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Solubility and Diffusivity of CO_2 in Triethanolamine Solutions

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The objective of this study was to measure directly the physical solubility and diffusivity of CO_2 in aqueous triethanolamine (TEA) solutions via the protonation method. The method is based on the protonation of TEA solutions by HCl prior to contacting the solutions to CO_2 to eliminate the solutions reactivity with CO_2. The properties were measured for concentrations of 10, 20, and 30 mass% TEA in the solution over the temperature range (20−60) °C. The volumetric and the wetted sphere methods were used to measure the solubility and diffusivity, respectively. The measured data of solubility and diffusivity were well fitted versus temperature by an exponential form. The measured properties by the protonation technique and the available literature values measured by the "N_2O analogy" method were compared. Good agreement between the two methods was found.

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1. Introduction

Natural gas, refinery gas, biogas, and synthetic gas usually contain undesirable compounds, called acid gases, like hydrogen sulfide (H_2S) and carbon dioxide (CO_2). In most cases these gases must be removed before the gas can be transported and processed. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diisoropanolamine (DIPA), and methyldiethanolamine (MDEA) are used to remove the acid gases.

Knowledge of the solubility and the diffusivity of acid gases in aqueous alkanolamine solutions, which are physical properties, are of primary importance for the prediction of mass-transfer rates in gas-treating processes and in the design of such units. These properties are needed at temperatures above ambient temperature as well as at various solution concentrations. The reaction that occurs between acid gases and alkanolamine solutions upon contacting makes the direct measurements of these properties difficult if not impossible. Because of molecular similarities between CO_2 and N_2O gases, the latter has been used to estimate CO_2 properties in reacting solutions.[1−9] This has been referred to as the "N_2O analogy ". This later has been extended to dissimilar gases such as COS and H_2S due to the lack of a method to estimate these properties.[10,11] The equations normally used to calculate the solubility and diffusivity via the N_2O analogy are[6]

$$H_{CO_2,\text{amine}} = k_1 H_{N_2O,\text{amine}} \tag{1}$$

with

$$k_1 = (H_{CO_2}/H_{N_2O})_{\text{water}} \tag{2}$$

$$D_{CO_2,\text{amine}} = k_2 D_{N_2O,\text{amine}} \tag{3}$$

with

$$k_2 = (D_{CO_2}/D_{N_2O})_{\text{water}} \tag{4}$$

where H and D are the Henry's constant and the diffusivity, respectively. Initially, k_1 and k_2 were assumed constants[1,2] regardless of the temperature, but later were evaluated as a function of temperature.[6−12] The latest correlations for k_1 and k_2 as a function of temperature was developed by Abu-Arabi et al.[12] as follows:

$$k_1 = 3.347 \exp(-272\text{K}/T) \tag{5}$$

$$k_2 = 0.688 \exp(128\text{K}/T) \tag{6}$$

The "protonation method" developed by Abu-Arabi et al.,[13] which is based on the elimination of the alkanolamine solutions reactivity with CO_2, was used in this work. The principle of this method is based on the protonation of alkanolamine solutions by hydrochloric acid (HCl) prior to contacting the solutions with CO_2. The solubility and diffusivity of CO_2 in diethanolamine solutions were determined by this method.[12] Therefore, the main objective of this research was to measure the solubility and diffusivity of CO_2 in protonated aqueous solutions of triethanolamine (TEA).

2. Experimental Procedure

2.1. Solution Preparation. The protonation method was followed in this study to prepare protonated aqueous TEA solutions. Hydrochloric acid (12 M) was added to the solutions until the end point was reached. The prepared solutions were 10, 20, and 30 mass % TEA after protonation. Reagent TEA with a purity of 98%, supplied by Across, was used. The purity of the CO_2 gas was ≥99.8%.

2.2. Solubility. The apparatus and the experimental technique used to measure the physical solubility are similar to those used by Haimour and Sandall.[7] The principal of the method is to bring a known volume of gas with a known volume of liquid. The amount of CO_2 gas absorbed in the protonated TEA solutions is measured volumetrically after equilibrium is reached between the gas phase and the solution at constant temperature and pressure. The volume of the gas absorbed is equal to the volume of liquid minus the measured change in volume.

