Hydrates of Carbon Dioxide and Methane Mixtures

Sanggono Adisasmito, Robert J. Frank, III, and E. Dendy Sloan, Jr.*

Department of Chemical Engineering and Petroleum Refining, Colorado School of Mines, Golden, Colorado 80401

Three-phase equilibrium conditions of hydrates (water-rich liquid, hydrate, and vapor) of carbon dioxide and methane binary mixtures were investigated in the temperature range of 273-288 K and the pressure range of 1.2-11.0 MPa. The vapor-phase concentrations were measured by a gas chromatograph. The results obtained were in good agreement with previous measurements done by researchers at the University of Michigan who had calculated the carbon dioxide concentration in the vapor phase. The data obtained in this work did not show unusual hydrate phenomena, as reported in a more recent publication by researchers in Hungary.

Introduction

Gas hydrates are crystalline molecules formed by a physical reaction between water and low molecular weight gases. The gas molecules occupy cavities in a network of water molecules composed of unit crystal structures, referred to as the body-centered cubic lattice of structure I or the diamond cubic lattice of structure II. In both hydrate structures, each cavity can contain at most one guest molecule. The occupation of hydrate cavities is determined to a large degree by the size of the gas molecules, and to a lesser degree by the chemical nature and the shape of the gas molecules, as summarized in the recent monograph by Sloan (*1*). Low molecular weight gases, such as methane and carbon dioxide, form structure I in hydrate equilibria.

Sediments containing carbon dioxide and methane hydrates are naturally found in regions of permafrost and beneath the sea in outer continental margins. Kvenvolden (*2*) estimated that the amount of carbon in methane hydrates is on the order of 10 000 Gtons. Because methane hydrates occur in the shallow geosphere, they are of interest as a potential resource of natural gas and as a possible cause of global warming due to the methane released to the atmosphere.

Information on the hydrate-forming conditions of the carbon dioxide mixtures is very important for natural gas handling, processing, and transportation. Carbon dioxide exhibits a high solubility in water due to the polar attractive forces that cause the mixture to be more susceptible for hydrate formation. Case et al. (*3*) reported unusual behavior of carbon dioxide-rich systems. At lower temperatures, liquid carbon dioxide was predicted to form and then dissolve hydrates in two-phase liquid-vapor equilibria. Although extensive hydrate equilibrium studies have been reported in the literature for hydrocarbons, there are only three studies for carbon dioxide binary mixtures with hydrocarbons: Unruh and Katz (*4*) in 1949 and Berecz and Balla-Achs (*5*) in 1974 for carbon dioxide-methane binary systems and Robinson and Mehta (*6*) in 1971 for carbon dioxide-propane binary systems. Robinson and Mehta reported that mixtures of carbon dioxide and propane did not appear to follow the *K*-factor concept introduced by Carson and Katz (*7*).

Unruh and Katz determined vapor-phase concentrations in the carbon dioxide and methane binary mixtures indirectly from calculations. At that time, there was not a device available for direct measurements of vapor compositions, such as a gas chromatograph. The vapor-phase composition of hydrate equilibria was determined on the basis of solubility data of carbon dioxide in water at a certain pressure and temperature. A vapor composition was assumed, and the quantities of each component in the liquid and in the vapor phases were calculated via a mass balance. If the overall composition did not agree with the actual vapor composition charged to the cell, the calculation was repeated.

Berecz and Balla-Achs showed that hydrates of carbon dioxide and methane mixtures exhibited instability at carbon dioxide vapor mole fractions of 50% and higher. A maximum and a minimum were reported in the hydrate isotherms and isobars.

The present work was done to resolve the discrepancy between results in the previous investigations. The work done by Unruh and Katz should be verified due to the lack of their vapor-phase concentration measurements. The very unusual results reported by Berecz and Balla-Achs should also be confirmed.

