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Solubility of Nitrous Oxide in Aqueous Blends of *N*-Methyldiethanolamine and 2-Amino-2-methyl-1-propanol

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The solubility of nitrous oxide in aqueous blends of *N*-methyldiethanolamine and 2-amino-2-methyl-1-propanol was measured over the temperature range 10−60 °C. The total composition of the alkanolamines in water ranged from 30 to 50 mass %. The experimental results were interpreted in terms of Henry's constants.

Introduction

Aqueous solutions of alkanolamines have application in acid gas treatment for the removal of acid gases such as carbon dioxide and hydrogen sulfide. More recently, attention is drawn to blended solutions of primary or secondary and tertiary amines for the simultaneous removal of CO_2 in the presence of H_2S (Chakravarty et al., 1985; Versteeg et al., 1990). One such system that has not been thoroughly investigated is the aqueous combination of the tertiary amine *N*-methyldiethanolamine (MDEA) and the secondary amine 2-amino-2-methyl-1-propanol (AMP). Several properties of the single amine solutions of AMP in water and MDEA in water have been reported previously in the literature (Haimour and Sandall, 1984; Versteeg and van Swaaij, 1988; Al-Ghawas et al., 1989; Bosch et al., 1990; Xu et al., 1991; Littel at al., 1992; Wang et al., 1992; Saha at al., 1993; Browning and Weiland, 1994; Rinker et al., 1995; Li and Lai, 1995). Densities and viscosities of aqueous blends of AMP and MDEA have been reported by Welsh and Davis (1995). Wang et al. (1992) reported the solubility of N_2O in aqueous blends of AMP and MDEA at 25 °C only. In this work, some additional results for density and Henry's constants for nitrous oxide solubility in aqueous blends of MDEA and AMP were determined over the temperature range of 10−60 °C. The solubility of N_2O is useful for estimating the physical solubility of CO_2 in reactive solvents by analogy (Laddha et al., 1981; Haimour and Sandall, 1984; Versteeg and van Swaaij, 1988; Xu et al., 1991; Littel et al., 1992; Wang et al., 1992; Saha et al., 1993; Browning and Weiland, 1994; Rinker et al., 1995; Li and Lai, 1995). Gas solubility is important for the design of gas-treating operations and in determining other physicochemical properties of this system such as the reaction kinetics of CO_2 with aqueous amine solutions.

Experimental Procedure

All liquid solutions were prepared from deionized, distilled water and 99+% (mass) pure MDEA and AMP supplied by Janssen Chimica. Prepared solutions were titrated with 1 M HCl to an end point of pH 4.5 with a Mettler DL12 autotitrator (Al-Ghawas et al., 1989). All reported liquid compositions are accurate to within ±0.05 mass %. Medical grade N_2O with a purity of 99+% was used in all the solubility experiments. The solutions were degassed before each experiment by heating under vacuum.

Density. Experiments to determine density were performed with a calibrated 25 cm^3 Gay-Lussac type pycnometer from Ace Glass Inc. The clean, dry pycnometer was weighed before each experiment on a Sartorius analytical balance, accurate to ±0.0002 g. The temperature was controlled by immersing the amine solution-charged pycnometer in a constant temperature bath for at least 30 min. The temperature of the bath was measured with a Fisher Scientific calibrated mercury-filled glass thermometer. The temperature was maintained to within ±0.05 °C of the set point. The density was found by dividing the difference in the mass of the charged and empty pycnometer by the calibrated pycnometer volume. The maximum error in the density measurements is estimated to be $\pm 0.001\ g\cdot cm^{-3}$.

Solubility. The solubility of N_2O in the aqueous amine solutions was determined by measuring the pressure change in a constant volume equilibrium cell after partially filling with a known aliquot of liquid sample. A Parr 300 mL stainless steel stirred reactor was used as an equilibrium cell. Initially, the cell was purged with humidified N_2O at room temperature. The gas was then partially evacuated from the cell under vacuum to lower the initial pressure in the cell below atmospheric pressure. The closed system was allowed to reach constant pressure and temperature before a known mass (approximately 100 g) of degassed liquid was injected into the cell. The temperatures of the gas and liquid in the cell were measured with type J thermocouples to within ±0.2 °C. The pressure of the gas phase was measured to within ±0.1 kPa with a calibrated pressure transducer supplied from Setra. The pressure in the cell ranged from 70 to 100 kPa during all experiments. The temperature of the cell was varied from 10 to 60 °C in 10 °C increments with an electric heating mantle and refrigerating bath. The system was assumed to be at equilibrium when the temperature and pressure stopped changing after a minimum of 1 h of continuous mixing.