For each solubility measurement, the absorption flask was first purged with CO_2 gas saturated with vapors of

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the desired solution at constant temperature. A predetermined volume of degassed solution, which was kept at the same temperature of the experimental run, was injected into the absorption flask. The liquid was agitated with a magnetic stirrer until there was no further change in gas volume.

The whole apparatus was kept at constant temperature inside a temperature-controlled bath within ±0.5 K. The experimental error in the reported data of solubility is <2%.

The solubility is calculated in terms of Henry's law constant as follows,

$$H_A = P_A/c_A^* \tag{7}$$

where c_A^* is the equilibrium concentration of CO_2, which was calculated from the total moles of gas absorbed in a volume of absorbing liquid. The partial pressure of CO_2 in the absorption apparatus was calculated from Raoult's law,

$$P_{CO_2} = P_{total} - x_{H_2O}P^v_{H_2O} - x_{amine}P^v_{amine} \tag{8}$$

where P_{total} is the total pressure (in this study it is atmospheric), x is the mole fraction, and P^V is the vapor pressure. The last term in eq 8 was very small for the temperature range covered in this study and was neglected. The vapor pressure of water was calculated from the following equation, which was taken from Al-Ghawas et al.:[9]

$$P^v_{H_2O}/\text{bar} = 1.33567 \times 10^6 \exp(-5243\text{K}/T) \tag{9}$$

2.3. Diffusivity. The wetted sphere apparatus used in this study is described in detail by Al-Ghawas et al.[9] To carry out the experimental runs, the solution was degassed by boiling the liquid with heating under vacuum. At the same time, a gas saturated with vapors of the desired solution was passed through the system long enough to completely flush the system of any air and fill the system with the saturated gas being absorbed. After the system was degassed and flushed, the solution was transferred to an overhead feed tank using pressurized nitrogen gas to prevent any contamination with atmospheric air. The temperature of the feed tank was held constant by a heating coil containing hot water. The solution and the gas passed through coils embedded in the water jacket surrounding the wetted-sphere absorber before entering the absorber.

Degassed solution flows by gravity through a rotameter and then enters the liquid distributor at the inlet of the absorber. Initially, the solution was pumped at a high flow rate to ensure complete wetting of the sphere surface; the flow rate was then reduced to a value such that the flow rate was in the range of 1.5 $cm^3 \cdot s^{-1}$ to achieve laminar flow conditions.

The temperature of the gas and liquid were measured to within ±0.2 K using a thermocouple located in the gas space surrounding the sphere and the liquid inlet to the sphere. The volumetric gas absorption rate was measured using a soap bubble meter. When the system reached steady state, the temperature, pressure, gas, and liquid flow rates were taken. Each run was repeated twice and the average is reported. Experimental errors were <2%.

The diffusivities of CO_2 in aqueous TEA solutions were calculated from the series solution developed by Olbrich and Wild[16] as follows,

$$R_A = Lc_A^*[1 - \sum \beta_i \exp(-\gamma_i \alpha)] \tag{10}$$

where

$$\alpha = 3.36\pi(2\pi g/3\nu)^{1/3} R_s^{7/3} L^{-4/3} D \tag{11}$$

R_A is the rate of absorption, c_A^* is the equilibrium concentration, L is the liquid flow rate, g is the acceleration of gravity, R_s is the radius of the sphere, ν is the kinematics viscosity, D is the diffusion coefficient, and β_i and γ_i are constants. An iterative procedure is required for the calculation of diffusivity from eq 10.

Table 1. Solubility of CO_2 in Protonated TEA Solutions

t	$H/(Pa \cdot m^3 \cdot mol^{-1})$		
°C	this work	Littel et al.[11]	Sotelo et al.[15,a]
		10 mass %	
20	2950	2850	2850
30	3515	3576	3590
37	3980		
40			4460
41	4265		
45		4750	
50	5011		
60	5946	6053	
		20 mass %	
20	3119	3002	
30	3761	3804	
37	4114		
42	4468		
45		4799	
50	5196		
60	6152	6066	
		30 mass %	
20	3266	3175	
30	3884	4072	
37	4347		
40	4479		
45		4907	
50	5353		
60	6212	6080	

[a] The data are for a 7.5 mass % TEA solution.

3. Results and Discussion

The reliabilities of the experimental apparatus and the procedure of calculating the solubility and diffusivity were tested by the well-known system CO_2 + water and were reported in a previous paper.[12] The results were in good agreement with the literature values.

