J. Chem. Eng. Data **1994,** *39,* 817−822

Physical Solubility of Carbon Dioxide in Aqueous Alkanolamines via Nitrous Oxide Analogy

Gregory J. Browning and Ralph H. Weiland*

Department of Chemical Engineering, University of Newcastle, Callaghan, New South Wales 2308, Australia

Van Krevelen coefficients for protonated monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), the carbamates of MEA and DEA, and the bicarbonate ion have been determined experimentally from measurements of the solubility of N_2O at 25 °C and atmospheric pressure in aqueous solutions of these ions. Measured values differ significantly from values recommended by others in the absence of experimental data. By analogy with N_2O, the solubility of carbon dioxide in the same solutions can be estimated.

Introduction

In the petrochemical and natural gas industry, the removal of carbon dioxide and hydrogen sulfide from process gas streams is commonly achieved by reacting these impurities with aqueous alkanolamines. Alkanolamines used for this purpose include monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) and, more recently, their mixtures.

In order to accurately design gas−liquid contacting equipment, information on the physical solubility of acid gases in single and blended alkanolamines is needed. In addition, a knowledge of the effect of acid gas loading on the solubility is also required. Currently, the experimental results available in these areas are either unreliable or nonexistent.

The measurement of the physical solubility is generally based on determining the concentration of gas absorbed in a solution at equilibrium. If the absorbed gas reacts with the solvent, then the physical equilibrium cannot be measured. As such, the physical solubility of carbon dioxide in alkanolamine solutions cannot be measured directly.

Clarke (1964) proposed the use of a similar gas that is unreactive in the test solution to measure the solubility. A proportionality constant is then used to calculate the solubility of carbon dioxide. Since then, nitrous oxide has been successfully used to predict the physical solubility of carbon dioxide by a number of researchers, including Al-Ghawas *et al.* (1989), Haimour and Sandall (1984), Laddha *et al.* (1981), and Weiland and Trass (1971). Nitrous oxide is used because it has a size, shape, electronic configuration, and Lennard-Jones potentials similar to those of carbon dioxide.

Haimour and Sandall (1984) expressed the N_2O analogy, at 25 °C, in the following form:

$$\frac{H_{(CO_2/soln)}}{H_{(N_2O/soln)}} = \frac{H_{(CO_2/H_2O)}}{H_{(N_2O/H_2O)}} = 0.73 \qquad (1)$$

where $H_{(CO2/H2O)}$ and $H_{(N2O/H2O)}$ are the Henry constants of carbon dioxide and nitrous oxide in pure water and $H_{(CO2/soln)}$ and $H_{(N2O/soln)}$ are their Henry constants in aqueous amine solution.

Laddha *et al.* (1981) performed solubility experiments on a number of organic compounds in aqueous solutions to test this relationship. The compounds chosen were glycol, 1-propanol, glycerol, 1,5-pentanediol, and diethylene glycol. They were selected for their structure similar to those of MEA and DEA. They found that all systems were in agreement with the nitrous oxide analogy to within 5%.

By measuring the Henry constant of nitrous oxide in solution, eq 1 can be used to predict the Henry constant of carbon dioxide in a solution of the same composition.

The aim of this work is to measure the physical solubility of nitrous oxide in partially loaded solutions of MEA, DEA, and MDEA and their blends and to develop empirical equations to predict the solubility at any amine concentration and carbon dioxide loading. These equations can then be used to predict the physical solubility of carbon dioxide via the nitrous oxide analogy.

Background

The solubility of a gas in a liquid can be expressed in terms of Henry's law which states that the partial pressure of a gas in equilibrium with a liquid is proportional to the concentration of the gas in the liquid, or

$$p = Hc \qquad (2)$$

where p = the partial pressure of the component (kPa), H = Henry's constant (kPa·L·mol^{-1}), and c = the concentration of the component in solution (mol·L^{-1}). This relationship holds for sparingly soluble gases in real solutions and for real gases at low pressures. Nitrous oxide obeys Henry's law well due to its low solubility in alkanolamine solutions. Some substances, such as sulfur dioxide in aqueous solution, do not follow Henry's law, even at low pressures, due to the effect of ionization.

Henry's constant is also a strong function of concentration. At present there is no way to predict the Henry constant of alkanolamine blends from data obtained for single amines. It is an aim of this work to develop an empirical equation which will achieve this.