Experimental Procedures

The equilibrium cell was a Jerguson sight glass model with a pressure rating of 2000 psig at 100 °F. The schematic diagram of the apparatus is shown in Figure 1. The cell volume was approximately 150 mL, including about 50 mL of liquid water. The gas and water in the cell were mixed by a rocking mechanism attached to the top of the cell, which allowed cell movement up to an angle of 35° on its longitudinal axis. A digital indicator attached to a platinum resistance thermometer with 1.0% accuracy in the 0-30 °F range was used to measure the temperature inside the cell. A gas sampling line was placed at the upper part of the cell to allow withdrawal of the vapor phase. The gas sample was then analyzed via a Hewlett-Packard Model 5890 gas chromatograph with automatic integration. The cell pressure was measured by a Heise pressure gauge (0-2000 psi), accurate to within 0.1%.

To control the temperature, the cell was immersed in a constant-temperature bath with a Plexiglass window to allow the monitoring of hydrate formation or dissociation. A mixture of 50% colorless ethylene glycol in water was used as the bath fluid. The bath was refrigerated by an immersion refrigeration unit, and the temperature was controlled by an immersion heater connected to a Bayley precision temperature controller, Model 122, with 0.001 K accuracy.

Bone-dry-grade carbon dioxide with 99.8% minimum purity and research-grade methane with 99.99% minimum purity were supplied by General Air Service and Supply. Double deionized water was used for all experiments.

Linear calibration curves were obtained from the plot of the pure-component pressure versus the area generated from the chromatogram that corresponds to the number of moles. Mixtures of carbon dioxide and methane were prepared by a gravimetric method and analyzed by the chromatograph to check the calibration accuracy. The concentration difference between the two methods of determination were always within 1%.

The equilibrium cell was charged with a mixture of methane and carbon dioxide. The system was cooled to about 5 K below the anticipated hydrate-forming temperature. Subcooling was necessary to induce initial crystal formation. When the hydrates formed, the temperature was elevated to dissociate the hydrates into a condition where the solid phase was in coexistance with the liquid water and vapor phases. The temperature

---

* To whom correspondence should be addressed.

0021-9568/91/1736-0068$02.50/0

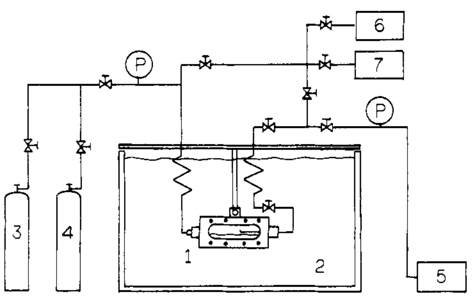

Figure 1. Schematic diagram of gas hydrate apparatus: (1) equilibrium cell; (2) constant-temperature bath; (3) carbon dioxide cylinder; (4) methane cylinder; (5) gas chromatograph; (6) vacuum pump; (7) vent. P = Pressure gauge.

Table I. Hydrate Equilibrium Temperature T, Experimental Pressure P_{exp}, Calculated Pressure P_{calc}, and Relative Percentage Deviation $\sigma_r(P)$ for Carbon Dioxide

T/K	P_{exp}/MPa	P_{calc}/MPa	$\sigma_r(P)$
274.3	1.42	1.41	-0.8
275.5	1.63	1.63	-0.1
276.8	1.90	1.91	0.6
277.6	2.11	2.12	0.3
279.1	2.55	2.57	1.0
280.6	3.12	3.15	1.0
281.5	3.51	3.57	1.6
282.1	3.81	3.88	1.8
282.9	4.37	4.34	-0.6

average absolute $\sigma_r(P)$ = 0.9

Table II. Hydrate Equilibrium Temperature T, Experimental Pressure P_{exp}, Calculated Pressure P_{calc}, and Relative Percentage Deviation $\sigma_r(P)$ for Methane

T/K	P_{exp}/MPa	P_{calc}/MPa	$\sigma_r(P)$
273.4	2.68	2.73	2.0
274.6	3.05	3.03	-0.6
276.7	3.72	3.68	-1.2
278.3	4.39	4.30	-2.1
279.6	5.02	4.91	-2.2
280.9	5.77	5.63	-2.4
282.3	6.65	6.57	-1.2
283.6	7.59	7.61	0.3
284.7	8.55	8.65	1.2
285.7	9.17	9.75	6.4
286.4	10.57	10.62	0.5

average absolute $\sigma_r(P)$ = 1.8

was kept constant until at least 8 h after the pressure stabilized. The temperature and pressure readings were then recorded as the L_w-H-V (water-rich liquid, hydrate, and vapor) equilibrium point.

