Solubility and Diffusivity of N_2O and CO_2 in Aqueous Solutions of 2-Amino-2-methyl-1-propanol

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The solubility and diffusivity of N_2O in 0.5, 1, 1.5, and 2 mol L^{-1} 2-amino-2-methyl-1-propanol in water were measured over a range of temperatures and at atmospheric pressure and correlated. The N_2O analogy was used to estimate the solubility and diffusivity of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol.

1. Introduction

Alkanolamines have become one of the most important classes of chemicals for the removal of acid gas components, H_2S and CO_2, from natural gases and synthesis gas streams. Monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), and *N*-methyldiethanolamine (MDEA) are some examples of industrially important amines widely used in gas sweetening processes. Except *N*-methyldiethanolamine, conventional alkanolamines exhibit a relatively low maximum capacity for carbon dioxide. Recently a new class of amines, sterically hindered amines, has been discovered (*1*). These amines are capable of much higher loadings of CO_2 because their carbamates are relatively unstable. 2-Amino-2-methyl-1-propanol (AMP), a hindered primary amine which forms a carbamate with a much lower stability than the carbamates of monoethanolamine and diethanolamine, may become a potential absorbent in future recirculatory gas sweetening processes.

Diffusivity and physical solubility data of CO_2 in the aqueous amine solutions are needed to analyze the results of absorption experiments in order to determine the reaction kinetics or to be used in models for predicting the gas absorption rate. But the diffusivity and solubility of CO_2 in aqueous amine solutions cannot be measured directly as CO_2 undergoes chemical reaction with these solvents. The similarity in mass, molecular structure, and molecular interaction parameters between CO_2 and N_2O led Clarke (*2*) to assume that the ratios of the solubilities and 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. This concept was later used by Sada et al. (*3*, *4*), Versteeg and van Swaaij (*5*), Al-Ghawas et al. (*6*), and Haimour (*7*) to estimate these parameters for CO_2 in various amine solutions. Laddha et al. (*8*) investigated the solubility of N_2O and CO_2 in aqueous solutions of organic alcohols that are nonreacting with respect to both solutes. From their work it was found that the solubilities of CO_2 and N_2O in the different solutions examined have a constant ratio of 1.37. For a change in temperature between 288 and 303 K the ratio of solubilities in water was found by them to be within 2% of 1.37. They also reported that Deckwer, in some independent measurements of the solubilities of CO_2 and N_2O in aqueous solutions of glycol and glycerol, observed the ratio of the solubilities in these solutions to be 1.37 ± 0.04. Thus, it has been proved that the "N_2O analogy" may be applied to estimate the solubility of CO_2 in aqueous amine solutions according to the following equation:

$$\text{solubility of } CO_2 \text{ in amine solution} = (1/A_1)(\text{solubility of } N_2O \text{ in amine solution}) \quad (1)$$

$$A_1 = \frac{\text{solubility of } N_2O \text{ in water}}{\text{solubility of } CO_2 \text{ in water}} \quad (2)$$

The value of A_1 is, in general, 1.37. But, for better accuracy of the estimated solubility data of CO_2, it is desirable to find the value of A_1 at the particular temperature at which the CO_2 solubility is required to be estimated. It may be seen from Table I that the value of A_1 has been found to be 1.376 at 298 K by us.

Sada et al. (*3*, *4*), Haimour and Sandall (*9*), and Al-Ghawas et al. (*6*) considered that the N_2O analogy can also be used to estimate the diffusivity of CO_2. Diaz et al. (*10*) proved this analogy from measurements on aqueous alcohol solutions. Xu et al. (*11*) considered that it is preferable to use the N_2O analogy to estimate the diffusivity of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol rather than the Stokes–Einstein relation. However, Versteeg and van Swaaij (*5*) thought that the analogue was not a general relation and suggested a modified Stokes–Einstein relation to calculate the diffusivity of CO_2 in amine solutions.