When carbon dioxide reacts with alkanolamines, the ions amine carbamate, bicarbonate, and protonated amine are formed, thereby changing the chemical composition of the solution. The increase in ionic strength causes a reduction in gas solubility. This phenomenon was first observed by Setschenow in 1892 and is referred to as the salting-out effect. Since then van Krevelen and Hoftijzer (1948) modified Setschenow's original equation to what is now

---

* To whom correspondence should be addressed. Present address: Optimized Gas Treating Inc., 15638 Whitewater Lane, Houston, TX 77079.

0021-9568/94/1739-0817$04.50/0

know as the van Krevelen correlation:

$$\log(H/H^*) = hI \tag{3}$$

Here, H and H^* are the Henry constants for the electrolyte solution and the pure molecular solvent, respectively, and I is the ionic strength of the solution, given by

$$I = (1/2)\sum c_i z_i^2 \tag{4}$$

where c and z are the concentration and charge of species i, respectively. Equation 3 holds for most systems for ionic strengths up to at least 2 mol·L^{-1}. The factor h is the sum of three constants which are dependent on the system:

$$h = h_+ + h_- + h_g \tag{5}$$

Here h_+ and h_- are the van Krevelen coefficients for the cations and anions in solution and h_g is the coefficient for the dissolving gas. These coefficients are independent of concentration, but may be a function of temperature.

In order for the van Krevelen coefficients to be consistent with each other, a standard reference system must be used. The system proposed by Ueyama and Hatanaka (1981) is based on values of $h_+(\mathrm{Na}^+) = 0.091$ L·mol^{-1} and $h_-(\mathrm{Cl}^-) = 0.021$ L·mol^{-1}. This basis was chosen because sodium chloride is most commonly used for salting-out experiments.

Joosten and Danckwerts (1972) proposed that, for mixed electrolyte solutions, the van Krevelen correlation could be expressed as

$$\log(H/H^*) = \sum h_i I_i \tag{6}$$

where h_i and I_i are the van Krevelen coefficient and ionic strength attributable to the electrolyte i. This proposed equation remains undemonstrated as there are no experimental data available to support either it or any other method of predicting the Henry constant for mixed electrolyte solutions from pure component or single electrolyte data.

In order to utilize eq 6, the ionic strength of the solution must be calculated. To find the ionic strength, the Deshmukh–Mather model (Deshmukh and Mather, 1981) can be used to speciate loaded solutions of single or blended amines. This model is based on an extension of the Debye–Hückel theory and has been fitted to all available vapor–liquid equilibrium data (Weiland *et al.*, 1993). Not only does the Deshmukh–Mather model allow the calculation of the concentrations of the ions in solution, but it can also be used to find the partial pressures of the components in the vapor phase.

Apparatus

The apparatus used in this work was based on similar equipment first used by Weiland and Trass (1971) and later by a number of researchers including Haimour and Sandall (1984) and Al-Ghawas *et al.* (1989). A schematic diagram of this equipment is shown in Figure 1.

The apparatus consisted of an equilibrium cell to which the liquid samples were introduced through a septum by a hypodermic syringe. The septum used was the same as used in gas chromatography injection systems and ensured no gas leakage. Liquid samples were agitated using a magnetic stirrer.

The gas volumes were measured by the mercury level in the buret stem. Atmospheric pressure was maintained inside the apparatus by adjustment of the movable barometric leg.

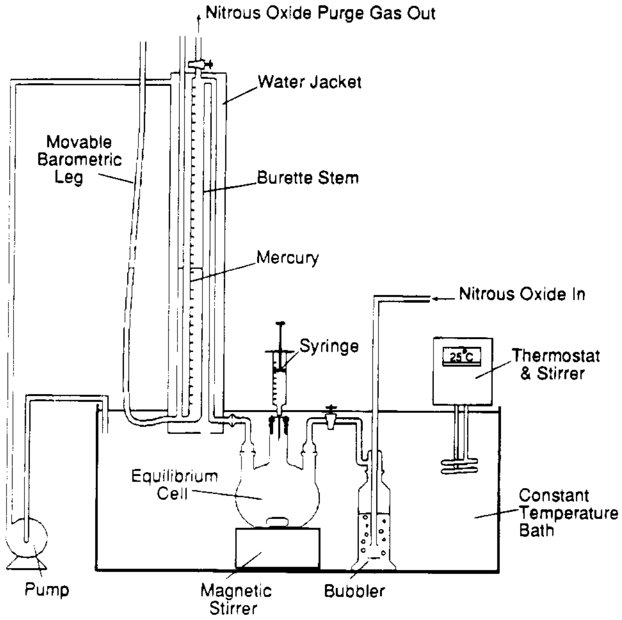

Figure 1. Schematic diagram of the experimental apparatus.

