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Diffusivity of Nitrous Oxide in Aqueous Solutions of *N*-Methyldiethanolamine and Diethanolamine from 293 to 368 K

A. Tamimi,[†] **E. B. Rinker, and O. C. Sandall**[*]

Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, California 93106-5080

The diffusion coefficients for nitrous oxide in aqueous solutions of diethanolamine (DEA) and *N*-methyldiethanolamine (MDEA) were determined using a wetted-sphere absorber over the temperature range 293–368 K. The ranges of amine concentrations covered in the experiments were 10–30 mass % for DEA and 10–50 mass % for MDEA. The diffusion coefficients indicated a linear dependence on amine concentration, but the temperature dependence was nonlinear. It was found that the diffusivity of N_2O in aqueous DEA is always less than that in aqueous MDEA under equivalent conditions of amine concentration and temperature.

Introduction

Diethanolamine (DEA) is used frequently in industry for the simultaneous removal of CO_2 and H_2S from gaseous streams, while *N*-methyldiethanolamine (MDEA) is used for the selective removal of H_2S in the presence of CO_2. Knowledge of the free molecular diffusivities of acid gases in aqueous alkanolamine solutions is of primary importance for the prediction of mass transfer rates in gas sweetening processes. The diffusion coefficient for CO_2 cannot be measured directly since CO_2 undergoes a chemical reaction with the solvent. The similarity in mass, molecular structure, and molecular interaction parameters between CO_2 and N_2O led Clarke (*1*) and Laddha et al. (*2*) to assume that the ratios of the diffusivities of CO_2 and N_2O in water and in aqueous solutions of organic solvents are similar within 5% or less at the same temperature. Thus, to implement this analogy method to predict the diffusivity of CO_2 in aqueous amine solutions, it is necessary to know the diffusion coefficient of N_2O in the same solution.

Although considerable work has been reported on measurements of gas diffusivities in aqueous alkanolamine solutions, relatively few measurements have been reported at temperatures greater than 333 K for gases in MDEA and DEA. In the amine stripping process, knowledge of the acid gas diffusivities in the amine solutions at high temperatures is of importance for the design of these processes. In the work reported here diffusivity measurements were made over the temperature range 293–368 K.

The experimental techniques used to measure the gas diffusivity in a liquid include laminar jet, laminar-film reactor, gas bubble, diaphragm cell, wetted wall, and wetted sphere. The latter technique, the wetted sphere, was used to measure the N_2O diffusivity in DEA and MDEA solutions in the work reported here. The wetted-sphere technique is a modification of the wetted-wall method which eliminates the problems of film ripples at low flow rates and end effects due to hydrodynamic instability (*3*). Wild and Potter (*4, 5*) and Davidson and Cullen (*6*) studied the diffusivity of sparingly soluble gases in water using the wetted-sphere apparatus over the temperature range 288–303 K. Their work included determination of diffusion coefficients of CO_2, N_2O, Cl_2, O_2, and H_2 in water under atmospheric conditions.

Sada et al. (*7*) measured the diffusivity of N_2O in various amine solutions including DEA at 298 K and 1 atm. The DEA concentrations covered the range 0.498–3.457 mol/L (5–36 mass % DEA).

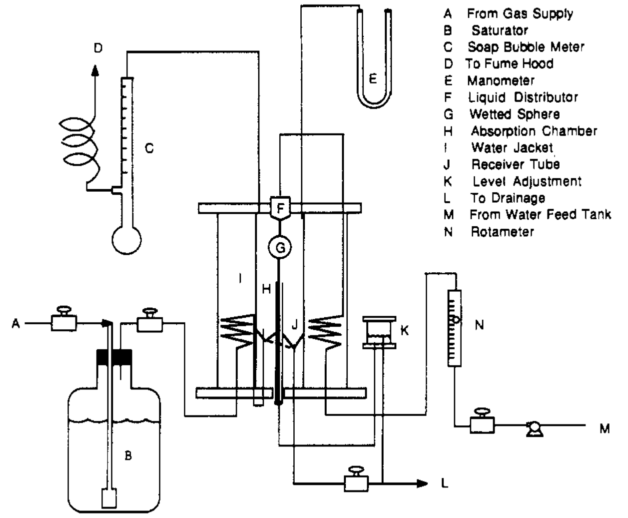

Figure 1. Schematic diagram of the wetted-sphere apparatus.

Haimour and Sandall (*8*) used a laminar-jet apparatus to measure the diffusivity of N_2O in aqueous MDEA solutions over the temperature range 288–308 K and at 1 atm. The amine concentrations considered were 0–20 mass % MDEA.

