		14.4	
25	25.6		
32		22.0	
37			31.8
40	38.5		
60	68.8		

The results are compared to those of Elliott<sup>7)</sup> and Mc Kee<sup>8)</sup> in Table 1. Fig. 3 presents all  $\text{CS}_2$  solubility data as a function of inverse temperature.

The measured solubilities of  $\text{CS}_2$  in aqueous solutions of Polyethylene glycol are shown in Fig. 4 and compared to those calculated by the  $\text{N}_2\text{O}$  analogy. The analogy predicts a slight rise in Henry's constant, while the experimental data, although being quite scattered, indicate an increase in solubility with higher Polyethylene glycol concentration, giving a lower Henry's constant.

The value for  $H_{\text{CS}_2/\text{water}}$  at 25°C is approximately 75 % higher than that reported by Elliot at 24°C for a liquid concentration of  $5 \times 10^{-4}$  mol/L solutions. However, Elliot did solubility measurements for different  $\text{CS}_2$  concentrations at this temperature, and found that the Henry's constant apparently varied significantly with  $\text{CS}_2$

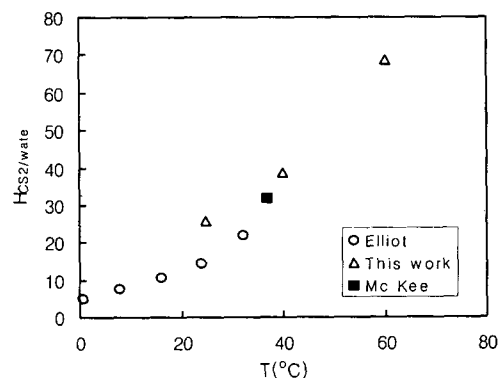


Fig. 3. Temperature dependence of  $\text{CS}_2$  solubility in water.

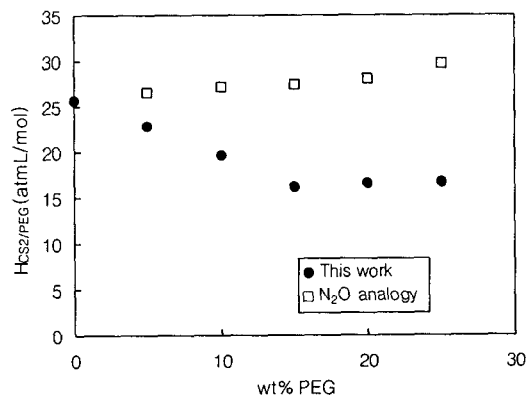
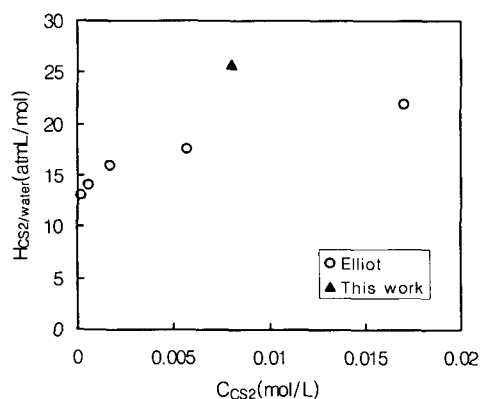


Fig. 4. Solubility of  $\text{CS}_2$  in Polyethylene glycol solutions.

Table 2. CS<sub>2</sub> concentration dependence of Henry's constant

C <sub>CS<sub>2</sub></sub> (mol/L)	H <sub>CS<sub>2</sub>/water</sub> (atm L/mol)	
	Elliot(24 °C)	This work(25 °C)
1.70 × 10 <sup>-2</sup>	21.93	25.8
8.00 × 10 <sup>-3</sup>		
5.67 × 10 <sup>-3</sup>	17.55	
1.70 × 10 <sup>-3</sup>	16.08	
5.67 × 10 <sup>-4</sup>	14.14	
1.70 × 10 <sup>-4</sup>	13.16	

Fig. 5. Concentration of CS<sub>2</sub> with Henry's constant.

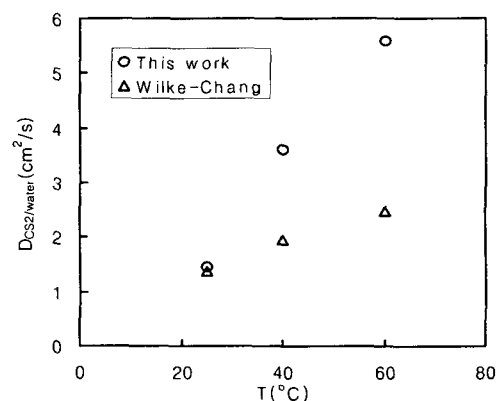
concentration as shown in Table 2 and Fig. 5.

Ideally, the Henry's constant is valid for infinitely dilute solutions, and at higher concentrations, deviations may occur. Although all the CS<sub>2</sub> concentrations considered here are low, the data in Table 2 may indicate that H changes with concentration of dissolved CS<sub>2</sub>. The measurements from this work also gives a straight line in Fig. 3, which supports the consistency of the data.