A gas sample was withdrawn and analyzed by the gas chromatograph. In order to avoid liquid formation, the high-pressure sample was depressurized in two stages before it entered the chromatograph at atmospheric pressure. Due to the apparatus limitations, the experiment was restricted to the L_w-H-V region.

Results and Discussions

Three-phase equilibrium data of water-rich liquid, hydrate, and vapor (L_w-H-V) for pure components are tabulated in Table I (carbon dioxide) and Table II (methane). The maximum pressure of carbon dioxide was selected not to exceed 4.37 MPa to avoid liquid carbon dioxide formation in the equilibria. Carbon dioxide data reported by Robinson and Mehta, Berecz and Balla-Achs, and Unruh and Katz are compared to this work, as shown in Figure 2. The data of Berecz and Balla-Achs do not compare well with the others, particularly at temperatures above 278 K. The carbon dioxide used by Berecz and Balla-Achs was of commercial grade with nitrogen impurity, compared to the 99.5% purity of that used by Unruh and Katz and the 99.8% purity of that used in this work.

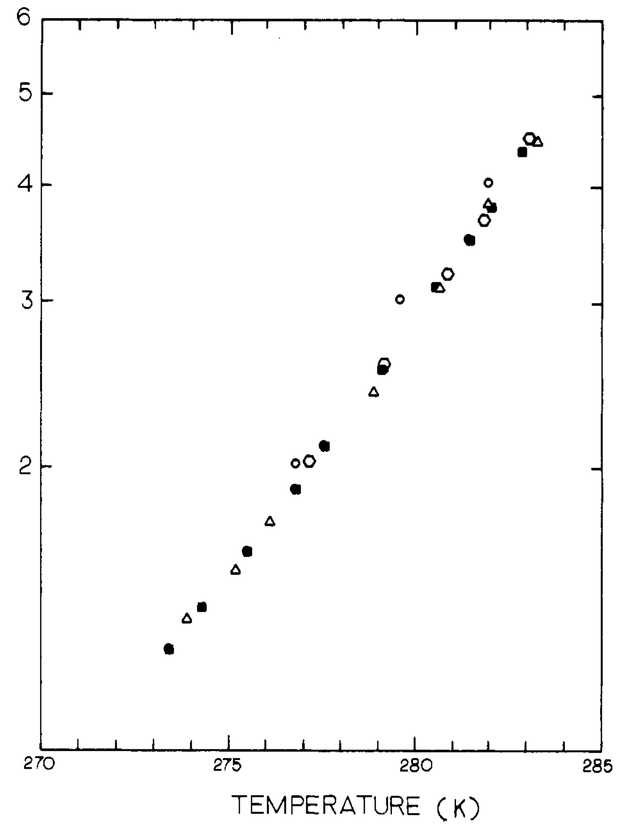

Figure 2. Hydrate equilibrium conditions of carbon dioxide: (■) this work; (O) ref 4; (O) ref 5; (Δ) ref 6.

