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Solubility and Diffusivity of Nitrous Oxide in Ternary Mixtures of Water, Monoethanolamine, and N-Methyldiethanolamine and Solution Densities and Viscosities

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The densities and viscosities of aqueous N-methyldiethanolamine/monoethanolamine (MDEA/MEA) blends containing 30 and 40 mass % total amine with MEA concentrations of 5, 10, and 15 mass % of the total amine concentration were measured at temperatures of 303, 313, and 323 K. The diffusion coefficients and Henry's law constants of N_2O in these solutions were also measured and were used to estimate the diffusion coefficients and Henry's law constants of CO_2 in these solutions according to the "N_2O/CO_2 analogy" technique.

Introduction

Recently, several researchers have suggested using aqueous mixtures of small amounts of monoethanolamine (MEA) and much larger amounts of N-methyldiethanolamine (MDEA) for the absorption of CO_2 and for the selective removal of H_2S from gas streams of mixtures of CO_2 and H_2S *(1–5)*. The objective of this paper is to provide values for some of the physical properties which are needed for the analysis of experimentally acquired data for the absorption of CO_2 into aqueous solutions of mixtures of MEA and MDEA. These physical properties are also needed for predicting the absorption rates and enhancement factors of CO_2 into aqueous blends of MDEA and MEA which are useful to process engineers who are interested in the problem of acid gas removal by aqueous blends of MEA and MDEA. The physical properties that were measured are the densities and viscosities of aqueous MDEA/MEA blends containing 30 and 40 mass % total amine with MEA concentrations of 5, 10, and 15 mass % of the total amine concentration at temperatures of 303, 313, and 323 K. The diffusion coefficients and Henry's law constants of N_2O in these solutions were also measured and were used to estimate the diffusion coefficients and Henry's law constants of CO_2 in these solutions according to the "N_2O/CO_2 analogy" technique *(6)*. The experimental apparatus and procedures that were used in our laboratory for these measurements have been described in detail previously *(6)*. The MDEA was purchased from Union Carbide with a purity of 99% or better, and the MEA was purchased from Fisher with a purity of 95% or better.

Results and Correlations

The equilibrium concentration of CO_2 in the liquid, u_{CO_2}, is related to its partial pressure in the gas phase, P_{CO_2}, by Henry's law constant, H_{CO_2}, according to the following equation:

$$u_{CO_2} = P_{CO_2}/H_{CO_2} \qquad (1)$$

Since CO_2 reacts in aqueous amine solutions, the solubility and diffusivity of CO_2 cannot be measured directly. In this work, the solubility and diffusivity of N_2O in aqueous MDEA/MEA mixtures were measured. The N_2O/CO_2 analogy technique *(7)* can then be employed to estimate the solubility and diffusivity of CO_2 in these mixtures. The similarity between CO_2 and N_2O in mass, molecular structure, and molecular interaction parameters led Clarke *(7)* to assume that the ratios of the solubilities or diffusivities of CO_2 and N_2O in water and in aqueous solutions of organic solvents are similar within 5% or better at the same temperature. Hence, according to the N_2O/CO_2 analogy, Henry's law constants of CO_2 and N_2O in the aqueous amine solutions and in pure water and the diffusion coefficients of CO_2 and N_2O in the aqueous amine solutions and in pure water are related by the following equations:

$$H_{CO_2}/H^{\circ}_{CO_2} = H_{N_2O}/H^{\circ}_{N_2O} \qquad (2)$$

$$D_{CO_2}/D^{\circ}_{CO_2} = D_{N_2O}/D^{\circ}_{N_2O} \qquad (3)$$

where superscript o refers to pure water. The values of Henry's law constants and diffusion coefficients of N_2O and CO_2 in pure water are reported in Table 1.

Table 1. Henry's Law Constants and Diffusion Coefficients of N_2O and CO_2 in Pure Water

T/K	$H^{\circ}_{N_2O}$ [a]/ (MPa·m³·kmol⁻¹)	$H^{\circ}_{CO_2}$ [a]/ (MPa·m³·kmol⁻¹)	$10^9 D^{\circ}_{N_2O}$ [a]/ (m²·s⁻¹)	$10^9 D^{\circ}_{CO_2}$ [b]/ (m²·s⁻¹)
303	4.35	3.39	1.607	2.16
313	5.02	4.25	1.679	2.71
323	5.37	5.17	1.868	3.34

[a] Reference 6. [b] Reference 8.