Although the N_2O analogy was used by many researchers previously to estimate the solubility and diffusivity of CO_2 in aqueous solutions of amines such as monoethanolamine, diethanolamine, *N*-methyldiethanolamine, di-2-propanolamine, etc., there are limited data in the open literature on these parameters of N_2O and CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol in spite of the emerging importance of this amine in industrial gas treating processes.

In the present work, new experimental results on the solubility and diffusivity of N_2O in four aqueous 2-amino-2-methyl-1-propanol solutions over a range of temperatures and atmospheric pressure are presented. Then, using these results and N_2O analogy the solubilities and diffusivities of CO_2 in aqueous amine solutions are estimated and presented. These data will be useful for the experimentalist or the process design engineer who is interested in the problem of acid gas removal using aqueous solutions of 2-amino-2-methyl-1-propanol. As a matter of fact these results are needed to analyze the experimental absorption data of a research work on the absorption of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol, currently in progress in our laboratory.

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Table I. Solubility of CO_2 and N_2O in Water

	T/K	H/(Pa m³ mol⁻¹)	reference
CO_2	298	2967	Versteeg and van Swaaij (5)
	298	3039	Versteeg and van Swaaij (5)
	298	2993	present work
N_2O	298	4132	Versteeg and van Swaaij (5)
	298	4115	Sada et al. (4)
	298	4120	present work

2. Experimental Section

2.1. Solubility. The apparatus and the experimental technique used for the free gas solubility determination are similar to those used by Haimour and Sandall (9). The principle of the method is to bring a known volume of liquid into contact with a known volume of gas at constant temperature and pressure. Equilibrium is established by agitation, and the remaining volume of gas (undissolved) is measured. The change in the gas volume gives the amount dissolved in the liquid.

A glass absorption flask with a volume of 0.25×10^{-3} m³ was used. The local pressure was 100 kPa. The system was first purged with saturated N_2O gas at constant temperature. A measured volume of 0.3×10^{-4} m³ of the aqueous solutions of 2-amino-2-methyl-1-propanol was then injected into the absorption flask, and the liquid was agitated with a magnetic stirrer until there was no further change in gas volume. This measured volume change is equal to the volume of the sample minus the volume of gas absorbed. The partial pressure of N_2O in the experiments was corrected for the vapor pressure of the solution. The temperatures of the water bath and environment were kept constant within ±0.1 and ±0.2 K, respectively. The maximum experimental error in the gas solubility was estimated to be ±2%, and the reproducibility between the various experiments was always within 1%.

The solubilities of N_2O and CO_2 in degassed water were measured with this apparatus before making measurements of solubility in 2-amino-2-methyl-1-propanol solutions.

Reagent grade 2-amino-2-methyl-1-propanol with a purity of 97%, supplied by Loba Chemie Indoaustranal Co., Bombay, was used. Distilled water degassed by extensive boiling was used to make the solutions. N_2O was supplied by Indian Oxygen Limited, and CO_2 was taken from a commercial cylinder. The purities of the gases were above 99.8% and above 99%, respectively.

2.2. Diffusivity. A 2.55×10^{-2} m o.d. stainless steel wetted wall column of standard design (12) was used to measure the diffusivities of N_2O in water and 2-amino-2-methyl-1-propanol solutions and CO_2 in water. The gas–liquid contact time could be varied from 0.23 to 0.7 s by varying the absorption length but keeping the liquid flow rate constant. The gas absorption rate was measured by the volume uptake method using a soap film meter. The liquid flow rate was measured with a rotameter that was calibrated at various experimental temperatures and concentrations. The temperature of absorption was controlled within ±0.1 K. The pressure in the absorption chamber was about 100 kPa. The experimental error was estimated to be ±5%. Reproducibility between the various experiments was always within 2%.

3. Result and Discussion

3.1. Solubility. The solubility data for CO_2 and N_2O in water from the present work are presented in Table I in combination with literature results. There is a good agreement between literature results and those of the present study, thus supporting the applicability of the present experimental method.