3.1. Solubility. Table 1 gives the solubility of CO_2 in protonated TEA solutions determined in this work by the "protonation method" together with the calculated values by the "N_2O analogy" method from the available literature data on N_2O solubility in TEA solutions. Littel et al.[11] presented the solubility of N_2O in TEA solutions and other alkanolamine solutions as a best-fit polynomial; their equation and equations (1−2, 5) were used in the calculations. The measured data of the present work were well fitted against temperature for each concentration by an exponential form as

$$H/(\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}) = A \exp(B\text{K}/T) \tag{12}$$

where A and B are constants of fitting and their values are given in Table 2 with the corresponding R^2. Figure 1 shows a plot of H versus T on a semilog scale for each concentration. The agreement between this work and the results calculated via the N_2O analogy method is good. The solubility of CO_2 in the three concentrations and in water are presented in Figure 2 for comparison. The data show good internal consistency and the consistency across tem-

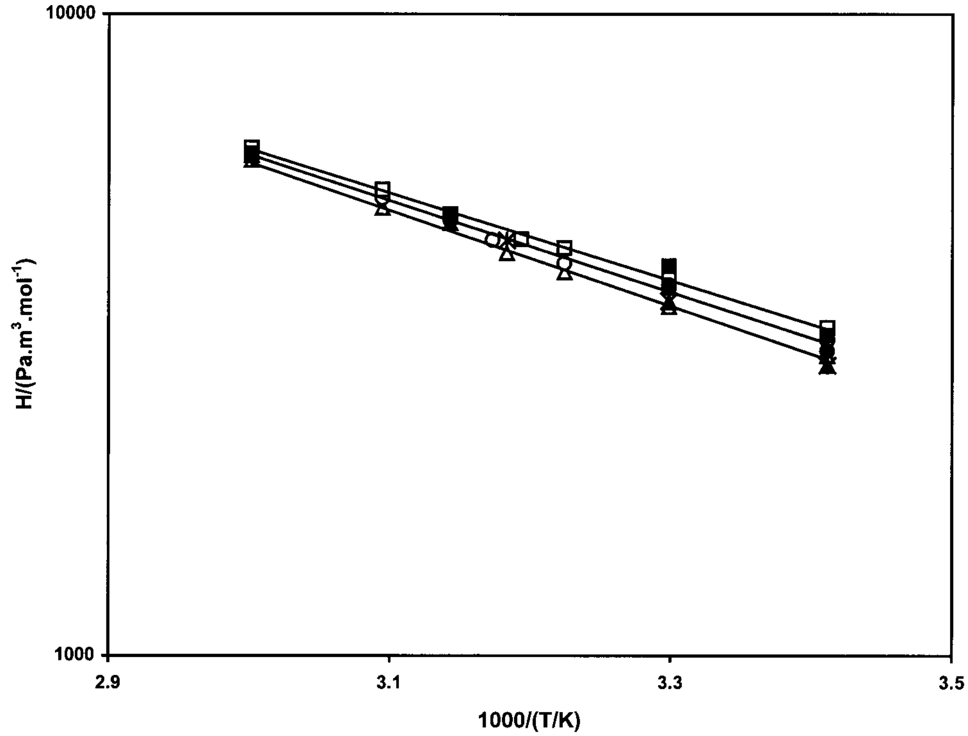

Figure 1. Solubility of CO_2 in protonated TEA solutions; this work (△, 10 mass %; ○, 20 mass %; □, 30 mass %); Littel et al.[11] (▲, 10 mass %; ●, 20 mass %, ■; 30 mass %); Sotelo et al.[15] (∗, 7.5 mass %); _, fitted line (this work).