Nitrous oxide of 99.5% purity was used for all experiments and was saturated with water vapor using a sintered glass Dreschel head bubbler.

All parts of the apparatus were jacketed with water to ensure constant temperature. A thermostat maintained the water temperature at 25 ± 0.1 °C.

Procedure

Prior to the testing of a sample, the apparatus was purged with water saturated nitrous oxide for about 1 h. Both taps were then closed so that the nitrous oxide was sealed inside the apparatus. The movable barometric leg was adjusted to produce equal mercury levels in the two glass legs. By doing this, the pressure inside the apparatus was made equal to the surrounding atmospheric pressure, which was measured separately by a mercury barometer.

Solubility measurements are sensitive to air dissolved in the solution because as gas is absorbed, it displaces dissolved air. Since the method we used measures the change in volume of the gas, concomitant desorption of air would introduce sizable error. To overcome this, all samples were vacuum degassed by spraying the sample into an evacuated flask, causing the solution to rapidly boil. By spraying the sample, a large surface area was produced, allowing complete degassing in a short period of time. Sample degassing was done quickly to ensure that carbon dioxide removal from preloaded solutions was minimal.

A 20 mL sample was taken by syringe and weighed on an analytical balance. The sample was injected through the septum into the equilibrium cell while atmospheric pressure was maintained inside the system by adjustment of the movable leg. Gas volume measurements were made every 4–5 min until equilibrium was reached. Equilibrium was said to have been achieved when three identical gas volume measurements were made several minutes apart. Samples were repeated until gas volume measurements were in agreement to within 0.1 mL.

When a species exists in solution, its partial pressure contributes to the overall pressure over the solution. When a carbon dioxide-loaded solution is injected into a CO_2-free atmosphere, sufficient CO_2 must be evolved to create this back-pressure. This evolution of CO_2 causes an increase in gas volume which leads to erroneous N_2O solubility measurements. However, once this CO_2 back-pressure has

Table 1. Experimentally Determined Values of *H* for N_2O in Water

sample	$H_{(N_2O/H_2O)}$/(kPa·L·mol^{-1})
1	4191.41
2	4230.06
3	4279.55
43	4252.90
5	4217.50
mean	4234.28
standard deviation	30.11

Table 2. Henry's Constant for N_2O in Water at 25 °C (from Haimour and Sandall, 1984)

source	H/(kPa·L·mol^{-1})
Joosten and Danckwerts (1972)	4151.27
Sada and Kitto (1972)	4168.50
Sada *et al.* (1977)	4116.83
Markham and Kobe (1941)	4209.02
Haimour and Sandall (1984)	4167.48
Al-Ghawas *et al.* (1989)	3909.16[a]
this work	4234 ± 45

[a] Not included in calculation of the mean value.

been formed, subsequent samples do not desorb CO_2, so any change in gas volume is due to N_2O absorption. For this reason, the result for the first sample was always discarded.

Sample Preparation

In order to determine the van Krevelen coefficient for the protonated amine, amine solutions were partially neutralized with sulfuric acid, producing protonated amine cations and sulfate anions. The van Krevelen coefficient for SO_4^{2-} is well established, leaving the coefficient for protonated amine as the only unknown.

All amine solutions were prepared with distilled water on a mass basis. To these solutions, 98% sulfuric acid was added to produce 20, 40, 60, 80, and 100% neutralization. The mass of acid added was recorded and used to calculate the mass fraction of acid.

For determining the coefficient for the carbamate ion, amine solutions were fully loaded by bubbling carbon dioxide through a sintered glass Dreschel head. Partially loaded solutions were then prepared by the mixing together of various proportions of the loaded solution with unloaded solution having the same amine concentration. A maximum loading of 0.4 mol of CO_2/mol of amine was used because the viscosity of highly loaded solutions made sample injection difficult. The amine concentration and loading of samples were also determined titrimetrically (Weiland and Trass, 1969).

Results and Discussion

In order to determine the accuracy of the experimental method, the Henry constant of nitrous oxide in water was measured repeatedly. Results are shown in Table 1.