The data for the solubility of N_2O in 0.5, 1, 1.5, and 2 mol L^{-1} aqueous solutions of 2-amino-2-methyl-1-propanol at four different temperatures are presented in Table II and plotted in Figures 1 and 2. As shown in Figure 1, the solubility of N_2O changes linearly with the amine concentration at a particular temperature within the range of amine concentrations and temperatures studied. The effect of temperature on the solubility of N_2O is shown in Figure 2 as an Arrhenius type of plot. Figure 2 shows that at a fixed concentration of the amine the solubility of N_2O changes exponentially with temperature. These results are in agreement with the trend in the results reported by Xu et al. (11). However, a comparison of the solubility data in a 2 mol L^{-1} 2-amino-2-methyl-1-propanol solution of the present study with those reported by Xu et al. (11) shows that the solubility values (H) presented by Xu et al. (11) are somewhat lower than those of the present study.

Table II. Solubility of N_2O for Various Concentrations of 2-Amino-2-methyl-1-propanol

	H/(Pa m³ mol⁻¹)			
T/K	0.5 mol L^{-1}	1.0 mol L^{-1}	1.5 mol L^{-1}	2.0 mol L^{-1}
288.5	3242.7	3413.0	3549.5	3716.7
293.0	3736.9	3941.1	4097.9	4293.0
298.0	4215.7	4445.6	4613.4	4825.9
303.0	4750.6	5005.6	5179.4	5404.6

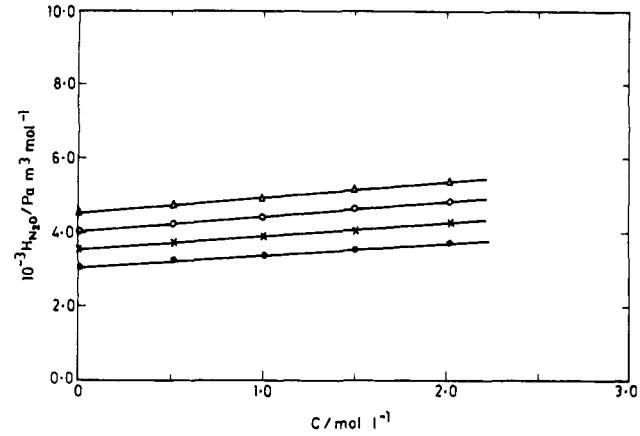

Figure 1. Solubility of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol: ●, 288.5 K; ×, 293 K; ○, 298 K; △, 303 K.

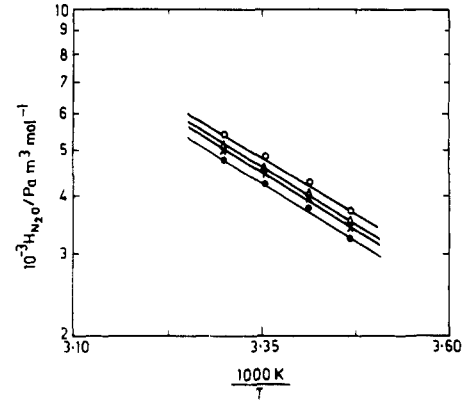

Figure 2. Solubility of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol: ●, 0.5 mol L^{-1}; ×, 1.0 mol L^{-1}; △, 1.5 mol L^{-1}; ○, 2.0 mol L^{-1}.

The experimental solubility data of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol of this work are correlated well by eq 3 within a maximum absolute deviation of 2.8%. In eq 3, H_{N_2O} is expressed in kPa m³ kmol⁻¹, C in kmol m⁻³, and T in K.