Versteeg and van Swaaij (*9*) studied the diffusivity of N_2O in aqueous MDEA solutions over the temperature range 293–333 K and at 1 atm. The amine concentration covered the range 237–2865 mol/m^3 (2.8–34.2 mass % MDEA).

Experimental Method

In this work, a wetted-sphere apparatus was used to measure the N_2O diffusivity in aqueous DEA and MDEA solutions over the temperature range 293–368 K and at 1 atm. The amine concentrations covered the ranges 10–30 mass % for DEA and 10–50 mass % for MDEA. The DEA used in this work was reagent grade with a stated purity greater than 99%. The MDEA was donated by Union Carbide and had a purity greater than 99% as determined by titration. The N_2O gas was medical grade with a stated purity of 99.99%. Deionized water was used in preparing the amine solutions which were degassed by heating to the boiling point and then applying a vacuum for a short time. Transfer of the degassed solution to the experimental setup was carried out using pressurized helium to prevent any absorption of atmospheric air during handling. The N_2O was saturated with the vapor

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[*] To whom correspondence should be addressed.

[†] On leave from the Chemical Engineering Department, Jordan University of Science and Technology, Irbid, Jordan.

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Table 1. Diffusivity, D, of N_2O in 10 mass % MDEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})	$D/(10^{-5}$ cm^2·s) (9)
293.15	1.36	0.017	1.15
298.15	1.41	0.007	1.34
303.15	1.60	0.002	
313.15	1.93	0.012	
333.15	3.20	0.007	
353.15	4.13	0.005	
368.15	4.86	0.181	

Table 2. Diffusivity, D, of N_2O in 20 mass % MDEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})	$D/(10^{-5}$ cm^2·s) (9)
293.15	1.06	0.005	0.8
298.15	1.11	0.006	1.0
303.15	1.25	0.021	
313.15	1.67	0.010	
333.15	2.71	0.005	2.75
353.15	3.93	0.004	
368.15	4.29	0.020	

Table 3. Diffusivity, D, of N_2O in 30 mass % MDEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})	$D/(10^{-5}$ cm^2·s) (9)
293.15	0.611	0.002	0.50
298.15	0.721	0.002	0.67
303.15	0.807	0.006	
313.15	1.27	0.008	
333.15	2.02	0.088	2.10
353.15	3.02	0.254	
368.15	3.71	0.017	

Table 4. Diffusivity, D, of N_2O in 40 mass % MDEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})
293.15	0.261	0.003
298.15	0.377	0.003
303.15	0.487	0.003
313.15	0.803	0.005
333.15	1.77	0.013
353.15	2.58	0.027
368.15	2.97	0.035

Table 5. Diffusivity, D, of N_2O in 50 mass % MDEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})
293.15	0.117	0.008
298.15	0.189	0.001
303.15	0.228	0.004
313.15	0.411	0.004
333.15	0.971	0.002
353.15	1.230	0.068
368.15	1.561	0.049

Table 6. Diffusivity, D, of N_2O in 10 mass % DEA

T/K	$D/(10^{-5}$ cm^2·s^{-1}) (this work)	$\sigma/(10^{-5}$ cm^2·s^{-1})	$D/(10^{-5}$ cm^2·s) (7)
293.15	1.23	0.024	
298.15	1.31	0.003	1.58
303.15	1.51	0.004	
313.15	1.71	0.014	
333.15	2.91	0.005	
353.15	3.95	0.034	
368.15	4.23	0.099	

of the particular amine solution before entering the absorber. A description of the experimental setup and methodology was given in detail in a previous paper (*10*). A schematic drawing of the apparatus is shown in Figure 1.

Results and Discussion

The diffusivities of N_2O in aqueous DEA and MDEA solutions were calculated from a series solution developed by Olbrich and Wild (*3*) as follows:

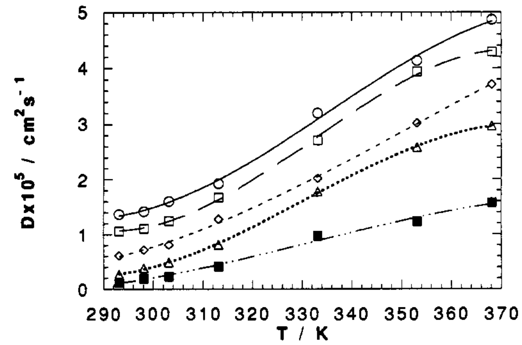

Figure 2. Diffusivity of N_2O in aqueous solutions of MDEA: ○, 10 mass % MDEA; □, 20 mass % MDEA; ◇, 30 mass % MDEA; △, 40 mass % MDEA; ■, 50 mass % MDEA.