Table 2 compares the value of the Henry constant in water determined in this work with values found by several researchers. From Table 2, the value for Henry's constant determined in this experiment was in basic agreement with literature values, although it lies about 1.7% above the mean. This deviation from the literature values may be indicative of a purge time of 1 h being insufficient to remove every trace of air from the apparatus. It should be noted that the result obtained by Al-Ghawas *et al.* (1989) was not included in the calculation of the mean value as it was significantly lower than those of other authors.

In Figures 2, 3 and 4, the Henry constant is a linearly increasing function of the unloaded amine concentration for all three amines. Thus, N_2O solubility decreases as water is replaced by amine. The solubility data for MDEA solutions are also compared to those of Haimour and Sandall (1984) and Al-Ghawas *et al.* (1989) in Figure 4. The data from these researchers are also linear functions of amine concentration with the exception of the pure water data points (zero mass fraction MDEA). As the value for the Henry constant for pure water is well established, this would indicate that their measured data for the amine solutions are low.

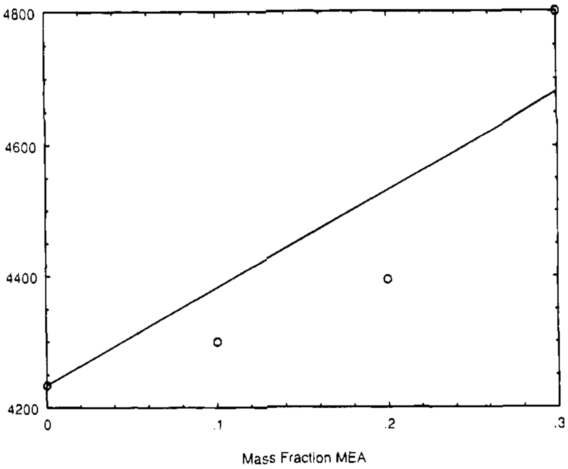

Figure 2. Henry's constant, *H*, for N_2O as a function of the mass fraction of MEA.

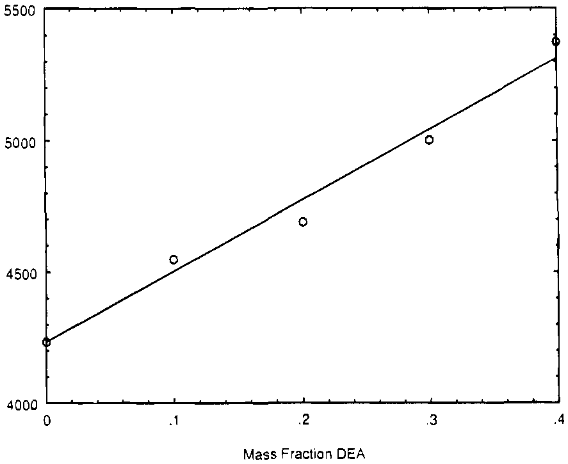

Figure 3. Henry's constant, *H*, for N_2O as a function of the mass fraction of DEA.

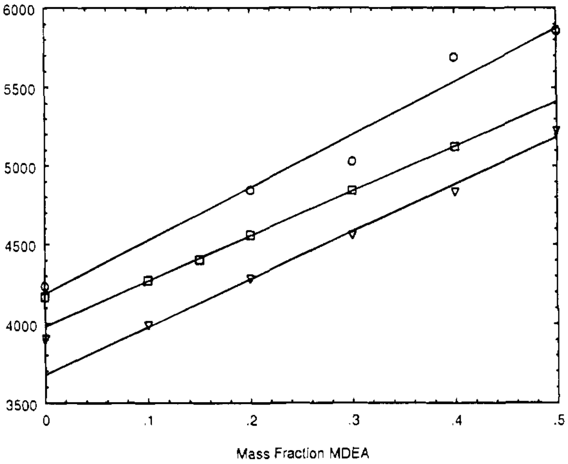

Figure 4. Henry's constant, *H*, for N_2O as a function of the mass fraction of MDEA: (□) Haimour and Sandall (1984), (▽) Al-Ghawas *et al.* (1989), (○) this work.