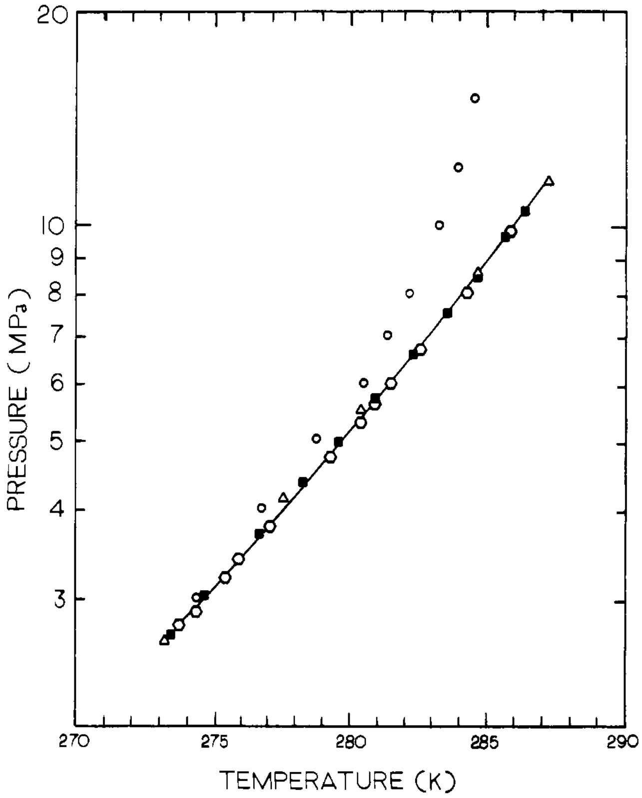

Figure 3. Hydrate equilibrium conditions of methane: (■) this work; (O) ref 8; (O) ref 5; (Δ) ref 9.

Methane data reported by Deaton and Frost (*8*), Berecz and Balla-Achs, and Jhaveri and Robinson (*9*) are compared to this work, as shown in Figure 3. The data reported by Berecz and

Table III. Hydrate Equilibrium Temperature T, Carbon Dioxide Mole Percent y_{CO_2}, Experimental Pressure P_{exp}, Calculated Pressure P_{calc}, and Relative Percentage Deviation $\sigma_r(P)$ for Carbon Dioxide and Methane Mixtures

$y_{CO_2}/\%$	T/K	P_{exp}/MPa	P_{calc}/MPa	$\sigma_r(P)$
10.0	273.7	2.52	2.51	-0.4
9.0	275.8	3.10	3.07	-0.9
8.0	277.8	3.83	3.78	-1.4
8.0	280.2	4.91	4.85	-1.1
8.0	283.2	6.80	6.80	0.0
8.0	285.1	8.40	8.53	1.5
9.0	287.2	10.76	10.99	2.1
14.0	274.6	2.59	2.61	0.8
13.0	276.9	3.24	3.29	1.5
13.0	279.1	4.18	4.13	-1.3
13.0	281.6	5.38	5.43	1.0
13.0	284.0	7.17	7.19	0.3
12.0	286.1	9.24	9.37	1.4
13.0	287.4	10.95	10.98	0.3
25.0	273.8	2.12	2.17	2.6
22.0	279.4	3.96	3.95	-0.3
22.0	283.4	6.23	6.27	0.7
21.0	285.2	7.75	7.88	1.7
25.0	287.6	10.44	10.49	0.5
44.0	273.7	1.81	1.82	0.7
42.0	276.9	2.63	2.58	-1.9
40.0	280.7	4.03	4.03	0.0
39.0	283.1	5.43	5.44	0.1
39.0	285.1	6.94	7.02	1.1
39.0	287.4	9.78	9.54	-2.5
50.0	275.6	1.99	2.12	6.4
47.0	278.5	2.98	2.98	0.0
40.0	280.9	4.14	4.13	-0.3
41.0	281.8	4.47	4.57	2.3
44.0	285.1	6.84	6.85	0.2
45.0	287.4	9.59	9.30	-3.0
73.0	274.6	1.66	1.65	-0.9
70.0	276.4	2.08	2.05	-1.5
68.0	278.2	2.58	2.56	-0.8
68.0	280.2	3.28	3.28	-0.1
67.0	282.0	4.12	4.14	0.5
79.0	273.7	1.45	1.44	-0.5
78.0	275.9	1.88	1.86	-1.1
76.0	277.8	2.37	2.35	-0.7
75.0	279.6	2.97	2.95	-0.6
74.0	281.6	3.79	3.84	1.2
85.0	282.7	4.37	4.32	-1.2

