Solubility of Carbon Dioxide and Nitrous Oxide in 50 mass % Methyldiethanolamine

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The partial pressure of carbon dioxide above a 50 mass % aqueous solution of methyldiethanolamine was measured as a function of the amount of carbon dioxide absorbed in the solution. Data were obtained over the temperature range 25 °C to 100 °C and for carbon dioxide loadings up to 0.5 mol CO_2/mol amine. Data were also obtained for the solubility of nitrous oxide in these solutions over the temperature range 25 °C to 80 °C. It is found that the solubility of nitrous oxide decreases significantly as the carbon dioxide loading increases. The data obtained in this study may be used with the nitrous oxide analogy method to estimate the physical solubility of carbon dioxide in 50 mass % methyldiethanolamine solutions as a function of carbon dioxide loading and temperature.

Introduction

Aqueous solutions of methyldiethanolamine (MDEA) are widely used in the petroleum and natural gas industries for the treatment of natural or refinery gases containing CO_2 and/or H_2S. One of the most important parameters needed to model absorption rates of CO_2 into aqueous amine solutions is the physical solubility of CO_2 in the amine solution. Since CO_2 reacts in the amine solution, its physical solubility cannot be measured directly. It is common practice to use the nitrous oxide analogy method originally proposed by Clarke[1] to estimate the physical solubility of CO_2. Since N_2O is similar to CO_2 with respect to molecular configuration, electronic structure, molecular weight, and molar volume, the effect of the amine on the physical solubility of CO_2 can be inferred from measurements with N_2O. Laddha et al.[2] verified the appropriateness of this method by measuring the physical solubilities of CO_2 and N_2O in various organic solvents. Haimour and Sandall[3] showed that predictions of physical solubility and diffusivity using the nitrous oxide analogy method can be used to predict absorption rates of CO_2 into aqueous MDEA under conditions of very short contact times where the chemical reaction does not affect the absorption rates.

The objective of the work presented here is to measure the total solubility of CO_2 in 50 mass % MDEA solutions over a wide range in temperature and CO_2 partial pressure and to measure the physical solubility of N_2O in these solutions as a function of the CO_2 loading.

Experimental Apparatus and Procedure

The solubility measurements presented here were carried out in a modified Zipperclave reactor. The reactor consists of a 1 L stainless steel cylindrical tank with an air-driven magnetically coupled stirrer on the top. There are valves for inlet of gas and liquid, and a connection to a vacuum pump. A thermocouple inserted in the cell measures the temperature to an accuracy of 0.1 K. The pressure is measured by a pressure transducer with an accuracy of 0.14 kPa.

Initially a weighed sample of approximately 500 g of liquid is sucked into the reactor. The temperature is then adjusted to the desired value through use of the external heating jackets. A vacuum is then pulled on the reactor so that the liquid exists under its own vapor pressure. This solution vapor pressure, P_v, is measured. A known quantity of CO_2, n_{CO_2}, is transferred to the reactor from a gas container of known volume

$$n_{CO_2} = \frac{V_T}{RT_a}\left(\frac{P_1}{z_1} - \frac{P_2}{z_2}\right) \qquad (1)$$

where V_T is the volume of the gas container, z_1 and z_2 are the compressibility factors corresponding to the initial pressure, P_1, and the final pressure, P_2, in the gas container before and after transferring the CO_2, and T_a is the ambient temperature. After transferring the CO_2 to the reactor, the stirrer is turned on and equilibrium is attained in about 20 min. This equilibrium pressure P_{CO_2} ($= P_{T_1} - P_v$) is measured, and the moles of CO_2 remaining in the gas phase are determined from

$$n^g_{CO_2} = \frac{V_g P_{CO_2}}{z_{CO_2} RT} \qquad (2)$$

The moles of CO_2 in the liquid are then determined from

$$n^l_{CO_2} = n_{CO_2} - n^g_{CO_2} \qquad (3)$$

The CO_2 loading in the liquid phase is defined as

$$L_{CO_2} = \frac{n^l_{CO_2}}{n_{Am}} \qquad (4)$$

where n_{Am} is the moles of MDEA in the liquid phase

$$n_{Am} = \frac{m_{MDEA}\rho V_l}{M_{MDEA}} \qquad (5)$$

where m_{MDEA} is the mass fraction of MDEA in the aqueous

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Table 1. Solubility of CO_2 in 50 mass % MDEA