The solubilities of CS<sub>2</sub> in Polyethylene glycol solutions as presented in Fig. 4 indicate an increase in solubility with Polyethylene glycol concentration, giving a lower Henry's constant for the higher concentrations of Polyethylene glycol which is the opposite trend of what the N<sub>2</sub>O analogy predicts. This behavior has been shown to be the case for H<sub>2</sub>S by Rinker<sup>9</sup>. The results for concentrations of 0-15% Polyethylene glycol show a close to linear behavior. The point for 20% PEG is much higher, indicating a substantial random experimental errors in the experiment.

Table 3. Diffusion coefficients for CS<sub>2</sub> in water at 25, 40 and 60 °C

T(°C)	D <sub>CS<sub>2</sub>/water</sub> (cm <sup>2</sup> /s)	
	This work	Wilke-Chang correlation
25	1.47 × 10 <sup>-5</sup>	1.37 × 10 <sup>-5</sup>
40	3.60 × 10 <sup>-5</sup>	1.96 × 10 <sup>-5</sup>
60	5.58 × 10 <sup>-5</sup>	2.48 × 10 <sup>-5</sup>

Fig. 6. Diffusion coefficients of CS<sub>2</sub> in water.

### 3.2. Diffusivity

The Wilke-Chang<sup>10</sup> equation is commonly used for estimating diffusivities of gases in liquids. This correlation is written as:

$$D_A = 7.4 \times 10^{-8} \left( \frac{(\phi M)^{1/2} T}{\mu V_m^{0.6}} \right) \quad (4)$$

Wilke and Chang recommends the value of to be 2.6 for water. The molal volume for CS<sub>2</sub> was found using the Le Bas additive method, as described by Dankwerts<sup>11</sup>, giving a value of 66 cm<sup>3</sup>/mol.

The diffusivity of CS<sub>2</sub> in water for 25, 40 and 60 °C was measured and is compared to the values estimated by the Wilke-Chang correlation in Table 3 and the results are shown in Fig. 6. The diffusivity measurements for CS<sub>2</sub> in water were performed using the wetted sphere under vacuum. This method is new, and opens for new random errors in the experiment. A leak of air into the cell would severely affect the measured gas absorption rates. The cell was extensively tested for leaks before operation. However, a small leak was at one point detected in the CS<sub>2</sub> container. The observed leak was stopped, but even a small leak in this con-

tainer would increase the observed absorption rate, as recorded from the soap bubble meter. Rinker found that the Wilke-Chang correlation predicted diffusivities for  $N_2O$  in solutions of DEA and MDEA within 19 % of the experimental results.

It was assumed that the liquid  $CS_2$  in the container kept constant temperature, giving a constant vapor pressure of  $CS_2$ . This requires that the heat transfer from the waterbath is faster than the loss of heat due to evaporation of  $CS_2$  as vapor in the wetted-sphere cell is absorbed. The temperature was monitored by a mercury thermometer with an accuracy of  $0.1^\circ C$ , and no change in temperature was observed during a run.

#### 4. Conclusions

The solubilities of  $CS_2$  in water at 25, 40 and  $60^\circ C$  has been measured. The data show fair agreement with previous literature values. The solubility experiments of  $CS_2$  in PEG do not give any conclusive results as to whether the  $N_2O$  analogy is valid or not. Lacking any other reliable methods to predict  $CS_2$  solubilities in DEA, the  $CS_2$ - $N_2O$  analogy has been used in this work. Since the analogy predicts a change in Henry's constant of no more than 15% for the case of 25 % DEA, the error resulting from this method is considered as acceptable in this work.

The diffusivities of  $CS_2$  in water and the reaction rate between  $CS_2$  and DEA has been measured at 25, 40 and  $60^\circ C$ , using a wetted sphere apparatus operated at approximately 1/3 atmospheres pressure, which is a previously untried method. As can be seen in table 3, the measured diffusion coefficient for  $25^\circ C$  agrees well with the value predicted by the Wilke-Chang equation, while the data point for 40 and  $60^\circ C$  is 85 % higher than the predicted value. Seen in light of this, it seems likely that a random experimental error, perhaps a leak, has disrupted the diffusivity measurement for  $40^\circ C$ . Therefore, it is recommended to repeat these diffusivity measurements.

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#### Nomenclature

- $C_A^*$  = concentration of gas at surface of solution, mol/L  
 $D_A$  = diffusion coefficient,  $cm^2/s$   
 $D_{A1}$  = diffusion coefficient,  $cm^2/s$   
 $D_{A2}$  = diffusion coefficient,  $cm^2/s$   
 $H$  = Henry's constant, atm  $cm^3/mol$   
 $H_A$  = Henry's law constant for considered gas and liquid, atm L/mol  
 $M$  = molecular weight of liquid  
 $P_A$  = partial pressure of gas species  $i$ , atm  
 $P_i$  = partial pressure of gas, atm  
 $R$  = ideal gas constant, 0.08205 atm L/mol K  
 $T$  = absolute temperature, K  
 $V_l$  = liquid volume, L  
 $V_g$  = vapor volume, L  
 $V_m$  = molal volume of gas,  $cm^3/mol$   
 $\mu$  = liquid viscosity, cP  
 $\phi$  = association parameter

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