$$H_{N_2O} = (5.52 + 0.7C) \times 10^6 \exp(-2166/T) \quad (3)$$

Table III. Estimated Solubility of CO_2 in Aqueous Solutions of 2-Amino-2-methyl-1-propanol Using the N_2O Analogy

	in water		in aqueous amine solutions		
T/K	H_{CO_2}/(Pa m^3 mol^{-1})	H_{N_2O}/(Pa m^3 mol^{-1})	C/(mol L^{-1})	H_{N_2O}/(Pa m^3 mol^{-1})	H_{CO_2}/(Pa m^3 mol^{-1})
288.5	2360.41	3107.38	0.5	3242.7	2463.2
			1.0	3413.0	2592.6
			1.5	3549.5	2696.2
			2.0	3716.7	2823.3
293.0	2638.22	3518.78	0.5	3736.9	2801.7
			1.0	3941.1	2954.8
			1.5	4097.9	3072.4
			2.0	4293.0	3218.7
298.0	2993.08	4120.12	0.5	4215.7	3062.5
			1.0	4445.6	3229.5
			1.5	4613.4	3351.4
			2.0	4825.9	3505.8
303.0	3321.24	4551.16	0.5	4750.6	3466.8
			1.0	5005.6	3652.9
			1.5	5179.4	3779.7
			2.0	5404.6	3944.0

Table IV. Diffusivity D of CO_2 and N_2O in Water

	T/K	10^9D/(m^2 s^{-1})	reference
CO_2	303	2.29	Davidson and Cullen (*13*)
	303	2.15	Taniguchi and Sakurada (*14*)
	303.2	2.18	present work
N_2O	302.9	2.27	Versteeg and van Swaaij (*5*)
	303.8	2.35	Davidson and Cullen (*13*)
	303.2	2.09	present work

As for the solubility of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol, it can be estimated directly by the N_2O analogy, that is, by using eqs 1 and 3. The solubilities of CO_2 thus found by the N_2O analogy are presented in Table III. In order to estimate the solubility of CO_2 in the amine solutions, the required solubility data of CO_2 and N_2O in water at 298 K, found experimentally in this work and presented in Table I, have been used. For other temperatures the solubilities in water have been found from the correlations proposed by Versteeg and van Swaaij (*5*).

3.2. Diffusivity. In Table IV the diffusivities of CO_2 and N_2O in water are presented together with the data published in the open literature. There is a good agreement between literature results and those of the present study, thus supporting the validity of the present experimental method.

The diffusivities of N_2O in 0.5, 1, 1.5, and 2 mol L^{-1} aqueous solutions of 2-amino-2-methyl-1-propanol at 294, 301.5, 311.5, and 318 K are presented in Table V and plotted in Figures 3 and 4. At a particular temperature diffusivity decreases with increasing amine concentration. Also, at a fixed concentration diffusivity changes exponentially with temperature. These results agree with the trend reported by Xu et al. (*11*).

It is observed from Table V that the experimental diffusivity results of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol do not follow the Stokes–Einstein relation ($D\mu/T$ = constant) strictly. Figure 5 shows the diffusivity data plotted as D/T vs μ. From this plot it is seen that the data are correlated well by

$$D\mu^{0.82}/T = 2.12 \times 10^{-14} \qquad (4)$$

within a maximum absolute deviation of 1.84%. In eq 4, D is expressed in m^2 s^{-1}, μ in N s m^{-2}, and T in K. Similar results were reported by Haimour and Sandall (*9*) for the diffusivity of N_2O in aqueous solutions of *N*-methyldiethanolamine.

In regard to estimating the diffusivity of CO_2 Sada et al. (*4*) considered that a relation similar to eq 1 could be applied. Haimour and Sandall (*9*) studied the absorption of CO_2 and

Table V. Diffusivity of N_2O in Different Aqueous Solutions of 2-Amino-2-methyl-1-propanol at Different Temperatures

T/K	C/(mol L^{-1})	10^9D/(m^2 s^{-1})	$10^3\mu$/(N s m^{-2})	$10^{15}(D\mu/T)$/(N K^{-1})
294	0.0	1.59	0.978	5.289
	0.5	1.57	1.171	6.253
	1.0	1.30	1.471	6.504
	1.5	1.09	1.833	6.796
	2.0	0.88	2.346	7.022
301.5	0.0	1.95	0.824	5.329
	0.5	1.83	0.986	5.985
	1.0	1.55	1.228	6.313
	1.5	1.30	1.531	6.601
	2.0	1.10	1.882	6.866
311.5	0.0	2.51	0.672	5.415
	0.5	2.30	0.789	5.826
	1.0	1.98	0.951	6.045
	1.5	1.68	1.157	6.240
	2.0	1.45	1.398	6.507
318	0.0	2.93	0.596	5.491
	0.5	2.70	0.668	5.672
	1.0	2.29	0.827	5.955
	1.5	2.01	0.972	6.144
	2.0	1.67	1.206	6.333