Analysis. The initial number of moles of N_2O in the equilibrium cell, before adding liquid, was calculated from the initial temperature and pressure assuming ideal gas behavior:

$$n_i = P_i V_i / R T_i \tag{1}$$

The compressibility factor for the mixtures of N_2O and H_2O in this investigation is practically unity ($Z > 0.99$) for the temperatures and pressures used here. The partial pressure of N_2O in the gas above the liquid was calculated assuming Raoult's law for water and amine:

$$P = P_T - \sum_{j \neq N_2O} x_j P_{vj} \tag{2}$$

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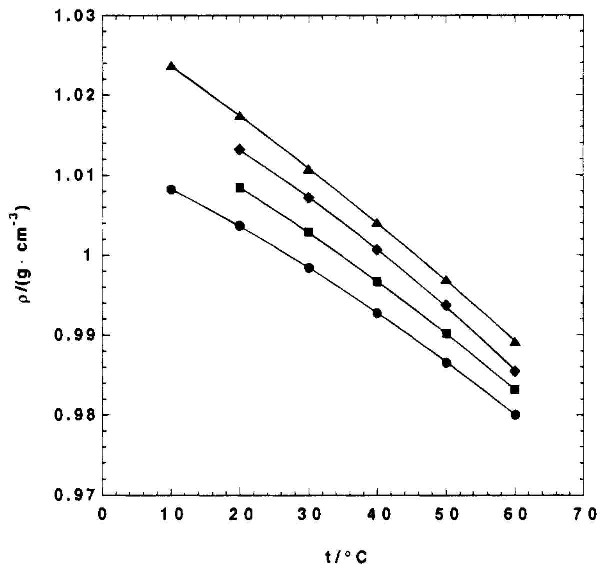

Figure 1. Density of aqueous blends of 25 mass % AMP and MDEA: ●, 5 mass % MDEA; ■, 10 mass % MDEA; ◆, 15 mass % MDEA; ▲, 20 mass % MDEA.

Table 1. Density of Water + AMP + MDEA Solutions

[AMP]/ (mass %)	[MDEA]/ (mass %)	t/ °C	ρ/ (g·cm^{-3})	[AMP]/ (mass %)	[MDEA]/ (mass %)	t/ °C	ρ/ (g·cm^{-3})
25	5	10	1.0083	25	15	20	1.0132
		20	1.0037			30	1.0072
		30	0.9985			40	1.0007
		40	0.9928			50	0.9937
		50	0.9866				
		60	0.9855				
		60	0.9801	25	20	10	1.0237
25	10	20	1.0085			20	1.0174
		30	1.0029			30	1.0108
		40	0.9967			40	1.0041
		50	0.9902			50	0.997
		60	0.9832			60	0.9892

where P_T is the total measured pressure, P_{vj} is the vapor pressure of pure species j at T_f, and x_j is the mole fraction of species j in the liquid. The terms representing amines in eq 2 were found to be negligible for the conditions of this investigation.

The final number of moles of N_2O in the gas phase after liquid injection was found in a similar way at each temperature. The volume occupied by the gas was taken as the difference between the initial volume of the empty cell and the volume of the liquid in the cell:

$$n_f = P_f(V_i - V_l)/RT_f \qquad (3)$$

where the liquid volume was calculated from the mass of liquid injected and the liquid density at the final temperature, T_f.

$$V_l = m_l/\varrho_l \qquad (4)$$

The total number of moles of N_2O absorbed at each final temperature was calculated from the difference between the initial and final number of moles of N_2O in the gas according to eqs 1 and 3. The concentration of dissolved gas was found from the number of moles of gas absorbed and the volume of liquid determined from the liquid density according to eq 4:

$$C = (n_i - n_f)/V_l \qquad (5)$$

The N_2O solubility was interpreted in terms of Henry's law constant for sparingly soluble gases in liquids:

$$H = P/C \qquad (6)$$

where P is the partial pressure of N_2O calculated according to eq 2.

