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Solubility and Diffusivity of CS_2 in DEA Solution

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1. Introduction

The removal of acid gas impurities like H2S, COS, and CS_2 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_2, H_2S, COS, and CS_2. H_2S is the most common sulfur species in natural gas, however, it is usually accompanied by COS and other sulfur compounds like CS_2. 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 studied solubility of CO_2 and N_2O with MDEA. Park et al. also have studied on the kinetics of the reaction of aqueous MEA with COS. Sharma 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. studied the physical properties and chemical kinetics of carbonyl sulfide in various amines, while Al-Ghawas investigated the absorption of carbonyl sulfide in MDEA. No literature has been found on the physical or chemical properties of CS2 in alkanolamines.

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 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 ±0.1℃. The pressure was measured by an Omega pressure transducer, with an accuracy of ±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, Pi. The system was then stirred for 5-10 minutes until the pressure reached a constant value and a gas-liquid equilibrium was assumed.

2.2. Diffusivity Measurements

CS_2 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_2 vapor was supplied from a round flask immersed in a water bath at 19℃ containing liquid CS_2. The CS_2 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_2 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.

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. The value for $HCS_{2/water}$ at 25℃ is approximately 75 % higher than that reported by Elliot at 24℃ for a liquid concentration of 5×10^{-4} mol/L solutions. However, Elliot did solubility measurements for different CS_2 concentrations at this temperature, and found that the Henry's constant apparently varied significantly with CS_2 concentration.

Table 1. Solubility data for CS_2 in water

C_{CS2} (mol/L)	$H_{CS2/water}$ (atm L/mol)	
	Elliot(24℃)	This work(25℃)
1.70×10^{-2}	21.93	
8.00×10^{-3}		25.8
5.67×10^{-3}	17.55	
1.70×10^{-3}	16.08	
5.67×10^{-4}	14.14	
1.70×10^{-4}	13.16	

Table 2. CS_2 concentration dependence of Henry's constant

T(℃)	$H_{CS2/water}$ (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		

3.2. Diffusivity

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

$$D_A = 7.4\times10^{-8}\left(\frac{(\phi M)^{1/2}T}{\mu V_m^{0.6}}\right)$$

Wilke and Chang recommends the value of to be 2.6 for water. The molal volume for CS_2 was found using the Le Bas additive method, as described by Dankwerts, giving a value of 66 cm^3/mol.

The diffusivity of CS_2 in water for 25, 40 and 60℃ was measured and is compared to the values estimated by the Wilke-Chang correlation in table 2.

Table 3. Diffusion coefficients for CS_2 in water at 25, 40 and 60℃

T(℃)	$D_{CS2/water}$ (cm^2/s)	
	This work	Wilke-Chang correlation
25	1.47×10^{-5}	1.37×10^{-5}
40	3.60×10^{-5}	1.96×10^{-5}
60	5.58×10^{-5}	2.48×10^{-5}

4. Conclusion

The solubilities of CS_2 in water at 25, 40 and 60℃ 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.

The diffusivities of CS_2 in water and the reaction rate between CS_2 and DEA has been measured at 25, 40 and 60℃, 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℃ agrees well with the value predicted by the Wilke-Chang equation, while the data point for 40 and 60℃ is 85 % higher than the predicted value.

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