Table 3. Pseudo Henry' Constants for Nitrous Oxide in Pure Components (for Use in Eq 7)

	H'/(kPa·L·mol^{-1})	σ		H'/(kPa·L·mol^{-1})	σ
water	4234.2	33.7	DEA	6942.1	372.3
MEA	5348.2	670.6	MDEA	7385.4	410.8

Table 4. Comparison of Predicted and Experimental Henry's Constants for N_2O in Amine Blends

blend as mass percent	H_{pred}/(kPa·L·mol^{-1})	H_{exp}/(kPa·L·mol^{-1})	deviation[a]/%
10% DEA + 40% MDEA	5765.6	5501.5	+4.8
20% DEA + 30% MDEA	5721.4	5544.9	+3.2
10% MEA + 40% MDEA	5606.2	5680.0	−1.3
20% MEA + 30% MDEA	5402.4	5464.8	−1.1

[a] $[((H_{pred} - H_{exp})/H_{exp}) \times 100]$

Table 5. Pseudo Henry's Constants for Carbon Dioxide in Pure Components (for Use in Eq 7)

	H'/(kPa·L·mol^{-1})		H'/(kPa·L·mol^{-1})
water	3090.7	DEA	5067.2
MEA	3903.8	MDEA	5390.8

Table 6. Solubility Data for N_2O in Partially Neutralized MEA Solutions

percentage neutralization	H/(kPa·L·mol^{-1})		
	10% MEA	20% MEA	30% MEA
0	4299.5	4395.4	4799.2
20	4659.6	5368.3	5766.8
60	5734.0	7262.5	9993.0
100	6880.9	9127.0	18378.0

Table 7. Solubility Data for N_2O in Partially Neutralized DEA Solutions

percentage neutralization	H/(kPa·L·mol^{-1})			
	10% DEA	20% DEA	30% DEA	40% DEA
0	4548.2	4689.5	5003.7	5375.9
20	4671.3	4984.0	5631.7	6663.6
40	4916.0	5638.7	7310.0	7859.3
60	4987.5	6310.4	7496.8	9532.5
80	5321.9	6104.9	9064.0	11196.2
100	5673.4	7998.2	10910.2	13912.8

Table 8. Solubility Data for N_2O in Partially Neutralized MDEA Solutions

percentage neutralization	H/(kPa·L·mol^{-1})			
	20% MDEA	30% MDEA	40% MDEA	50% MDEA
0	4845.0	5031.1	5691.3	5860.4
20	5211.2	5544.9	6279.9	6746.2
40	5459.5			
60	5829.8	7212.4	7803.5	9844.6
80	5930.2			
100	6449.3	8185.3	9808.8	13448.2

Table 9. van Krevelen Coefficients for Cations

cation	h_+/(L/mol)	cation	h_+/(L/mol)
protonated MEA	0.055 ± 0.006	protonated MDEA	0.041 ± 0.007
protonated DEA	0.047 ± 0.005	ammonium ion, NH_4^+	0.028

Table 10. Solubility Data for N_2O in Partially CO_2 Loaded MEA Solutions

CO_2 loading/(mol of CO_2/mol of MEA)	H/(kPa·L·mol^{-1})		
	10% MEA	20% MEA	30% MEA
0	4299.5	4395.4	4799.2
0.1	4660.9		
0.15		4819.8	5766.2
0.25	4757.8	5411.5	6683.5
0.35		6211.7	7406.3
0.4	5051.4		

In order to correlate the data for amine concentration effects on the Henry constant, we used the following mixing rule:

$$H_{\text{mixture}} = \sum m_i H'_i \qquad (7)$$

where m_i is the mass fraction of water or amine and the H'_i are the corresponding Henry constants for the pure components. (We also tried a mole fraction based rule but found eq 7 gave a superior fit to the data.)

While the value of Henry's constant for water was determined experimentally, the values for the amines were found by minimizing the discrepancy between the mixing rule and the results. These values for the amines, therefore, are not really the true pure component Henry constants. They can be thought of as pseudo Henry's constants or fitting parameters. In fact, DEA, being a solid at 25 °C, does not have a Henry constant at all. For each amine, a pseudo pure component value was found; the results are shown in Table 3.

Equation 7 was also used to *predict* the Henry constant of unloaded MEA/MDEA and DEA/MDEA blends. From Table 4, the use of eq 7 gives good estimates for the value of Henry's constant for nitrous oxide in blended alkanolamines. The deviations from the experimental values appear to be randomly distributed and are most likely due to a combination of the errors associated with determining the pseudo Henry constants for the pure components and errors in the mixed amine solubility measurements themselves.

By applying the nitrous oxide analogy, the solubility of carbon dioxide in alkanolamine solutions can also be predicted from eq 7. Table 5 shows the pseudo Henry constants for carbon dioxide in the pure components.