average absolute $\sigma_r(P)$ = 1.1

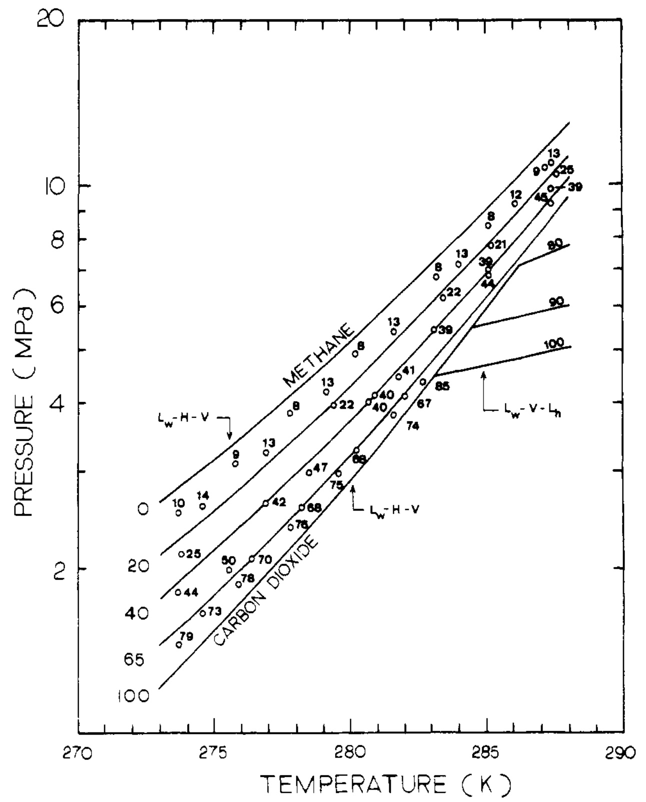

Figure 4. Hydrate equilibrium conditions of carbon dioxide and methane mixtures: L_w = water-rich liquid; L_h = hydrate-former-rich liquid; H = hydrate; V = vapor. Numbers indicate carbon dioxide mole percent in the vapor phase (water-free basis).

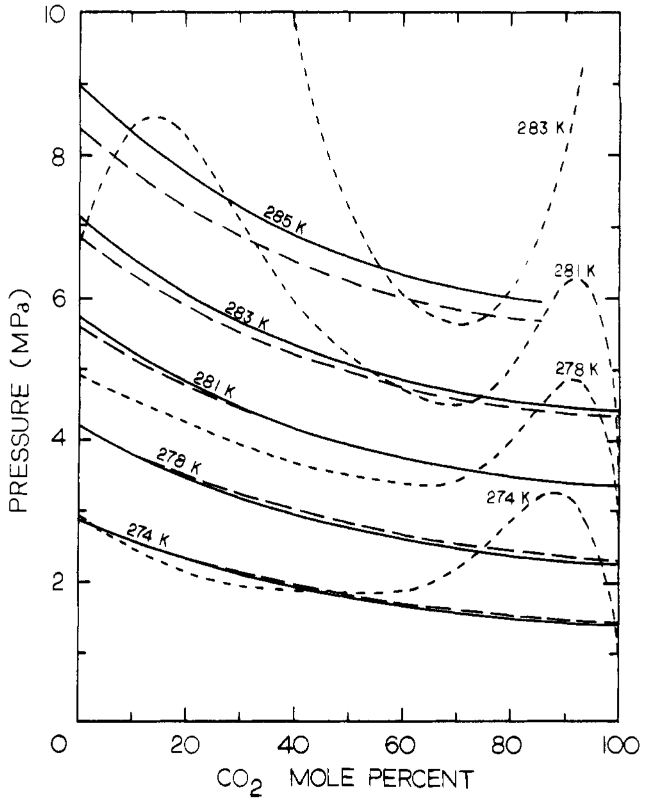

Figure 5. Hydrate equilibrium isotherms of carbon dioxide and methane mixtures: (—) this work; (– –) ref 4; (- -) ref 5.