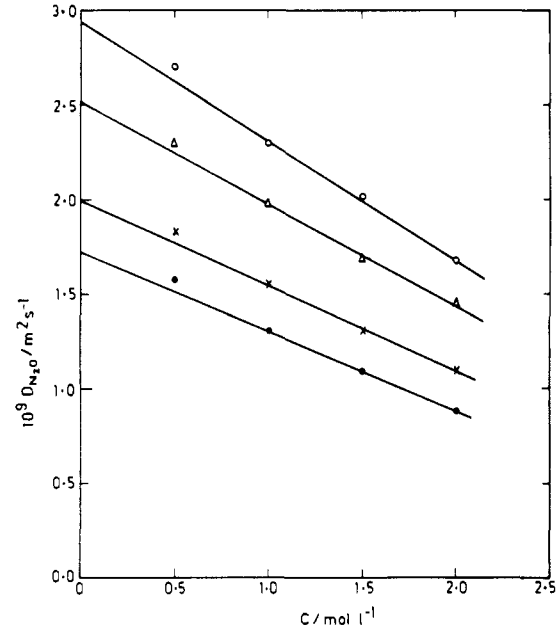

Figure 3. Diffusivity of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol: ●, 294 K; ×, 301.5 K; △, 311.5 K; ○, 318 K.

N_2O in aqueous solutions of *N*-methyldiethanolamine at various temperatures in a laminar liquid jet. At very short contact times the absorption of CO_2 can be considered as physical absorption without any enhancement due to chemical reaction, and therefore it was possible to verify for this particular solution the N_2O analogy for both solubility and diffusivity. From their results it could be concluded that for aqueous *N*-methyldiethanolamine solutions the N_2O analogy holds for both the parameters solubility and diffusivity. Diaz et al. (*10*) measured the rates of absorption of CO_2 and N_2O in aqueous solutions of organic alcohols (glycerol and 1,5-pentanediol) that are nonreacting with respect to both CO_2 and N_2O, by the laminar jet technique and proved that the "analogy" holds true for the diffusivities of CO_2 and N_2O in these liquids. These results indicate that it will be reasonable to use the N_2O analogy, as expressed by eq 5, to estimate the diffusivity of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol.

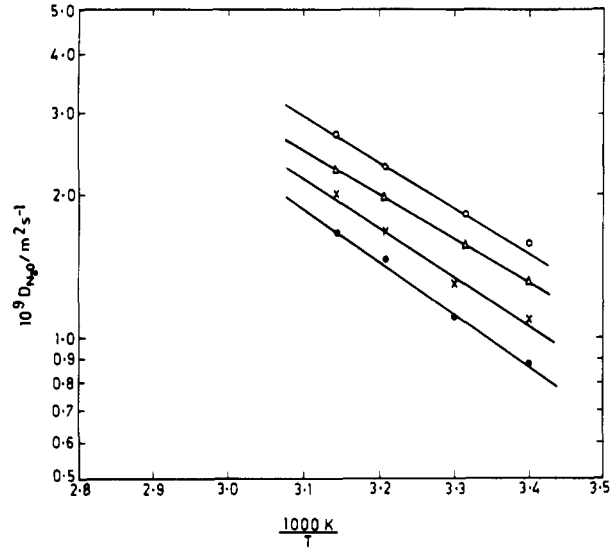

Figure 4. Diffusivity of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol: ○, 0.5 mol L^{-1}; △, 1.0 mol L^{-1}; ×, 1.5 mol L^{-1}; ●, 2.0 mol L^{-1}.