To adequately describe the effect of carbon dioxide loading on the solubility, values of the van Krevelen coefficients for the protonated amines, amine carbamates, and the bicarbonate ion need to be determined. In the past, the value of these have been assumed to be the same as those of similar ions. Protonated amines have been considered the same as the ammonium ion and carbamates and bicarbonate the same as carbonate.

The values for the protonated amines were determined using the amine solutions partially neutralized with sulfuric acid. The solubility data for these partially neutralized solutions are given in Tables 6, 7 and 8 for MEA, DEA, and MDEA, respectively. From the slope of a plot of log(H/H^*) versus ionic strength and a van Krevelen coefficient for the sulfate ion of 0.022 L·mol^{-1} (Ueyama *et al.*, 1982), the value for h_+ was determined. These values were found to be independent of amine concentration, as was expected.

Table 9 shows the values obtained for the protonated amines, together with the value for the ammonium ion for comparison. It can clearly be seen that the value for the ammonium cation is much lower than those any of the protonated amines. As such, any estimates of Henry's constant using the ammonium ion approximation will be lower than what would be found in practice. (It should be noted that Henry's constant is exponentially sensitive to errors in the van Krevelen constants.)

The values of h_- for the amine carbamates and bicarbonate ions were found from the experiments performed on the solutions partially loaded with carbon dioxide. The solubility data for the CO_2 loaded solutions are given in Tables 10, 11 and 12. From the slope of a plot of log(H/H^*) versus ionic strength and the values for h_+ determined for protonated amines using the partially neutralized solutions, h_- for the anions was calculated. Examples of these plots for partially neutralized and CO_2 loaded solutions are given in Figures 5 and 6, respectively.

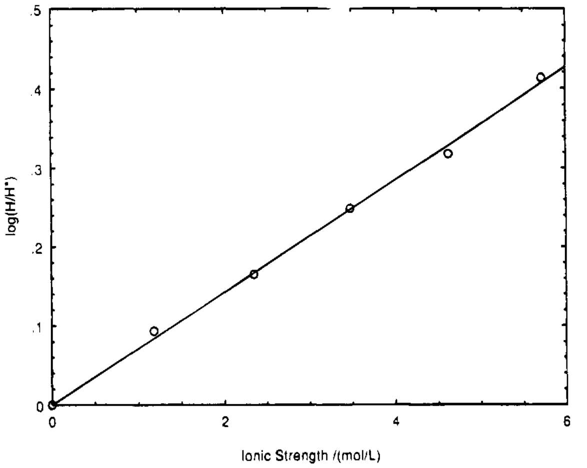

Figure 5. log(*H*/*H**) vs ionic strength for partially neutralized 40% DEA.

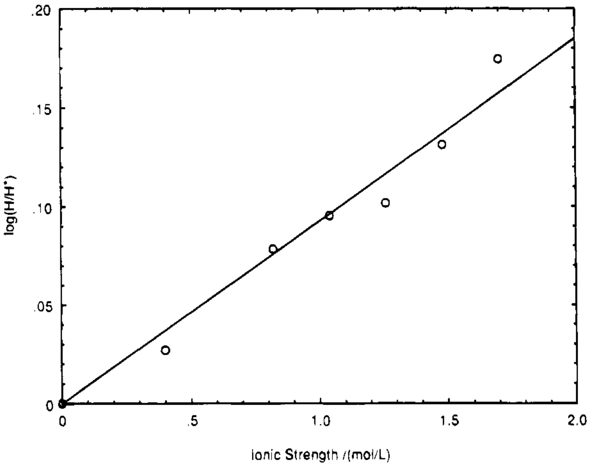

Figure 6. log(*H*/*H**) vs ionic strength for CO_2 loaded 40% DEA.

Table 11. Solubility Data for N_2O in Partially CO_2 Loaded DEA Solutions

CO_2 loading/ (mol of CO_2/mol of DEA)	*H*/(kPa·L·mol^{-1}) 10% DEA	20% DEA	30% DEA	40% DEA
0	4548.2	4689.5	5002.7	5375.9
0.05	4588.4	4776.8	5051.0	
0.1	4651.0	4960.8	5102.0	5719.7
0.15	4610.0	4985.8	5410.7	
0.2	4643.4	5228.2	5470.2	6439.0
0.25			5782.3	6696.6
0.3	4791.7	5389.8		6796.2
0.35		5402.8		7257.4
0.4	5012.4	5502.1	6688.9	8033.2

