

## Physical Solubility of Nitrous Oxide in Aqueous Amine Solutions

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One of the most important parameters required to model the absorption of CO<sub>2</sub> into aqueous alkanolamine solutions is physical solubility. However, since CO<sub>2</sub> reacts in amine solutions, its physical solubility cannot be measured directly. As a result, a nonreacting gas which is similar to CO<sub>2</sub> has to be used such as N<sub>2</sub>O.

The solubility of nitrous oxide (N<sub>2</sub>O) in aqueous solutions of 0wt% - 50wt% MDEA, 0wt% - 30wt% DEA, and 50wt% total amine with DEA/MDEA molar ratios of 0.05, 0.25, 0.5, and 0.67 was measured using a modified Zipperclave reactor over a temperature range of 293-353 K with near atmospheric partial pressures of N<sub>2</sub>O. The solubility data from this work were found to be in good agreement with previously reported data where available.

Key words : physical solubility, nitrous oxide, modified Zipperclave reactor, alkanolamine

### 1. Introduction

The removal of carbon dioxide and hydrogen sulfide from process gas streams in the petrochemical and natural gas industry is commonly achieved by reacting these impurities with aqueous alkanolamines. The alkanolamines used for this purpose include diethanolamine (DEA), methyldiethanolamine (MDEA), and, more recently, a mixture of the two.

In order to accurately design gas-liquid contacting equipment, information is needed on the physical solubility of acid gases in single and blended alkanolamines. In addition, an understanding of the effect of acid gas loading on their solubility is also required. Currently, the experimental data available in these areas are either unreliable or nonexistent. Moreover, since CO<sub>2</sub> reacts in amine solutions, its physical solubility cannot be measured directly. As a result, a nonreacting gas which is similar to CO<sub>2</sub> has to be used such as N<sub>2</sub>O. Clarke (1964) originally proposed the use of a similar gas that is unreactive

in the test solution for measuring the solubility. A proportionality constant is then used to calculate the solubility of carbon dioxide. Accordingly, 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), and Laddha et al. (1981). Nitrous oxide is used because it has a similar size, shape, electronic configuration, and Lennard-Jones potential to those of carbon dioxide. The resulting N<sub>2</sub>O solubility data for aqueous MDEA and aqueous DEA solutions can then be fitted using the extended scaled-particle model proposed by Li and Mather (1994).

The purpose of this work was to measure the physical solubility of nitrous oxide in partially loaded solutions of DEA, MDEA, and their blends and 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.

## 2. Materials and Methods

### 2.1. Henry's Law

Henry's law states that the partial pressure of a gas is proportional to the concentration of that gas dissolved in a solution at equilibrium :

$$P_i = H_i C_i \quad (1)$$

where  $P_i$  is the partial pressure of species  $i$  in the gas phase;  $H_i$  is Henry's law constant; and  $C_i$  is the concentration of species  $i$  in the liquid phase. Henry's law is only valid for sparingly soluble gases at relatively low pressures. Since  $N_2O$  is sparingly soluble in aqueous alkanolamine solutions, its solubility in these solutions can be adequately described by Henry's law.

Henry's law constant is a strong function of temperature and a much weaker function of concentration. Accordingly, the  $H_i$  logarithm can be described as an inverse linear function of temperature ( $T$ ). However, the composition dependence of  $H_i$  is not well defined.

### 2.2. $N_2O$ Analogy

Clarke (1964) originally proposed the use of  $N_2O$  as a simulant gas to infer the physical solubility of  $CO_2$  in alkanolamine solutions because  $N_2O$  is similar to  $CO_2$  in configuration, electronic structure, molecular weight, and molar volume. Laddha et al. (1981) measured the physical solubilities of  $CO_2$  and  $N_2O$  in organic solvents in which neither gas reacts, and found that the ratio of the gas solubilities was constant. Accordingly, the  $N_2O$  analogy can be written in terms of Henry's law constants as:

$$\frac{H_{CO_2}}{H^o_{CO_2}} = \frac{H_{N_2O}}{H^o_{N_2O}} \quad (2)$$

where  $H_{CO_2}$  and  $H_{N_2O}$  are the Henry's law constants for  $CO_2$  and  $N_2O$  in a solution, and  $H^o_{CO_2}$  and  $H^o_{N_2O}$  are the Henry's law constants for  $CO_2$  and  $N_2O$  in pure water. Haimour and Sandall (1984) used a laminar-liquid jet apparatus to measure the absorption rate of  $CO_2$  into aqueous MDEA over very short contact times under conditions where the reaction does not affect the absorption rate. Their results indicate that the  $N_2O$  analogy holds in aqueous MDEA solutions. Several authors have used the  $N_2O$  analogy to obtain physical solubility

