1506 J. Chem. Eng. Data **2002,** *47,* 1506−1509

Solubility of Carbon Dioxide and Nitrous Oxide in Water + Methyldiethanolamine and Ethanol + Methyldiethanolamine Solutions

Hanna Kierzkowska-Pawlak* and Roman Zarzycki

Faculty of Process and Environmental Engineering, Technical University of Łódź, 90-924 Łódź, Poland

The solubility of carbon dioxide and nitrous oxide in water + methyldiethanolamine and ethanol + methyldiethanolamine (MDEA) solutions was investigated over the whole range of amine concentrations. Experiments were performed in a reaction calorimeter at 293 K at constant atmospheric pressure. From the measurements of the solubilities of N_2O in aqueous MDEA and of CO_2 in pure amine, it was found that a "N_2O analogy" for the prediction of CO_2 solubility could not be used over the whole composition range of the aqueous MDEA solutions. In the case of ethanol + MDEA solutions, both gases show opposite trends for physical solubility as a function of amine concentration. These results disqualify the use of the "N_2O analogy" in the estimation of CO_2 solubility in ethanol + MDEA solutions.

1. Introduction

Absorption by aqueous alkanolamine solutions is the dominant industrial process for removing acid gases such as CO_2 and H_2S, from industrial and natural gas streams. Mixtures of water, organic solvent, and the amine are also used, as in the case of the Shell-Sulfinol process.[1] The amines that have been proved to be of principal commercial interest for gas purification are monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). In the past decade interest in using methyldiethanolamine, which is a tertiary amine, has increased significantly. The main advantage of MDEA is its ability to selectively absorb H_2S from gas streams containing CO_2 and H_2S. Other advantages of MDEA as a solvent are a small enthalpy of reaction with acid gases and its low vapor pressure.

Several authors have studied the mechanism and kinetics of the reaction between CO_2 and tertiary amines in its aqueous solutions. It was concluded that because of the N atom in the amine, which does not have a free hydrogen atom, no carbamate ions can be formed. However, in the presence of water, hydration of CO_2 occurs, resulting in bicarbonate and protonated tertiary alkanolamines. According to the generally accepted reaction mechanism in water-free tertiary amines, CO_2 dissolves only physically.[2]

For the design and operation of absorption equipment for gas-treating processes it is necessary to have information on the mass transfer coefficient, reaction kinetics, and fundamental physicochemical properties such as the solubility of acid gas components in the various solutions. The physical solubility of CO_2 in aqueous solutions of alkanolamines cannot be measured directly because CO_2 reacts with the amines. So this property must be estimated from the corresponding data of similar nonreacting systems. Nitrous oxide is an inert gas, which is very similar to CO_2 in many physical properties. It was first found by Clarke et al.[3] that both these gases behave similarly in nonreacting low-viscosity liquids.

Laddha et al.[4] investigated the solubility of N_2O and CO_2 in the aqueous solutions of selected alcohols that are nonreacting with respect to both solutes and have a somewhat similar structure to MEA and DEA. From this work it was concluded that the ratio of solubilities of the two gases, expressed by Henry's law constants (k_H), was the same in the aqueous solutions of selected alcohols as that in water at the same temperature. Therefore, from the solubility of N_2O, values of Henry's law constant can be estimated for CO_2 according to the equation

$$k_{H,CO_2} = C_1 k_{H,N_2O} \tag{1}$$

with

$$C_1 = \frac{k_{H,CO_2}(\text{water})}{k_{H,N_2O}(\text{water})}$$

Several authors used the "N_2O analogy" for the estimation of CO_2 solubility in the aqueous solutions of alkanolamines and used these data in the determination of absorption kinetics. However, a direct check whether the N_2O solubility can predict the CO_2 solubility in solutions when it reacts is not possible. Haimour and Sandall[5] used a laminar jet apparatus to measure the CO_2 absorption rate into aqueous MDEA over very short contact times under conditions where the reaction did not affect the absorption rate. Their results indicate that the "N_2O analogy" holds in aqueous MDEA solutions.