CO_2 loading (mol CO_2/ mol MDEA)	P_{CO_2} (kPa)			
	$t = 25$ °C	$t = 50$ °C	$t = 75$ °C	$t = 100$ °C
0.2574	8.27			
0.2988	10.34			
0.4923	19.72			
0.0150		0.78		
0.0442		2.47		
0.0740		4.87		
0.1315		11.67		
0.1916		17.36		
0.2420		24.46		
0.3190		38.75		
0.3854		53.04		
0.4529		70.92		
0.4884		76.19		
0.0162			3.62	
0.0334			7.92	
0.0420			9.72	
0.0537			13.72	
0.0770			21.31	
0.1010			31.11	
0.1330			45.39	
0.1656			61.88	
0.1946			78.87	
0.0087				5.00
0.0164				11.40
0.0261				20.29
0.0350				30.38
0.0476				45.27
0.0656				68.45
0.0827				95.83
0.1080				140.40

solution, ρ is the solution density, V_l is the volume of liquid in the cell, and M_{MDEA} is the molecular weight of MDEA.

To measure the solubility of N_2O in the CO_2-loaded solutions, a known quantity of N_2O is transferred to the Zipperclave reactor containing the CO_2-loaded amine from a gas container. The mass of N_2O transferred is determined in the same manner as for CO_2 (see eq 1). After transferring N_2O to the reactor, the stirrer is turned on. An equilibrium is achieved after about 10 min, and the total pressure, P_{T_2}, is measured. The partial pressure of N_2O, P_{N_2O}, is calculated from

$$P_{N_2O} = P_{T_2} - P_{CO_2} - P_v \tag{6}$$

The moles of N_2O in the gas phase are determined from P_{N_2O} by

$$n^g_{N_2O} = \frac{P_{N_2O}V_g}{z_{N_2O}RT} \tag{7}$$

The moles of N_2O dissolved in the liquid are given by

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O} \tag{8}$$

We define Henry's law as

$$P_{N_2O} = H_{N_2O}c_{N_2O} \tag{9}$$

where c_{N_2O} is the concentration of N_2O in the liquid.

The Henry's law coefficient, H_{N_2O}, is calculated from eq 9 with c_{N_2O} given by

$$c_{N_2O} = n^l_{N_2O}/V_l \tag{10}$$

Experimental Results and Discussion

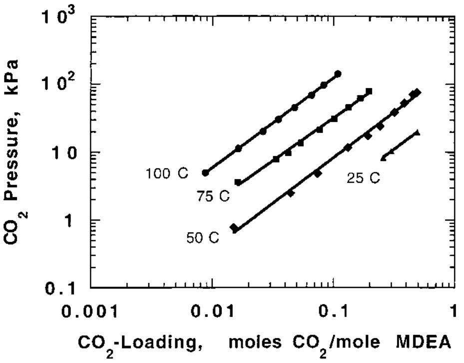

Figure 1. Solubility of CO_2 in 50 mass % MDEA solution.

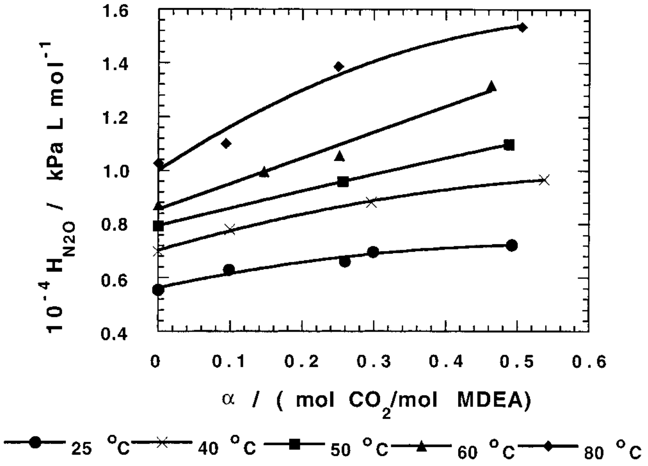

Figure 2. Henry's constant for N_2O in 50 mass % MDEA as a function of CO_2 loading.

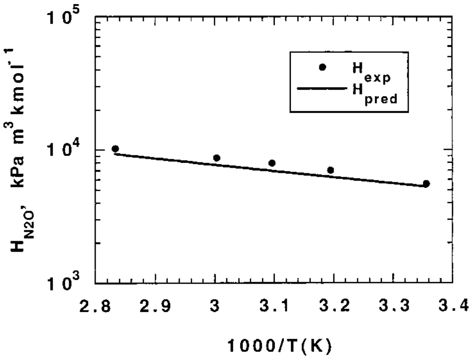

Figure 3. Comparison of the N_2O solubility measured in this work for no CO_2 loading with the correlation of Wang et al.