Table 12. Solubility Data for N_2O in Partially CO_2 Loaded MDEA Solutions

CO_2 loading/ (mol of CO_2/mol of MDEA)	*H*/(kPa·L·mol^{-1}) 20% MDEA	30% MDEA	40% MDEA	50% MDEA
0	4845.0	5031.1	5691.3	5860.4
0.1	4998.4	5658.2		6379.8
0.15	4999.7		6351.5	
0.25	5182.9	6461.1	6945.2	8110.0
0.35	5483.2		7603.4	
0.4	5565.0	7477.1		9654.9

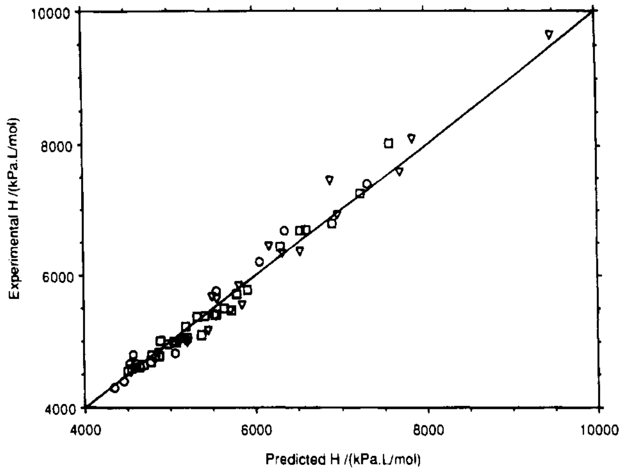

Figure 7. Comparison of predicted with experimentally determined Henry's constants for N_2O in single amine solutions: (○) MEA solutions, (□) DEA solutions, (▽) MDEA solutions.

Table 13. van Krevelen Coefficients for Anions

anion	h_-/(L/mol)	anion	h_-/(L/mol)
MEA carbamate	0.054 ± 0.003	bicarbonate, HCO_3^-	0.073 ± 0.025
DEA carbamate	0.043 ± 0.003	carbonate, CO_3^{2-}	0.021

Table 14. Solubility Data for N_2O in Partially CO_2 Loaded Amine Blends

CO_2 loading/ (mol of CO_2/ mol of MDEA)	*H*/(kPa·L·mol^{-1}) 10% MEA + 40% MDEA	20% MEA + 30% MDEA	10% DEA + 40% MDEA	20% DEA + 30% MDEA
0	5679.6	5464.8	5544.9	5501.5
0.1	6268.7			
0.15		6565.0	6400.4	6552.8
0.25	7784.8	7532.2	7211.2	7167.1
0.35		8781.5	7772.9	7507.4
0.4	9331.6			

As the values for the protonated amine were calculated on a standard basis, the values for the anions were determined on the same basis. Table 13 shows the values of h_- found experimentally; the literature value for carbonate, which has commonly been used to approximate the carbamates, is listed for comparison. As with the h_+ values, the van Krevelen coefficients for the anions were also independent of concentration.

Once again, the experimentally determined values for bicarbonate and carbamate ions are significantly higher than for the carbonate ion. Henry's constant predictions made in the past using ammonium and carbonate as analogs for loaded amine solutions were always too low, and by a sizable amount.

By combining the van Krevelen correlation (eq 2) and eq 7, an expression can be produced which will predict the Henry constant at any concentration of a single amine and carbon dioxide loading, at 25 °C:

$$\log(H) = (h_+ + h_- + h_g)I + \log(\sum m_i H'_i) \qquad (8)$$

For predicting the solubility of nitrous oxide in alkanolamine solutions at 25 °C, the coefficients in Table 3 should be used with an h_g value of 0. For carbon dioxide solubility, the coefficients in Table 5 and an h_g value of -0.019 L·mol^{-1} should be used (Danckwerts, 1970).

The ability of eq 8 to predict the Henry constant of nitrous oxide in single amine solutions is demonstrated in Figure 7. This compares the predicted value with the experimentally determined value and shows good agreement between the two.