data for  $CO_2$  in various alkanolamine solutions, including Weiland and Trass (1971), Browning and Weiland (1994), Laddha et al. (1981), Haimour and Sandall (1984), and Al-Ghawas et al. (1989). Still others have reported  $N_2O$  solubility data in DEA and MDEA solutions, including Versteeg and van Swaaij (1988), Littel et al. (1992), Haimour (1990), and Sada et al. (1978).

### 2.3. Experimental

The solubility experiments were carried out in a modified Zipperclave reactor shown in Figure 1. The DEA was obtained from Fisher Scientific with a minimum purity of 99 mass%. The MDEA was donated by Union Carbide Corp. with a minimum purity of 99 mass%. The nitrous oxide was medical grade with a stated purity of 99.99%. The water used in this work was deionized. The concentration of the amine in a solution was determined by titration with hydrochloric acid.

A weighed sample of approximately 400g of the test solution was injected into a  $1.02815 \times 10^{-3} \text{ m}^3$  (at 298 K) stainless steel chamber. The reactor was then sealed and heated or cooled to the

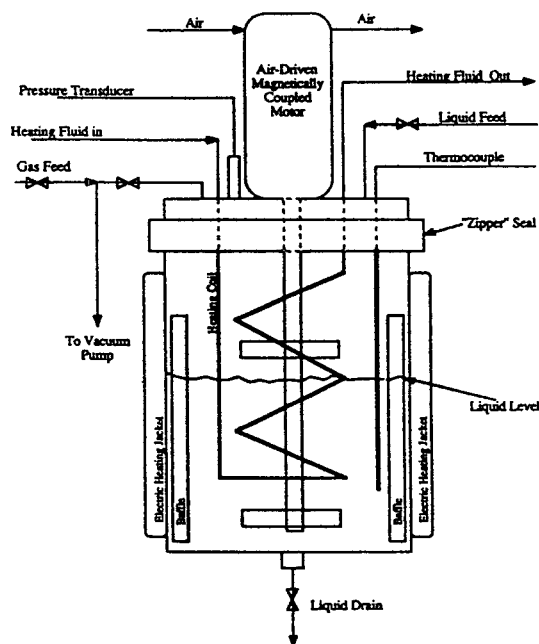


Fig. 1. Schematic diagram of modified Zipperclave reactor.

desired temperature by two external electric heating jackets and an internal heating/cooling coil through which an antifreeze/water solution was circulated by an external constant temperature circulator. The temperature was maintained within  $\pm 0.1$  K, and the absorption chamber and tubing were insulated. The solution was degassed in the absorption chamber in a vacuum while being stirred with an attached Magnedrive packless stirrer. The vacuum was shut off after the pressure steadied, and the system was allowed to come to a vapor-liquid equilibrium. At this equilibrium, the pressure was measured and recorded as the vapor pressure of the test solution ( $P_v$ ). With the stirrer shut off, the gas was allowed to flow through a coil submerged in the external constant temperature bath into the absorption chamber until an arbitrary pressure was reached. This pressure was recorded as the initial pressure ( $P_i$ ). The absorption chamber was then resealed by closing the valve connecting it to the gas storage chamber, and the stirrer was started at about 1500 rpm. The system was allowed to reach a vapor-liquid equilibrium at which point the final pressure ( $P_f$ ) was measured and recorded. The Henry's law constant,  $H$ , was then calculated using the following equation:

$$H = \frac{(P_f - P_v)V_l}{(P_i - P_f)V_g} RT \quad (3)$$

where  $V_l$  and  $V_g$  are the liquid and gas volumes, respectively;  $R$  is the ideal gas constant ( $8.314 \times 10^{-3}$  MPa m<sup>3</sup>/kmol K); and  $T$  is the absolute temperature (K).

All pressures were measured with an Omega pressure transducer to within  $\pm 0.15 \times 10^{-3}$  MPa. The temperature dependence of the pressure transducer was compensated for by calibrating the transducer over a temperature range of 20 to 100 °C. The temperature was measured to within  $\pm 0.1$  K with a type J thermocouple mounted in a stainless steel thermal well which was inserted into the absorption chamber.