Balla-Achs show disagreement with those of other investigations, almost in the entire range of temperatures. The methane used by Berecz and Balla-Achs was of 98.0% purity, compared to the 99.0% purity of that used by Unruh and Katz and the 99.9% purity of that used in this work.

Carbon dioxide concentrations in the carbon dioxide–methane binary mixtures were varied between 0 and 100%, as shown in Table III. Since each data point differed in concentration, a polynomial was fit to the data and used to draw constant carbon dioxide concentration lines, as shown in Figure 4. The fit equation is

$$\ln (P_{calc}/\mathrm{MPa}) = A + B(T/\mathrm{K})^{-1} + Cy + D(T/\mathrm{K})^{-2} + Ey(T/\mathrm{K})^{-1} + Fy^2$$

where P_{calc} = calculated pressure, T = temperature, y = mole percent of carbon dioxide in the vapor phase (water-free basis), and the values for the constants are A = 175.3, B = -89 009, C = 0.073 92, D = 1.1307 × 10^7, E = -23.392, and F = 3.9566 × 10^{-5}. In Figure 4, lines of L_w–V–L_h (water-rich liquid, vapor, and hydrate-former-rich liquid, respectively) were approximated by using the EQUI-PHASE program (*10*), based upon the Peng–Robinson equation of state. The experimental data point, the calculated value from the fit, and the deviation of each data point are given in Tables I and II for pure components and Table III for mixtures. The average absolute deviation of the fit for pure components and mixtures is 1.3%. The error bounds of the smoothed data are within this average deviation.

The experimental data were cross-plotted to obtain equilibrium isotherms, as shown in Figure 5. The cross plot of the data of this work did not show maximum and minimum pressures, as reported by Berecz and Balla-Achs. The cross-plotted data reported by Unruh and Katz compare well to the data of this work up to 281 K. At temperatures above 283 K, there are significant discrepancies in the isotherms. We note that Unruh and Katz had only 5 data points compared to our 14 data points above 283 K.

There may be several reasons to describe the discrepancies reported by Berecz and Balla-Achs. They did not report the exact procedures they used to measure carbon dioxide concentrations. Apparently, they reported concentrations at loading (before hydrate formation) and they did not measure the vapor composition at the equilibria. If that is the case, the concentration differences due to carbon dioxide solubility may have been neglected. Discrepancies may also have occurred due to the impurities they had either in their carbon dioxide or in their methane. It may be noted that the impurities become very significant if they are hydrate-formers.

Conclusions

Hydrate equilibrium data of carbon dioxide and methane binary mixtures are presented and compared to the previous data published in the literature. The data reported by Unruh and Katz compare well to those of this work up to 281 K, although they had calculated the carbon dioxide concentration in the vapor phase. This work does not show unusual hydrate phenomena as reported by Berecz and Balla-Achs, whose pure-components impurities may have caused the discrepancies.

Literature Cited

(1) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker, Inc.: New York, 1990; 641 pp.
(2) Kvenvolden, K. A. *Chem. Geol.* **1988**, *71*, 41.
(3) Case, J. L.; Ryan, B. F.; Johnson, J. E. *Oil Gas J.* **1985**, *83*, (May 13), 103.
(4) Unruh, C. H.; Katz, D. L. *Pet. Trans. AIME* **1949**, *186*, 83.
(5) Berecz, E.; Balla-Achs, M. Research Report No. 37 (185-XI-1-1974 OGIL), NME, Technical University of Heavy Industry, Miskolc, Hungary, as summarized in: *Gas Hydrates*; Studies in Inorganic Chemistry, Vol 4; Elsevier: New York, 1983; 343 pp.
(6) Robinson, D. B.; Mehta, B. R. *J. Can. Pet. Technol.* **1971**, *10*, 133.
(7) Carson, D. B.; Katz, D. L. *Pet. Trans. AIME* **1942**, *146*, 150.
(8) Deaton, W. M.; Frost, E. M., Jr. *U.S. Bur. Mines Monogr.* **1946**, 8.
(9) Jhaveri, J.; Robinson, D. B. *Can. J. Chem. Eng.* **1965**, *43*, 75.
(10) *EQUI-PHASE phase behavior program*; D. B. Robinson & Associates Ltd.: Edmonton, Alberta, Canada.