The densities and viscosities of aqueous MDEA/MEA blends containing 30 and 40 mass % total amine with MEA concentrations of 5, 10, and 15 mass % of the total amine concentration were measured at temperatures of 303, 313, and 323 K and are reported in Tables 2 and 3, respectively. Henry's law constants and the diffusion coefficients of N_2O in these solutions were measured and are reported in Tables 4 and 5, respectively. Henry's law constants and diffusion coefficients of CO_2 which were estimated from eqs 2 and 3 are reported in Tables 6 and 7, respectively. These properties were correlated as functions of temperature and

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Table 2. Density ϱ of Aqueous MDEA/MEA Solutions

	$10^{-3}\varrho/(\text{kg·m}^{-3})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	1.0229	1.021 72	1.021 19	1.020 28	1.0322	1.030 90	1.030 18	1.029 36
313	1.0180	1.016 56	1.015 07	1.013 94	1.0266	1.025 21	1.024 41	1.023 75
323	1.0130	1.010 43	1.009 69	1.009 12	1.0204	1.019 27	1.018 24	1.017 76

[a] Reference 6.

Table 3. Viscosity μ of Aqueous MDEA/MEA Solutions

	$10^{3}\mu/(\text{kg·m}^{-1}\text{·s}^{-1})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	2.612	2.601	2.559	2.542	4.359	4.279	4.189	4.097
313	1.937	1.944	1.915	1.892	3.112	3.035	3.011	2.913
323	1.505	1.506	1.490	1.477	2.309	2.255	2.241	2.214

[a] Reference 6.

Table 4. Henry's Law Constants for N_2O in Aqueous MDEA/MEA Solutions

	$H_{N_2O}/(\text{MPa·m}^3\text{·kmol}^{-1})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	5.10	5.14	5.27	5.36	5.43	5.58	5.67	5.85
313	5.90	6.10	6.29	6.48	6.21	6.27	6.34	6.44
323	6.07	6.35	6.55	6.59	6.22	6.29	6.32	6.43

[a] Reference 6.

Table 5. Diffusion Coefficients of N_2O in Aqueous Solutions of MDEA/MEA

	$10^{9}D_{N_2O}/(\text{m}^2\text{·s}^{-1})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	1.032	1.136	1.267	1.393	0.824	0.844	0.905	0.973
313	1.240	1.265	1.345	1.450	1.108	1.159	1.207	1.288
323	1.421	1.488	1.564	1.656	1.269	1.305	1.391	1.471

[a] Reference 6.

Table 6. Estimated Henry's Law Constants for CO_2 in Aqueous MDEA/MEA Solutions According to the N_2O/CO_2 Analogy Technique

	$H_{CO_2}/(\text{MPa·m}^3\text{·kmol}^{-1})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	3.98	4.01	4.11	4.18	4.24	4.35	4.43	4.56
313	4.99	5.17	5.32	5.49	5.25	5.31	5.36	5.46
323	5.84	6.11	6.30	6.34	5.99	6.05	6.08	6.18

[a] Reference 6.

Table 7. Estimated Diffusion Coefficients of CO_2 in Aqueous Solutions of MDEA/MEA According to the N_2O/CO_2 Analogy Technique

	$10^{9}D_{CO_2}/(\text{m}^2\text{·s}^{-1})$ at w_{MDEA}/w_{MEA} =							
T/K	0.30/0[a]	0.285/0.015	0.27/0.03	0.255/0.045	0.40/0[a]	0.38/0.02	0.36/0.04	0.34/0.06
303	1.387	1.545	1.723	1.895	1.108	1.148	1.231	1.323
313	2.001	2.047	2.176	2.346	1.788	1.875	1.953	2.084
323	2.541	2.665	2.801	2.966	2.264	2.337	2.491	2.634

[a] Reference 6.