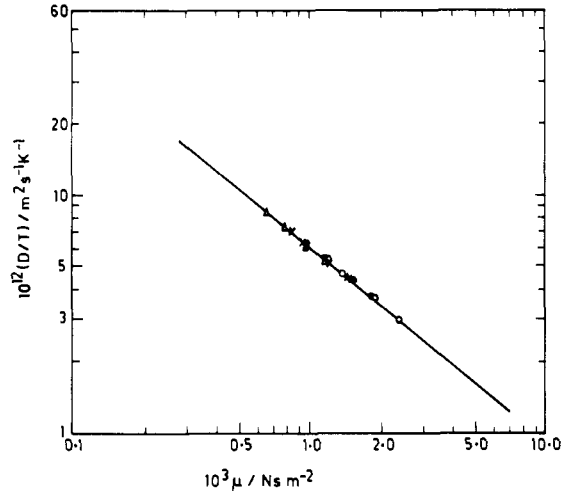

Figure 5. Correlation for diffusivity of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol: △, 0.5 mol L^{-1}; ×, 1.0 mol L^{-1}; ●, 1.5 mol L^{-1}; ○, 2.0 mol L^{-1}.

diffusivity of CO_2 in amine solution =

$$A_2(\text{diffusivity of } N_2O \text{ in amine solution}) \quad (5)$$

$$A_2 = \frac{\text{diffusivity of } CO_2 \text{ in water}}{\text{diffusivity of } N_2O \text{ in water}} \quad (6)$$

Diffusivity data of CO_2 thus estimated using eqs 4 and 5 are presented in Table VI.

The required density and viscosity values for the aqueous solutions of 2-amino-2-methyl-1-propanol shown in Figures 6 and 7, respectively, were obtained experimentally.

4. Conclusions

The results of the present work lead to the following conclusions.

(1) The solubility of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol changes exponentially with temperature at a constant concentration of the amine. At constant temperature the solubility is a linear function of the concentration of 2-amino-2-methyl-1-propanol. Under the experimental conditions of this work, the solubility of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol can be represented by eq 3. The solubility of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol can be estimated by the N_2O analogy.

(2) The diffusivity of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol changes with temperature at the same concentration of the amine in an exponential fashion. The

Table VI. Estimated Diffusivity of CO_2 in Aqueous Solutions of 2-Amino-2-methyl-1-propanol Using the N_2O Analogy

	in water		in aqueous amine solutions		
T/K	$10^9 D_{CO_2}$/ (m^2 s^{-1})	$10^9 D_{N_2O}$/ (m^2 s^{-1})	C/ (mol L^{-1})	$10^9 D_{N_2O}$/ (m^2 s^{-1})	$10^9 D_{CO_2}$/ (m^2 s^{-1})
294.0	1.74	1.59	0.5	1.57	1.72
			1.0	1.30	1.42
			1.5	1.09	1.19
			2.0	0.88	0.96
301.5	2.08	1.95	0.5	1.83	1.95
			1.0	1.55	1.65
			1.5	1.30	1.39
			2.0	1.10	1.17
311.5	2.61	2.51	0.5	2.30	2.39
			1.0	1.98	2.06
			1.5	1.68	1.75
			2.0	1.45	1.51
318.0	3.00	2.93	0.5	2.70	2.76
			1.0	2.29	2.34
			1.5	2.01	2.06
			2.0	1.67	1.71

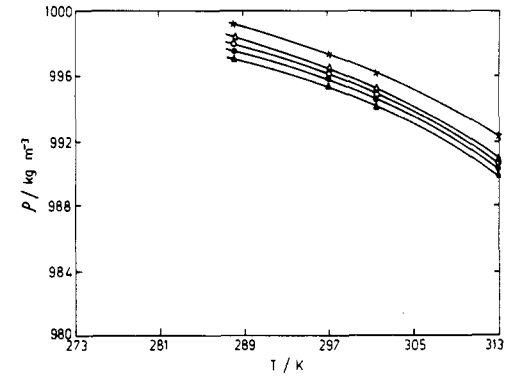

Figure 6. Density of aqueous solutions of 2-amino-2-methyl-1-propanol: ×, 0 mol L^{-1}; △, 0.5 mol L^{-1}; ○, 1.0 mol L^{-1}; ●, 1.5 mol L^{-1}; ▲, 2.0 mol L^{-1}.