### 3. Results and Discussion

In order to determine the accuracy of the experimental method, the Henry constant of nitrous oxide in water was measured repeatedly. As the value for the Henry constant for pure water is well established, the comparative values could indicate

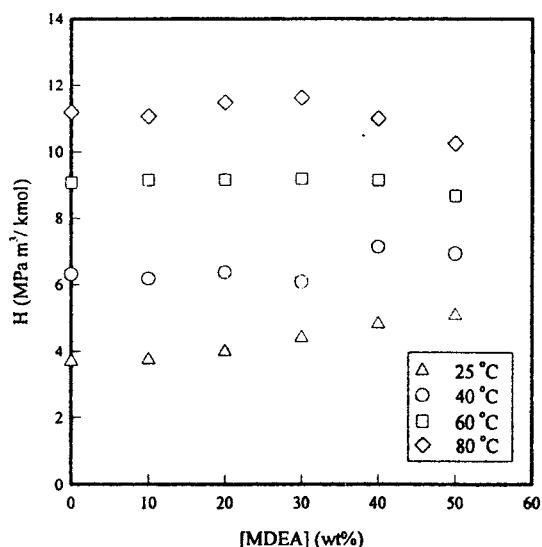


Fig. 2. Henry constants for N<sub>2</sub>O in aqueous MDEA.

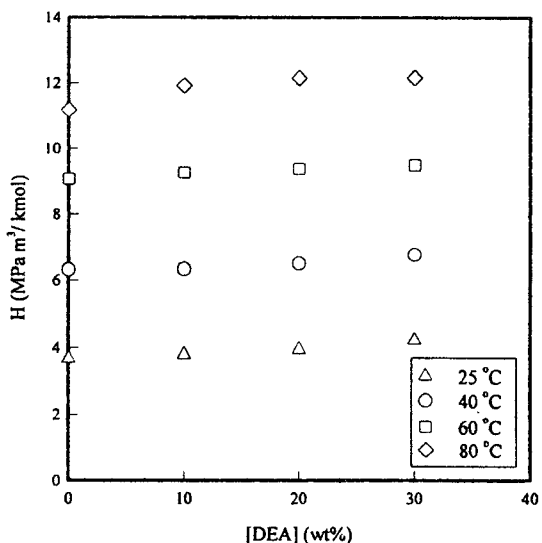


Fig. 3. Henry constants for N<sub>2</sub>O in aqueous DEA.

whether the measured data for the amine solutions was low or not.

The experimental Henry constants determined in the present work for N<sub>2</sub>O in aqueous solutions of 0-50 wt % MDEA, 0-30 wt % DEA, and 50 wt % total amine with DEA/MDEA molar ratios varying from 0.05, 0.25, 0.50, to 0.67 over a temperature range of 293-353 K are listed in Tables 1, 2, and 3, respectively. The Henry constants from

Tables 1, 2 and 3 are plotted in Figures 2, 3, and 4, respectively. In Figures 2, 3, and 4, the Henry constant is a linearly increasing function of the unloaded amine concentration for all three amines. Accordingly,  $N_2O$  solubility decreases as water is replaced by amine. The solubility data for MDEA solutions were also compared to that of Haimour and Sandall(1984) and Al-Ghawas et al.(1989). The data from these researchers were also linear functions of the amine concentration with the exception of the pure water data points. As the value for the Henry constant for pure water is well established, the comparative values indicated that the measured data for the amine solutions was low. In Figure 2, the  $N_2O$  solubility data of Versteeg and van Swaaij (1988), Al-Ghawas et al. (1989), and Haimour and Sandall(1984) are included for comparison. The data of Littel et al. (1992) and Haimour (1990) are plotted in Figure 3 for comparison.

Table 1. Henry's law constants for  $N_2O$  in aqueous 0-50 wt% MDEA

Temp. (°C)	MDEA (wt%)	$H_{N_2O}$ (MPa m <sup>3</sup> /kmol)
20	0	3.69
	10	3.74
	20	3.99
	30	4.42
	40	4.83
	50	5.09
40	0	6.32
	10	6.19
	20	6.38
	30	6.10
	40	7.16
	50	6.96
60	0	9.08
	10	9.16
	20	9.17
	30	9.20
	40	9.17
	50	8.69
80	0	11.19
	10	11.07
	20	11.49
	30	11.63
	40	11.01
	50	10.27