Received for review February 9, 1990. Revised July 5, 1990. Accepted July 9, 1990. We acknowledge the World Bank Development Project XVII with the Institute of Technology, Bandung, Indonesia, for their partial support of this work.

Physical Properties of Aqueous AMP Solutions

Shuo Xu, Frederick D. Otto, and Alan E. Mather*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

The solubility and diffusivity of N_2O in 2 and 3 M AMP (2-amino-2-methyl-1-propanol) solutions were measured and correlated with temperature. The N_2O analogy was used to estimate the solubility and diffusivity of CO_2 in AMP solutions. The density of aqueous AMP solutions was determined over a wide range of temperatures and compositions. The viscosity of 2 and 3 M AMP solutions was measured over the temperature range 23-77 °C.

1. Introduction

There are many advantages in the use of aqueous AMP (2-amino-2-methyl-1-propanol) solutions for the removal of the acid gas compounds H_2S and CO_2 from various types of gases (*1*, *2*). For the determination of reaction kinetics and in the design of suitable gas-liquid absorbers, it is necessary to use the physicochemical properties of aqueous AMP solutions, such as the density and viscosity of the solutions, as well as the solubility and diffusivity of the acid gas in the solutions. The literature data are insufficient or unavailable, and it is necessary to determine these physicochemical properties of AMP solutions.

Due to the chemical reaction that occurs in the solution when it mixes with the acid gas, it is impossible to obtain these transfer properties directly. In view of the similarities with regard to configuration, molecular volume, and electronic structure, N_2O is often used as a nonreacting gas to estimate the properties of CO_2. It has been proved that "N_2O analogy" may be applied to estimate the solubility of CO_2 in aqueous alkanolamine solutions according to the following equation (*3*, *5*):

$$(\text{solubility of } CO_2) = C_1(\text{solubility of } N_2O) \qquad (1)$$

with

$$C_1 = \frac{(\text{solubility of } CO_2 \text{ in water})}{(\text{solubility of } N_2O \text{ in water})} \qquad (2)$$

The estimation of the diffusivity of CO_2 in alkanolamine solutions may be done in different ways. Sada et al. (*6*) and Haimour and Sandall (*7*) considered that the N_2O analogy can be used to estimate the diffusivity of CO_2. Diaz et al. (*4*) proved this analogy by using aqueous alcohol solutions. However, Versteeg et al. (*8*) thought that the analogue was not a general relation and suggested a modified Stokes-Einstein relation to calculate the diffusivity of CO_2:

$$(D_{N_2O}\eta^{0.8})_{\text{am soln}} = \text{constant} = (D_{N_2O}\eta^{0.8})_{\text{water}} \qquad (3)$$

For convenience, Versteeg et al. (*8*) correlated the data of solubility and diffusivity of N_2O and CO_2 in water based on their own and other experimental results. These correlations are as follows:

$$H_{N_2O} = 8.55 \times 10^6 \exp(-2284/T) \qquad (4)$$

$$H_{CO_2} = 2.82 \times 10^6 \exp(-2044/T) \qquad (5)$$

$$D_{N_2O} = 5.07 \times 10^{-6} \exp(-2371/T) \qquad (6)$$

$$D_{CO_2} = 2.35 \times 10^{-6} \exp(-2119/T) \qquad (7)$$

---

* To whom correspondence should be addressed.

0021-9568/91/1736-0071$02.50/0