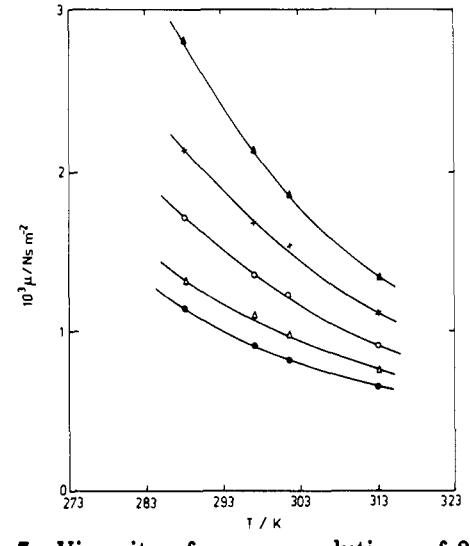

Figure 7. Viscosity of aqueous solutions of 2-amino-2-methyl-1-propanol: ●, 0 mol L^{-1}; △, 0.5 mol L^{-1}; ○, 1.0 mol L^{-1}; ×, 1.5 mol L^{-1}; ▲, 2.0 mol L^{-1}.

diffusivity of N_2O in aqueous solutions of 2-amino-2-methyl-1-propanol can be obtained from eq 4.

The diffusivity of CO_2 in aqueous solutions of the amine can be estimated directly by the N_2O analogy, that is, by using eqs 4 and 5.

Glossary

A_1	constant defined by eqs 1 and 2
A_2	constant defined by eqs 5 and 6
C	concentration of 2-amino-2-methyl-1-propanol in solution
D	diffusivity
H	Henry's coefficient
T	temperature
μ	viscosity
ρ	density

Subscripts

CO_2	carbon dioxide
N_2O	nitrous oxide

Literature Cited

(1) Sartori, G.; Savage, D. W. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 238.
(2) Clarke, J. K. A. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 239.
(3) Sada, E.; Kumazawa, H.; Butt, M. A. *J. Chem. Eng. Data* **1977**, *22*, 277.
(4) Sada, E.; Kumazawa, H.; Butt, M. A. *J. Chem. Eng. Data* **1978**, *23*, 161.
(5) Versteeg, G. F.; van Swaaij, W. P. M. *J. Chem. Eng. Data* **1988**, *33*, 29.
(6) Al-Ghawas, H. A.; Hagewiesche, D. P.; Ruiz-Ibanez, G.; Sandall, O. C. *J. Chem. Eng. Data* **1989**, *34*, 391.
(7) Haimour, N. M. *J. Chem. Eng. Data* **1990**, *35*, 177.
(8) Laddha, S. S.; Diaz, J. M.; Danckwerts, P. V. *Chem. Eng. Sci.* **1981**, *36*, 288.
(9) Haimour, N.; Sandall, O. C. *Chem. Eng. Sci.* **1984**, *39*, 1791.
(10) Diaz, J. M.; Vega, A.; Coca, J. *J. Chem. Eng. Data* **1988**, *33*, 10.
(11) Xu, S.; Otto, F. D.; Mather, A. E. *J. Chem. Eng. Data* **1991**, *36*, 71.
(12) Danckwerts, P. V. *Gas Liquid Reactions*; McGraw-Hill: New York, 1970.
(13) Davidson, J. F.; Cullen, E. *J. Trans. Inst. Chem. Eng.* **1957**, *35*, 51.
(14) Taniguchi, M.; Sakurada, *J. J. Soc. Chem. Ind., Jpn.* **1955**, *8*, 584.

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