The present study was designed to check whether this analogy is valid for ethanol + MDEA solutions. Therefore, the absorption of carbon dioxide and nitrous oxide was carried out in the alcoholic solutions of MDEA. The experiments were performed in a reaction calorimeter at 293 K at a constant pressure close to $P = 0.1$ MPa. Additionally, some N_2O solubility measurements in the aqueous solutions over the range of (0 to100) mass % MDEA were performed to compare with the existing literature data and to check if the analogy was maintained over the whole range of MDEA concentrations. The data previously obtained on N_2O solubility in the aqueous

---

* Corresponding author. Fax: 48-42-6368133. E-mail: kierzkow@ck-sg.p.lodz.pl.

10.1021/je020093v CCC: $22.00 © 2002 American Chemical Society
Published on Web 09/13/2002

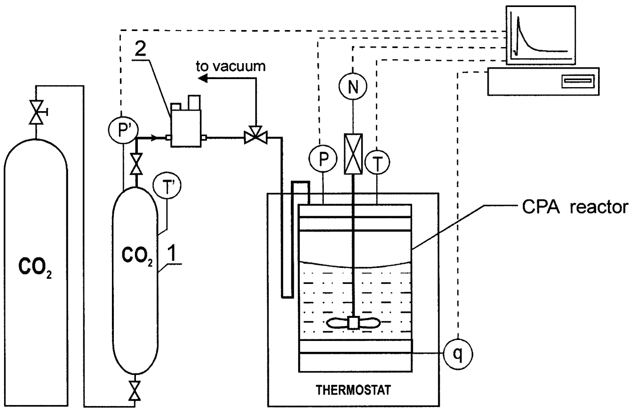

Figure 1. Experimental setup: 1, storage tank; 2, downstream pressure regulator; N, stirring speed transducer; T, temperature sensor in the reactor; T′, temperature sensor in the storage tank; P′, pressure transducer; q, heat flow transducer.

MDEA usually cover a limited range of amine concentration up to 30 mass %.

2. Experimental Section

2.1. Apparatus. The solubility measurements were performed in a commercially available reaction calorimeter (Chemical Process Analyzer, ChemiSens AB, Sweden) which is a fully automated and computer-controlled stirred reactor vessel with the possibility of an on-line measurement of the thermal power developed by the process. Its heart is a mechanically agitated stainless steel/glass reactor with an effective volume of 250 cm^3. While in use, it is submerged in the thermostating liquid bath. A Peltier element mounted inside the bottom of the reactor serves as an efficient heating and cooling device and keeps the temperature constant to ±0.1 K. Ports in the lid enable charging and sampling from both the gas and liquid phases. All operating conditions, including the reactor temperature, the stirring speed, and the system pressure as a function of time, are recorded using the special data acquisition system.

2.2. Procedure. In this work the experimental procedure involved measurements of the gas-phase pressure in the storage tank with respect to time during semibatch isothermal absorption of the gas. The schematic diagram of an experimental setup, modified with the aim of absorption studies, is shown in Figure 1. The gas was charged from the storage tank of known volume (75 or 504 cm^3) to the reactor by a special feed line through the downstream pressure controller (Brooks, 5866), which allowed the constant total pressure (P) of 0.1 MPa to be maintained in the reactor. After the reactor was filled with the desired solution, the liquid was degassed and heated to a given temperature. After equilibrium was established, the stirring was stopped for a moment. Then, under the solution vapor pressure, pure carbon dioxide or nitrous oxide was introduced during a short time to the upper part of the cell. After a few seconds, when the pressure in the reactor reached the set value of 0.1 MPa, the process was initiated by switching on the stirrer at about 1500 rpm. The subsequent decline of the gas pressure in the storage tank $p_A'(t)$ was recorded as a function of time until the equilibrium state was reached. The pressure in the storage tank, p_A', was measured by means of an IDA transducer (Nobel Electronik) with the accuracy of 0.005 MPa. The total pressure drop in the storage tank was necessary for calculating the amount of gas absorbed in the liquid. The total pressure change in our experiments was in the range of (0.1 to 1) MPa depending on the volume of the storage tank applied and the system studied.