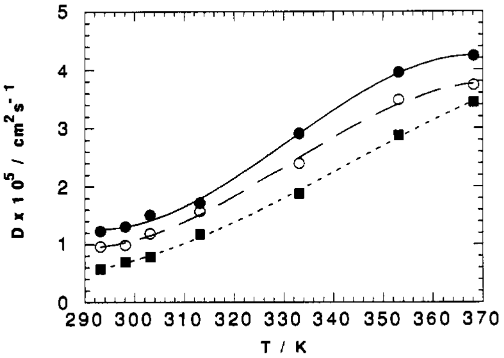

Figure 3. Diffusivity of N_2O in aqueous solutions of DEA: ●, 10 mass % DEA; ○, 20 mass % DEA; ■, 30 mass % DEA.

$$G = (P_{N_2O}/H)m_L[1 - \sum_i b_i \exp(\lambda_i^2\epsilon)] \tag{1}$$

where

$$\epsilon = 13.5(gr_s^7/\nu m_L^4)^{1/3}D \tag{2}$$

G = rate of absorption, mol·s^{-1}, H = Henry's constant, atm·cm^3·mol^{-1}, p_{N_2O} = partial pressure of N_2O, atm, m_L = liquid flow rate, cm^3·s^{-1}, b_i and λ_i = constants, g = acceleration of gravity, cm·s^{-2}, r_s = radius of the sphere, cm, ν = kinematic viscosity, cm^2·s^{-1}, and D = diffusion coefficient, cm^2·s^{-1}. An iterative procedure was developed to calculate the diffusivity from eq 1.

The values of H, Henry's law constant, were deduced from the work of Versteeg and van Swaaij (*9*) over the concentration range 10–30 mass % for both DEA and MDEA in the temperature range 293–333 K. Above these ranges the values of H were obtained by correlating and extrapolating their data for temperature and amine concentration up to 368 K and 50 mass % MDEA. The partial pressure of N_2O in the absorption apparatus was calculated from Raoult's law and the total pressure from

$$p_{N_2O} = P_{tot} - x_{H_2O}P^v_{H_2O} - x_{amine}P^v_{amine} \tag{3}$$

where P_{tot} = total pressure, atm, x_{H_2O} = mole fraction of water, $P^v_{H_2O}$ = vapor pressure of water, atm, and x_{amine} = mole fraction of the amine. The last term in eq 3 was very small for the conditions of our experiments and was neglected.

Tables 1–5 give the diffusion coefficients for MDEA together with available literature values. There is fair agreement between our results and those of Versteeg and van Swaaij (*9*) for the diffusivity of N_2O in aqueous MDEA. Each value reported in these tables for this work represents the

Table 7. Diffusivity, *D*, of N_2O in 20 mass % DEA

T/K	$D/(10^{-5}\ cm^2 \cdot s^{-1})$ (this work)	$\sigma/(10^{-5}\ cm^2 \cdot s^{-1})$	$D/(10^{-5}\ cm^2 \cdot s)$ (7)
293.15	0.957	0.005	
298.15	0.984	0.109	1.42
303.15	1.186	0.009	
313.15	1.57	0.022	
333.15	2.40	0.041	
353.15	3.48	0.168	
368.15	3.73	0.183	

Table 8. Diffusivity, *D*, of N_2O in 30 mass % DEA

T/K	$D/(10^{-5}\ cm^2 \cdot s^{-1})$ (this work)	$\sigma/(10^{-5}\ cm^2 \cdot s^{-1})$	$D/(10^{-5}\ cm^2 \cdot s)$ (7)
293.15	0.569	0.003	
298.15	0.693	0.005	1.24
303.15	0.780	0.006	
313.15	1.17	0.008	
333.15	1.88	0.025	
353.15	2.88	0.051	
368.15	3.44	0.197	

average of at least three runs with the standard deviations listed.

Tables 6–8 report the diffusivity results for DEA. Each value reported for this work represents the average of at least three runs with the standard deviation of these measurements reported in the tables. In the case of DEA, there is only one value reported by Sada et al. (7) at 298 K for comparison.

The average diffusivity values obtained in this work are shown plotted in Figures 2 and 3.

Conclusion

Diffusivities of N_2O in aqueous DEA and MDEA solutions were measured using a wetted-sphere apparatus over the temperature range 293–368 K and at 1 atm. The results indicated that the effect of temperature is more pronounced than that of amine concentration. The diffusivity increases with increasing temperature. The effect of amine concentration is almost linear, with the diffusivity decreasing with an increase in amine concentration.

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