Table 2. Coefficients of Eqs 12 and 13

eq 12, $H/(\mathrm{Pa \cdot m^3 \cdot mol^{-1}}) = A \exp(B/(T/\mathrm{K}))$			
system	A	B	R^2
CO_2 + 10 mass % TEA	1 013 271	−1716	0.998
CO_2 + 20 mass % TEA	834 629	−1642	0.995
CO_2 + 30 mass % TEA	683 392	−1568	0.998

eq 13, $D/(10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}) = A' \exp(B'/(T/\mathrm{K}))$			
system	A'	B'	R^2
CO_2 + 10 mass % TEA	3146	−2286	0.997
CO_2 + 20 mass % TEA	5374	−2557	0.999
CO_2 + 30 mass % TEA	7085	−2757	1

Table 3. Diffusivity of CO_2 in Protonated TEA Solutions

t	$10^5 D/(\mathrm{cm^2 \cdot s^{-1}})$		
°C	this work	Sada et al.[14]	Ko et al.[17]
		10 mass %	
20	1.29	1.71	
25			
30	1.67		1.91
35			2.15
40	2.14		2.36
50	2.67		
60	3.27		
		20 mass %	
20	0.88	1.39	
25			
30	1.15		1.68
35			1.85
40	1.55		1.99
50	1.99		
60	2.47		
		30 mass %	
20	0.58	0.79	
25			
30	0.80		1.32
35			1.43
40	1.08		1.66
50	1.40		
60	1.78		

perature and concentration appears to be good. At high temperatures, the solubility of CO_2 in water and in protonated TEA solutions converges.

3.2. Diffusivity. Table 3 gives the diffusion coefficients determined in this work and calculated based on the N_2O analogy method from data reported in the literature on N_2O diffusivity in TEA solutions and equations (3−4,6). Ko et al.[17] reported their concentration of TEA solutions in $\mathrm{kmol \cdot m^{-3}}$. The corresponding concentrations for the 10, 20, and 30 mass % TEA solutions used in this work are 0.68, 1.37, and 2.08 $\mathrm{kmol \cdot m^{-3}}$, respectively. These values of the concentration were used to find the diffusivity of N_2O from Ko et al. work by interpolation. For the measurements of the diffusivity, Ko et al. used a short wetted wall column absorber, and Sada et al.[14] used a laminar liquid-jet apparatus.

The diffusivity measured in this work was well fitted by exponential form as

$$D/(\mathrm{cm^2 \cdot s^{-1}}) = A' \exp(B'\mathrm{K}/T) \qquad (13)$$

where A' and B' are constants of fitting; their values are given in Table 2 with the corresponding R^2. The plots of diffusivity of CO_2 in water and in the solutions as a function of temperature are shown in Figure 3. Good internal consistency between the data obtained in this work is evident and the consistency across temperature and concentration is good. The diffusivity of CO_2 in the TEA solutions should be lower than that in pure water, which is not the case for the 10 mass % calculated based on the data of Ko et al. This indicates that their data are shifted systematically upward.

4. Conclusions

The solubility and diffusivity of CO_2 in (10, 20, and 30) mass % TEA solutions as a function of temperature is now available via the protonation method. The good agreement