The chemicals employed, CO$_2$ (99.995 vol % pure), N$_2$O (99.995 vol % pure, medical grade), ethanol (99 mass % pure), and MDEA (Riedel-de Haën, 98.5 mass % pure), were used without any further purification. In the preparation of aqueous alkanolamine solutions, distilled, deionized water was used. Because of the fact that even a small amount of water has a significant contribution to the mechanism of absorption and thus influenced the measured solubility, all nonaqueous solutions were stored over molecular sieves prior to use. However, totally water-free liquids could not be obtained. The lowest water content that could be achieved during the experiments was around 0.1 mass %.

To provide additional data on the gas solubility, the measurements were carried out over the whole range of the MDEA concentrations. All experiments were done at 293 K. The total pressure in the reactor was always kept at 0.1 MPa. The volume of the liquid loaded in the reactor was kept at 150 cm^3. Each absorption experiment for given conditions was repeated at least twice. The reproducibility of the solubility measurements was better than 3%. The estimated maximum error in the reported values of gas solubility was less than 4%.

3. Results and Discussion

The apparatus and method were verified by studying the solubility of carbon dioxide in water and those of nitrous oxide in water and in aqueous alkanolamine and comparing the results with those of other investigators. The solubility was expressed by Henry's law constant according to the equation

$$p_i = \mathrm{k}_{\mathrm{H},i} c_{i\mathrm{L}} \tag{2}$$

where p_i is the partial pressure of species i in the gas phase, $k_{\mathrm{H},i}$ is the Henry's law constant, and $c_{i\mathrm{L}}$ is the concentration of species i in the liquid phase. The partial pressure of the absorbed gas in the reactor was calculated according to the measured total pressure in the system (0.1 MPa) corrected for solution vapor pressure by use of Raoults's law. In these calculations the MDEA vapor pressure was neglected, as it was very small compared to the solvent vapor pressure. The number of moles of absorbed gas, necessary for calculating the gas concentration in the liquid phase, was determined from the total pressure decrease in the storage tank. It should be noted that, contrary to the cases of previous works, a nonideal behavior of the gas phase was assumed. In calculations the Beatty−Bridgeman state equation was applied. The experimental results on N$_2$O solubilities in aqueous solutions of MDEA and on CO$_2$ and N$_2$O solubilities in ethanol solutions of MDEA over the whole range of amine concentrations are listed in Table 1, where the average values are reported.

For the CO$_2$ + water system the Henry's law constant of 2.61 MPa·m^3·kmol^{-1} was found in this work, which was in fair agreement with the value of 2.59 MPa·m^3·kmol^{-1} obtained by Al-Ghawas et al.[6] and also with the value of 2.64 MPa·m^3·kmol^{-1} reported by Versteeg et al.[7] The solubility data for N$_2$O in the (0 to 30) mass % aqueous MDEA from this work are presented in Figure 2 along with the data published in the literature. From Figure 2 it can be seen that the Henry's law constants extracted from this apparatus match qualitative results and trends of other investigators very well. Especially the agreement with the data of Al-Ghawas et al.[6] for (10 to 30) mass % MDEA solutions is very good, and the deviation does not exceed

Table 1. Experimental Results of Gas Solubility for Different Mass Fractions of MDEA, w_2, at 293 K

$100w_2$	$k_H{}^a/\mathrm{MPa \cdot m^3 \cdot kmol^{-1}}$	$100w_2$	$k_H{}^a/\mathrm{MPa \cdot m^3 \cdot kmol^{-1}}$
	N_2O in Water (1) + MDEA (2)		
0	3.49	60	4.35
10	3.54	70	4.11
20	3.82	85	3.31
30	4.05	90	2.82
50	4.52	100	1.61
	CO_2 in Ethanol (1) + MDEA (2)		
0	0.949	60	0.150
10	0.371	70	0.117
20	0.288	85	0.085
30	0.223	100	0.076
50	0.184		
	N_2O in Ethanol (1) + MDEA (2)		
0	0.803	60	1.185
10	0.834	70	1.305
20	0.895	85	1.564
30	1.036	100	1.610
50	1.142		

[a] The averages of several measured values.