A number of partially loaded amine blends were tested, and the data are presented in Table 14. There is no accepted way to adapt the van Krevelen correlation to predict the solubility behavior of amine blends from single amine data. An attempt to adapt the Joosten–Danckwerts equation (eq 6) to predict the solubility of amine blends was made but proved unsuccessful. The problem with this approach lies in the calculation of the ionic strength of the ion pairs in solution. When, for example, CO_2 is added to an MDEA/DEA blend, the following reactions take place.

$$\mathrm{MDEA} + \mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{MDEAH^+} + \mathrm{HCO_3^-} \quad (9)$$

$$2\mathrm{DEA} + \mathrm{CO_2} \rightarrow \mathrm{DEAH^+} + \mathrm{DEACOO^-} \quad (10)$$

$$\mathrm{HCO_3^-} + \mathrm{MDEA} \rightarrow \mathrm{MDEAH^+} + \mathrm{CO_3^{2-}} \quad (11)$$

$$\mathrm{HCO_3^-} + \mathrm{DEA} \rightarrow \mathrm{DEAH^+} + \mathrm{CO_3^{2-}} \quad (12)$$

Some of the bicarbonate ions formed in eq 9 react to form carbonate ions by the transfer of a proton to the remaining amine (eqs 11 and 12). This presents the problem of deciding which cations should be paired with which anions. As all the ions are randomly distributed in solution, this pairing should be able to be done arbitrarily. However, the presence of carbonate ions in solution, with a valency of 2+, will cause its ion pair to have a disproportionate influence on the final result. This is because the charge on an ion is squared in the calculation of ionic strength (eq 4). Since the way the ions are paired affects the final answer, the use of eq 6 is inappropriate for blended amine solutions. (If all the ions present were univalent, the method of pairing would not affect the outcome.)

Conclusion

The solubility of nitrous oxide in various alkanolamine solutions was measured at 25 °C and atmospheric pressure. From these measurements, pseudo Henry's constants for the pure amines were determined. These can be used to predict the Henry constant for an unloaded solution of any amine composition on a mass fraction basis.

By making solubility measurements on amine solutions partially neutralized with sulfuric acid and partially loaded with carbon dioxide, van Krevelen coefficients for the protonated amines, MEA and DEA carbamates, and bicarbonate ion were calculated. These were found to be significantly higher than the values for NH_4^+ and CO_3^{2-} which have previously been recommended as substitutes for values corresponding to the actual amine–CO_2 reaction products.

By combining the equations developed for representing the Henry constant for unloaded amine solutions with the van Krevelen equation, an expression has been developed which will allow the calculation of the Henry constant for nitrous oxide in all the single alkanolamine solutions studied. The nitrous oxide solubility can be translated into carbon dioxide solubility by application of the nitrous oxide analogy. The method for predicting solubility in multiple component solutions proposed by Joosten and Danckwerts (1972) was found to be inappropriate for blended alkanolamine solutions.

Literature Cited

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

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

Deshmukh, R. D.; Mather, A. E. A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions. *Chem. Eng. Sci.* **1981**, *36*, 355–362.

Danckwerts, P. V. *Gas-Liquid Reactions*; McGraw-Hill: New York, 1970.

Haimour, N.; Sandall, O. C. Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine. *Chem. Eng. Sci.* **1984**, *39* (12), 1791–1796.

Joosten, G. E. H.; Danckwerts, P. V. Solubility and Diffusivity of Nitrous Oxide in Equimolar Potassium Carbonate - Potassium Bicarbonate Solutions at 25 °C and 1 atm. *J. Chem. Eng. Data* **1972**, *17* (4), 452–454.

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.

Ueyama, K.; Hatanaka, J. Salt Effect on Solubility of Nonelectrolyte Gases and Liquids. *Chem. Eng. Sci.* **1982**, *37* (5), 790–792.

Weiland, R. H.; Trass, O. Titrimetric Determination of Acid Gases in Alkali Hydroxides and Amines. *Anal. Chem.* **1969**, *41*, 1709.

Weiland, R. H.; Trass, O. Absorption of Carbon Dioxide in Ethylenediamine Solutions. *Can. J. Chem. Eng.* **1971**, *49*, 767–781.

Weiland, R. H.; Chakravarty, T.; Mather, A. E. Solubility of Carbon Dioxide and Hydrogen Sulfide in Aqueous Alkanolamines. *Ind. Eng. Chem. Res.* **1993**, *32* (7), 1419–1430.

Received for review March 1, 1994. Accepted June 17, 1994.[®] This paper is a partial account of work sponsored by the Gas Research Institute and the Gas Processors Association under Contract Number 5091-260-2310, administered by Dr. Jeffrey L. Savidge, Senior Project Manager, GRI, and a grant from the Australian Research Committee, administered by the University of Newcastle. The amines used in this work were supplied by Texaco Chemical Co., courtesy of Mr. Tom Kenney.

[®] Abstract published in *Advance ACS Abstracts,* September 1, 1994.