Table 1 gives the data for the partial pressure of CO_2 above CO_2-loaded solutions. These data are shown plotted in Figure 1. Table 2 lists the data for the solubility of N_2O, and these data are shown in Figure 2. Figure 2 shows that the solubility of N_2O in these CO_2-loaded MDEA solutions decreases significantly as the CO_2-loading increases. The solubility data for no CO_2 loading are compared to the correlation of Wang et al.[4] in Figure 3. The experimental Henry constants of this work are approximately 10% higher than those predicted from the correction of Wang et al.

In the analysis of the data for H_{N_2O} it has been assumed that, because of the low concentration of N_2O in the liquid phase, the CO_2 equilibrium is unchanged by the addition of N_2O. In another study in our laboratory with a different aqueous amine, we tested this hypothesis by varying c_{N_2O} at a constant CO_2 loading. We found that H_{N_2O} remained constant within experimental error.

Jou et al.[5] measured the total solubility of CO_2 in aqueous MDEA solutions. Their data are compared to the

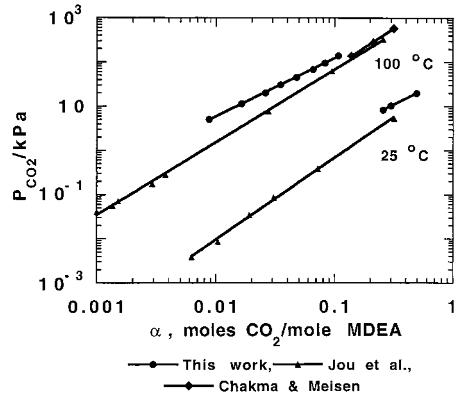

Figure 4. Comparison of the CO_2 solubility measurements of this work with the results of Jou et al. and Chakma and Meisen.

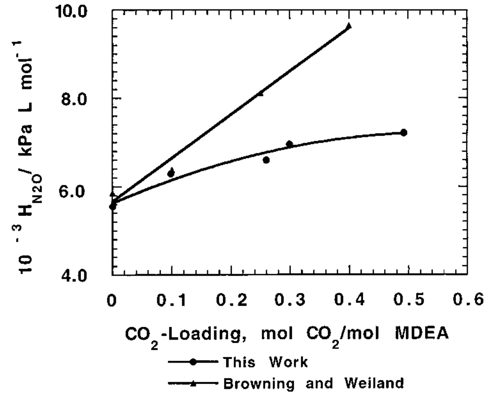

Figure 5. Comparison of N_2O solubility with data of Browning and Weiland at 25 °C.

results of this work in Figure 4 for temperatures of 25 °C and 100 °C, where the data overlap. The partial pressure deviations between the measurements of Jou et al. and this work are larger at the lower CO_2 loadings, but the agreement becomes closer at higher CO_2 loadings. Figure 4 also shows the data of Chakma and Meisen[6] for 50 mass % MDEA at 100 °C. The Chakma and Meisen data appear to lie between the results of this work extrapolated to higher CO_2 loadings and the data of Jou et al. The pressure transducers used in this work had an accuracy of 0.14 kPa. Since the CO_2 partial pressure is obtained as a difference between two pressure measurements, the estimated error in the CO_2 partial pressures reported here is ±0.28 kPa.

Figure 5 compares the N_2O solubility measurements for 25 °C with the results obtained by Browning and Weiland.[7] There is good agreement at the lower CO_2 loadings up to 0.1 mol CO_2/mol MDEA, but we find a higher N_2O solubility (lower H_{N2O}) at the higher loadings. The N_2O partial pressures measured in this work were approximately 100 kPa, and the estimated maximum error in the reported values of H_{N_2O} is less than 10%.

Table 2. Physical Solubility of N_2O in 50 mass % MDEA As a Function of CO_2 Loading

CO_2 loading (mol CO_2/	H_{N_2O} (kPa m^3 mol^{-1} × 10^{-3})				
mol MDEA)	t = 25 °C	t = 40 °C	t = 50 °C	t = 60 °C	t = 80 °C
0.0000	5549	6979	7933	8713	10273
0.0983	6288				
0.2597	6597				
0.2988	6955				
0.4923	7215				
0.0991		7803			
0.2960		8806			
0.5377		9670			
0.2566			9582		
0.4884			10977		
0.1465				9963	
0.2516				10556	
0.4631				13173	
0.0933					10992
0.2499					13865
0.5065					15346

Conclusions

In this investigation, we have measured the total solubility of CO_2 as a function of partial pressure of CO_2 in 50 mass % MDEA solutions over a wide temperature range. These data should be useful for the design of absorption columns using MDEA to remove CO_2. The nitrous oxide analogy method may be used with the H_{N_2O} data presented here to estimate the physical solubility of CO_2 as a function of temperature and CO_2 loading. The physical solubility of CO_2 is the key physicochemical property needed to predict CO_2 mass transfer rates.

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