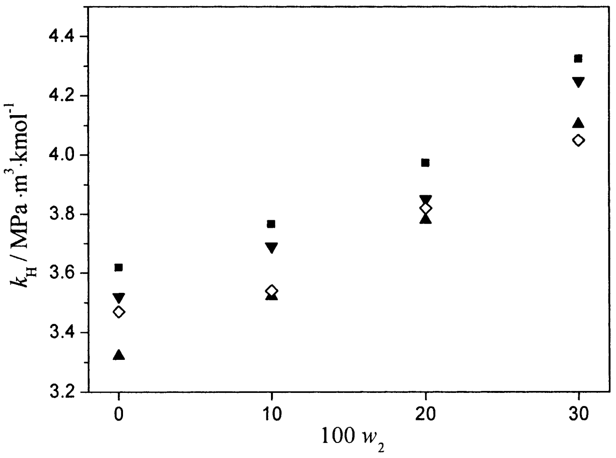

Figure 2. Henry's law constants for N_2O solubility in water (1) + MDEA (2) solutions at 293 K: ▲, Al-Ghawas et al.;[6] ▼, Versteeg et al.;[7] ■, Rinker et al.;[8] ◇, this work.

3% in this case. The above consistency supports the technique applied here.

For the interpretation of experimentally determined Henry's law constants over the whole range of MDEA concentration, they were recalculated in terms of the distribution coefficient, which is defined by the equation

$$m_i = \frac{c_{iL}}{c_{iG}} \tag{3}$$

To check if the system can be treated as ideal, all recalculated experimental results on the $N_2O + H_2O +$ MDEA system were plotted against mole fraction of the amine, as shown in Figure 3. Additionally, in Figure 3 the following relationship

$$\ln m_{\text{mix}} = \sum_{j=1}^{2} x_j \ln m_i \tag{4}$$

is plotted which predicts the solubility in mixed solvents, m_{mix}, by the ideal mixing rule. The subscript j in eq 4 refers to a liquid component in the solution (water and MDEA in this case). As can be seen from Figure 3, initially with an increasing MDEA concentration, the N_2O solubility decreases. Then from about a MDEA mole fraction of 0.13, the solubility increases. It is clear from this figure that the system studied cannot be treated as an ideal one.

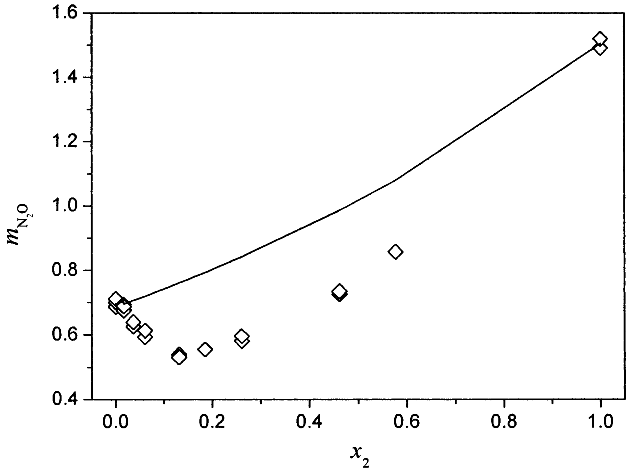

Figure 3. Distribution coefficient, m, of N_2O for water (1) + MDEA (2) solutions at 293 K. Comparison with ideal mixing rule: ◇, experimental data; —, ideal mixing rule.