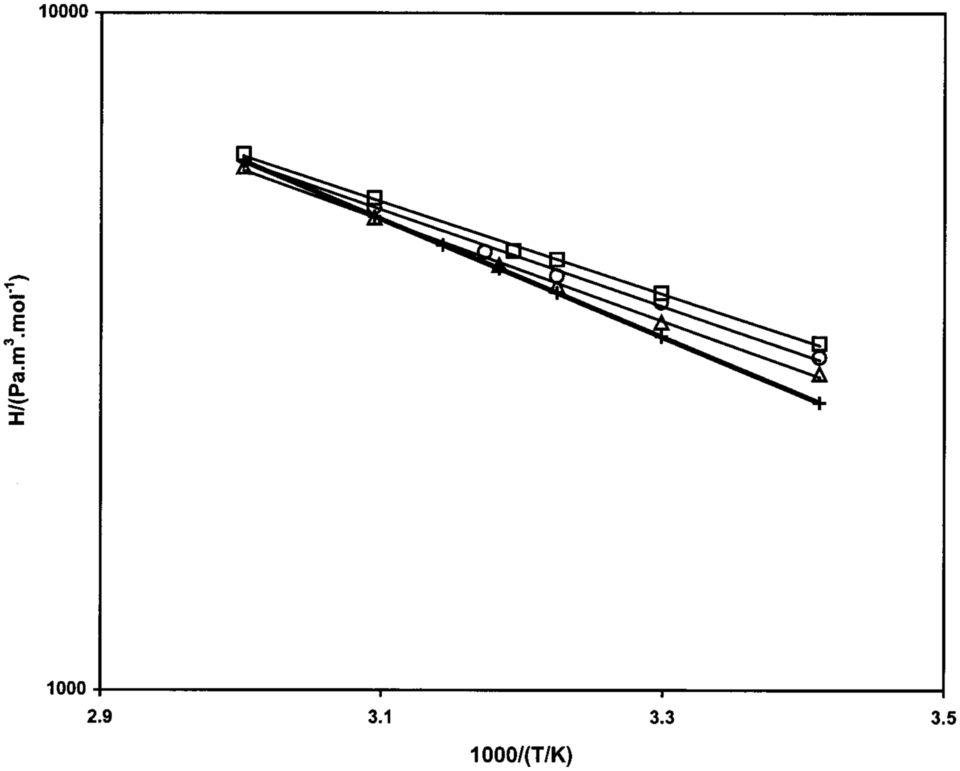

Figure 2. Solubility of CO_2 in water and in protonated TEA solutions; △, 10 mass %; ○, 20 mass %; □, 30 mass %; _, fitted line (this work); __, water.[12]

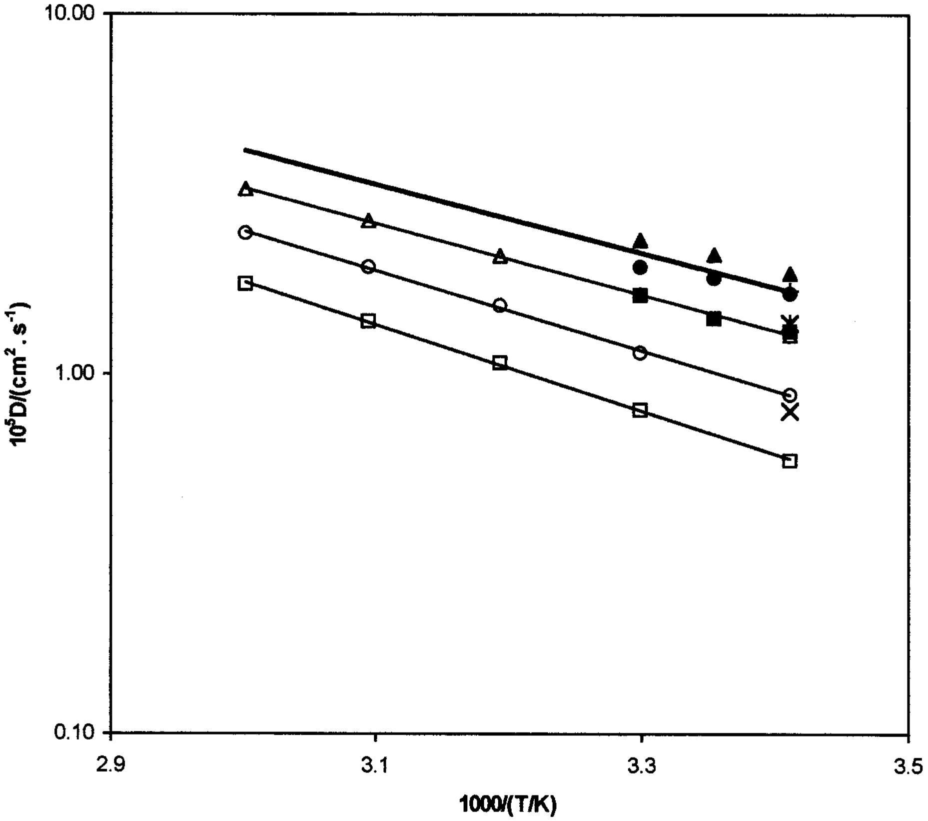

Figure 3. Diffusivity of CO_2 in water and in protonated TEA solutions; this work (△, 10 mass %; ○, 20 mass %; □, 30 mass %); Sada et al.[14] (+, 10 mass %; ∗, 20 mass %; ×, 30 mass %); Ko et al.[17] (▲, 10 mass %; ●, 20 mass %, ■; 30 mass %); _, fitted line (this work); __, water.[12]

between the results of this work and those based on the N_2O analogy indicates that the protonation method can be used effectively in direct measurement of the solubility and the diffusivity of any acid gas in alkanolamine solutions. This technique avoids any possibility of reaction that may affect the measured solubility and diffusivity.

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