Table 2. Henry's law constants for  $N_2O$  in aqueous 0-30 wt% DEA

Temp. (°C)	DEA (wt%)	$H_{N_2O}$ (MPa m <sup>3</sup> /kmol)
20	0	3.69
	10	3.80
	20	3.95
	30	4.23
40	0	6.32
	10	6.34
	20	6.51
	30	6.77
60	0	9.08
	10	9.27
	20	9.38
	30	9.50
80	0	11.19
	10	11.92
	20	12.15
	30	12.16

The  $N_2O$  solubility data determined in the present work show a reasonable agreement with the above-mentioned authors. Not included in Figures 2 and 3 are the data for  $N_2O$  solubility in water reported by Jou et al. (1992) and the data of Browning and Weiland (1994) for  $N_2O$  solubility in 20-50 wt% MDEA and 10-30 wt% DEA at 298 K. The  $N_2O/H_2O$  solubility data from the current study agreed to within 5% with the data of Jou et al. (1992). Based on Figure 4, table 3 can provide good estimates for the value of Henry's constant for nitrous oxide in blended alkanolamines. Any deviations from the experimental values appear to be randomly distributed and are most likely due to a combination of errors associated with determining the pseudo Henry constants for the pure components and errors in the mixed amine solubility measurements themselves.

The model predictions in this work agree to within 2.5% with the data of Browning and Weiland (1994) at 298 K. It should also be noted that the data of Al-Ghawas et al. (1989) at temperatures higher than 298 K are not in agreement with the results of the present work. It is believed that there were systematic errors associated with their experimental results at temperatures higher than 298 K. The

$N_2O$  solubility data in Tables 1 and 2 were fitted, and the best fits are shown in Figures 2 and 3, respectively. Using the parameter estimates determined in the present work, shown in Table 3, the equations were then used to predict the Henry's constants for  $N_2O$  in the DEA-MDEA- $H_2O$  solutions, and the results are plotted in Figure 4.

The solubility of nitrous oxide ( $N_2O$ ) in aqueous solutions of 0wt% - 50wt% methyldiethanolamine, 0wt% - 30wt% diethanolamine, and 50wt% total amine with diethanolamine/methyldiethanolamine molar ratios of 0.05, 0.25, 0.5, and 0.67 was measured using a modified Zipperclave reactor over a temperature range of 293-353 K with near-atmospheric partial pressures of  $N_2O$ . The solubility data from this work were found to be in fair agreement with previous literature where data were available. The predicted Henry's constants showed a fairly good agreement with an average deviation of only 4.1% from the experimental data.

Table 3. Henry's law constants for  $N_2O$  in aqueous blends of DEA and MDEA with a 50 wt% total amine concentration

Temp. (°C)	DEA/MDEA (molar ratio)	$H_{N_2O}$ (MPa m <sup>3</sup> /kmol)
20	0.00	5.09
	0.05	4.94
	0.25	5.04
	0.50	5.12
	0.67	5.04
40	0.00	6.96
	0.05	6.98
	0.25	7.70
	0.50	7.17
	0.67	7.05
60	0.00	8.69
	0.05	8.76
	0.25	8.96
	0.50	9.05
	0.67	9.22
80	0.00	10.27
	0.05	10.48
	0.25	10.80
	0.50	10.89
	0.67	10.84

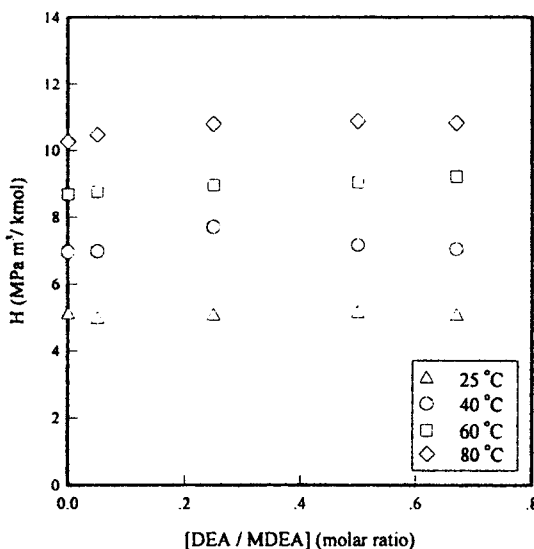


Fig. 4. Henry constants for  $N_2O$  in aqueous blend solutions of DEA/MDEA.

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