From data on solubilities of both gases in pure water, the constant C_1 in eq 1 can be obtained. At 293 K, $C_1 = 1.34$, which is in good agreement with the value 1.37 reported by Laddha et al.[4] However, the CO_2 solubility in pure MDEA, $m_{CO_2} = 31.7$, was found to be much higher than that in pure water and also much higher than the N_2O solubility in pure MDEA, $m_{N_2O} = 1.5$. At the temperature 293 K, the ratio of CO_2/N_2O solubility in pure MDEA is thus 21, while in water the ratio is only 1.34. According to the "N_2O analogy", both ratios should be equal. Even if it is assumed that the residual small amount of water or other contaminants (primary or secondary amines) reacts completely with dissolved CO_2, the measured solubility in pure MDEA is still much higher. It is also higher than that measured by Kreulen et al.,[9] who reported the ratio of CO_2/N_2O solubility in pure MDEA to be 3.4 at 298 K. Despite this difference, a similar conclusion to that in the work of Kreulen et al.[9] can be drawn from the present results that the "N_2O analogy" for prediction of the CO_2 solubility cannot be used over the whole composition range of the aqueous MDEA solutions.

The surprising results were obtained while measuring the CO_2 and N_2O solubilities in ethanol solutions of MDEA. As pointed out in the Introduction, no chemical reaction should be observed in nonaqueous solutions of amine. Both gases should dissolve only physically, and because of the main assumptions underlying the "N_2O analogy", the solubilities of these gases should be similar. However, as can be seen from the tabulated data, the solubility of CO_2 is much higher than that of N_2O, and it increases with amine concentration, as opposed to the case for nitrous oxide. This is in strong contradiction with the trends predicted by the "N_2O analogy". This is clearly illustrated in Figures 4 and 5, in which relationship 4 is plotted together with the presently recalculated solubility data in terms of distribution coefficient. As can be seen, the N_2O solubility in ethanol solutions of MDEA decreases about twice going from ethanol to pure MDEA, and it seems that the data can be exactly described by the ideal mixing rule. The solubility of CO_2 increases several orders of magnitude over a range of (0 to 100) mass % MDEA, and the experimental measured values are higher than the ones predicted by the ideal mixing rule. It is clear from the present results that the solubility of CO_2 in alcoholic solutions of MDEA cannot be inferred from measurements

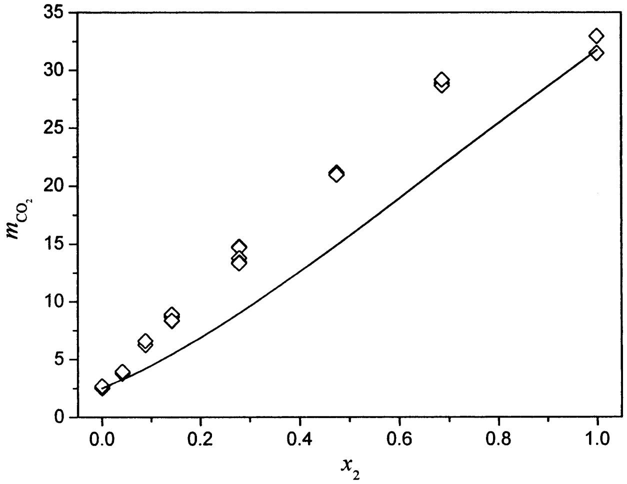

Figure 4. Distribution coefficient, *m*, of CO_2 for ethanol (1) + MDEA (2) solutions at 293 K: ◇, experimental data; —, ideal mixing rule.

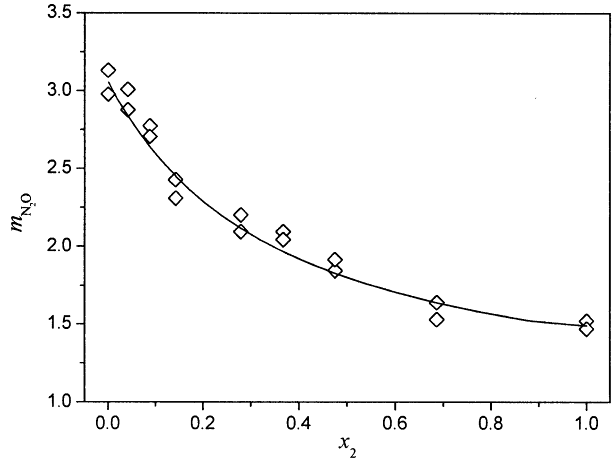

Figure 5. Distribution coefficient, *m*, of N_2O for ethanol (1) + MDEA (2) solutions at 293 K: ◇, experimental data; —, ideal mixing rule.

with N_2O. According to the generally accepted reaction mechanism of CO_2 in aqueous tertiary amines, no chemical reaction should take place between CO_2 and MDEA molecules in nonaqueous solvents. The only explanation of such a high solubility of CO_2 appears to be a different character of interactions of dissolved CO_2 with the solvent molecules than that of N_2O, where undoubtedly only physical absorption occurs.