concentration according to the following equations:

solubility (Henry's law constant) of N_2O

$$\ln(H_{N_2O}/(\text{MPa·m}^3\text{·kmol}^{-1})) = A_1 + B_1/(T/\text{K}) \quad (4)$$

estimated solubility (Henry's law constant) of CO_2

$$\ln(H_{CO_2}/(\text{MPa·m}^3\text{·kmol}^{-1})) = A_2 + B_2/(T/\text{K}) \quad (5)$$

density ϱ of aqueous MDEA/MEA solution

$$\varrho/(\text{kg·m}^{-3}) = A_3 + B_3(T/\text{K}) \quad (6)$$

viscosity μ of aqueous MDEA/MEA solution

$$\ln(\mu/(\text{kg·m}^{-1}\text{·s}^{-1})) = A_4 + B_4/(T/\text{K}) \quad (7)$$

A_k and B_k are correlated with the mass fractions of MDEA (w_{MDEA}) and MEA (w_{MEA}) in the solution according to the following equations:

$$A_k = a_k + b_k w_{MDEA} + c_k w_{MEA} \quad (8)$$

$$B_k = d_k + e_k w_{MDEA} + f_k w_{MEA} \quad (9)$$

The values of the constants a_k, b_k, c_k, d_k, e_k, and f_k are

Table 8. Constant Coefficients for Calculating A_k and B_k, k = 1−4, Which Are Required in Eqs 4−7

	$A_k = a_k + b_k w_{MDEA} + c_k w_{MEA}$			$B_k = d_k + e_k w_{MDEA} + f_k w_{MEA}$		
k	a_k	b_k	c_k	d_k	e_k	f_k
1	9.007562	−13.34430	−15.10479	−2288.484	4236.726	5133.326
2	12.14463	−13.39581	−15.20839	−3317.018	4252.902	5165.193
3	1124.340	204.8350	283.2410	−0.4311301	−0.3575680	−0.7899637
4	−12.19713	−8.905239	−4.823588	1438.717	4218.749	2697.360

Table 9. Constant Coefficients for Calculating the Diffusion Coefficients of N_2O and CO_2 in Aqueous Solutions of MDEA/MEA According to Eqs 10 and 11 Along with the Mean Deviations for These Equations

	$D_{N_2O}/(m^2 \cdot s^{-1}) = \alpha(\mu/(kg \cdot m^{-1} \cdot s^{-1}))^{\beta}(T/K)$			$D_{CO_2}/(m^2 \cdot s^{-1}) = \gamma(\mu/(kg \cdot m^{-1} \cdot s^{-1}))^{\delta}(T/K)$		
w_{MDEA}/w_{MEA}	α	β	mean deviation/%	γ	δ	mean deviation/%
0.30/0	2.145301×10^{-13}	−0.4654931	0.55	1.313257×10^{-14}	−0.9862939	1.78
0.285/0.015	3.999079×10^{-13}	−0.3742148	1.54	2.700742×10^{-14}	−0.8801191	0.33
0.27/0.03	8.381405×10^{-13}	−0.2666473	2.29	5.431339×10^{-14}	−0.7780113	1.12
0.255/0.045	1.409513×10^{-12}	−0.1952480	2.30	9.219197×10^{-14}	−0.7044025	1.24
0.40/0	1.166238×10^{-13}	−0.5833275	3.03	1.394693×10^{-14}	−1.030384	4.45
0.38/0.02	1.164062×10^{-13}	−0.5869788	3.76	1.518429×10^{-14}	−1.018302	4.89
0.36/0.04	1.213190×10^{-13}	−0.5886689	2.75	1.485901×10^{-14}	−1.029997	4.00
0.34/0.06	1.390204×10^{-13}	−0.5740574	2.40	1.604657×10^{-14}	−1.023848	3.33

reported in Table 8 for k = 1−4. The mean deviations for eqs 4−7 are 2.70%, 1.61%, 0.03%, and 0.64%, respectively. The diffusion coefficients of N_2O and CO_2 were correlated according to the following equations:

diffusivity of N_2O

$$D_{N_2O}/(m^2 \cdot s^{-1}) = \alpha(\mu/(kg \cdot m^{-1} \cdot s^{-1}))^{\beta}(T/K) \qquad (10)$$

estimated diffusivity of CO_2

$$D_{CO_2}/(m^2 \cdot s^{-1}) = \gamma(\mu/(kg \cdot m^{-1} \cdot s^{-1}))^{\delta}(T/K) \qquad (11)$$

The values of α, β, γ, and δ along with the mean deviations for eqs 10 and 11 are reported in Table 9.

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