The methyldiethanolamine has one amino group and can combine with another amine molecule as well as the hydroxyl group of the solvent through hydrogen bonding. Moreover, it seems to be possible in this case for the nitrogen atom to interact with the CO_2 molecule through hydrogen bonding. Such a difference in the solubilities of both gases in alcoholic solutions of MDEA can be thus tentatively interpreted in terms of structural changes in the solution due to hydrogen bonding.

4. Conclusions

In the present study the solubility of CO_2 and N_2O in aqueous and nonaqueous solutions of MDEA was investigated by the use of a reaction calorimeter. The experimental method applied avoids analysis of the gas and liquid phases, which introduces uncertainties and allows us to determine the amounts of gas absorbed in the liquid from the pressure decrease in the storage tank.

The comparison of the Henry's law constants for the $N_2O + H_2O +$ MDEA systems obtained in this work with those published by others demonstrates very good agreement. In the case of pure MDEA, the CO_2 solubility was found to be much higher than that of N_2O, which was in disagreement with the predictions using the "N_2O analogy". The present results indicate that this analogy cannot be used over the whole composition range of the aqueous MDEA solutions in predicting the CO_2 solubility.

In the case of ethanol solutions of MDEA, both gases show opposite trends for solubility as a function of amine concentration. The N_2O solubility into ethanol solutions of MDEA decreases with the rise of amine concentration, while the CO_2 solubility strongly increases. The reason for such different behavior of N_2O and CO_2 in nonaqueous solutions of MDEA is unclear, assuming that they both dissolve only physically. It seems to be possible that the high solubility of CO_2 can be attributed to the additional interactions in the solution through the hydrogen bonding. However, the mechanism of CO_2 absorption into nonaqueous MDEA solutions needs to be further investigated.

Literature Cited

(1) Kohl, A. L.; Riesenfeld, F. C. *Gas Purification*, 5th ed.; Gulf Publishing: Houston, TX, 1997.

(2) Versteeg, G. F.; Van Dijck, L. A. J.; Swaaij, W. P. M. On the Kinetics Beetween CO_2 and Alkanolamines Both in Aqueous and Nonaqueous Solutions. An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113−158.

(3) Clarke, J. K. A. Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 239−245.

(4) Laddha, S. S.; Diaz, J. M.; Danckwerts, P. V. The N_2O Analogy: The Solubilities of CO_2 and N_2O in Aqueous Solutions of Organic Compounds. *Chem. Eng. Sci.* **1981**, *36*, 228−229.

(5) Haimour, N.; Sandall, O. C. Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine. *Chem. Eng. Sci.* **1984**, *39*, 1791−1796.

(6) Al-Ghawas, H. A.; Hagewiesche, D. P.; Ibanez, G.; Sandall, O. C. Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine. *J. Chem. Eng. Data* **1989**, *34*, 385−391.

(7) Versteeg, G. F.; Swaaij, W. P. M. Solubility and Diffusivity of Acid Gases (CO_2, N_2O) in Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data* **1988**, *33*, 29−34.

(8) Rinker, E. B.; Ashour, S. S.; Sandall, O. C. Kinetics and Modelling of Carbon Dioxide Absorption into Aqueous Solutions of *N*-Methyldiethanolamine. *Chem. Eng. Sci.* **1995**, *50*, 755−768.

(9) Kreulen, H.; Smolders, C. A.; Versteeg, G. F.; van Swaaij, W. P. M. Selective Removal of H_2S from Sour Gases with Microporous Membranes. Part II. A Liquid Membrane of Water-Free Tertiary Amines. *J. Membr. Sci.* **1993**, *82*, 185−197.

Received for review May 16, 2002. Accepted August 7, 2002.

JE020093V