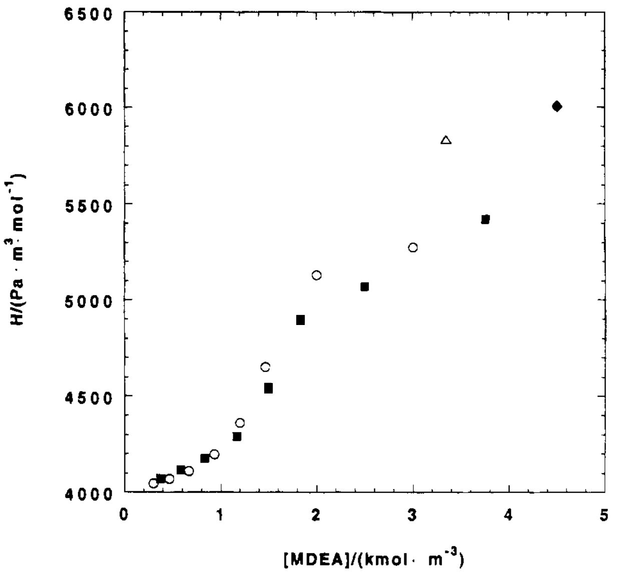

Figure 2. Solubility of N_2O in aqueous blends of AMP and MDEA at 25 °C: ■, [AMP]/[MDEA] = 0.2 (Wang et al., 1992); ◆, [AMP]/[MDEA] = 0.2 (this work); ○, [AMP]/[MDEA] = 0.5 (Wang et al., 1992); △, [AMP]/[MDEA] = 0.5 (this work).

Table 2. Solubility of N_2O in Water

t/°C	H/(Pa·m^3·mol^{-1})	ref
25.0	4173	Haimour and Sandall (1984)
	4132	Versteeg and van Swaaij (1988)
	3910	Al-Ghawas et al. (1989)
	4176	Xu et al. (1991)
	4120	Saha et al. (1993)
	4234	Browning and Weiland (1994)
	4101	Rinker et al. (1995)
	4179	this work
50.0	7407	Versteeg and van Swaaij (1988)
	5369	Al-Ghawas et al. (1989)
	7254	Xu et al. (1991)
	7214	Rinker et al. (1995)
	7264	Li and Lai (1995)
	7260	this work

Results and Discussion

Density experiments were performed for aqueous amine solutions of 25 mass % AMP and 5–20 mass % MDEA over the temperature range 10–60 °C, extending the range of compositions reported previously (Welsh and Davis, 1995). The results for density are listed in Table 1 and plotted as a function of temperature in Figure 1. The maximum error in the density results was estimated to be ±0.0015 g·cm^{-3}.

The solubility of N_2O in aqueous AMP solutions and aqueous blends of AMP and MDEA is reported here for liquid phase compositions and temperatures beyond the range of those reported previously in the literature (Bosch et al., 1990; Xu et al., 1991; Littel et al., 1992; Wang et al., 1992; Saha et al., 1993; Li and Lai, 1995). The experimental procedure for determining the solubility was validated by comparing our results for the solubility of N_2O in water with recently reported values listed in Table 2. With the exception of the results of Al-Ghawas et al. (1989), our results agree within 1% of the mean value at each tem-

Table 3. Solubility of N_2O in Aqueous Blends of AMP and MDEA

[AMP]/ (mass %)	[MDEA]/ (mass %)	t/°C	H/ ($Pa \cdot m^3 \cdot mol^{-1}$)	[AMP]/ (mass %)	[MDEA]/ (mass %)	t/°C	H/ ($Pa \cdot m^3 \cdot mol^{-1}$)	[AMP]/ (mass %)	[MDEA]/ (mass %)	t/°C	H/ ($Pa \cdot m^3 \cdot mol^{-1}$)
0	50	10	4075	25	5	10	3771	25	25	10	4503
		20	5258			20	4938			20	5478
		30	6481			30	6210			30	6481
		40	7713			40	7656			40	7562
		50	9119			50	8952			50	7852
		60	10451			60	10918			60	8639
10	40	10	4379	25	10	10	4019	30	20	10	4614
		20	5667			20	5172			20	5554
		30	6534			30	6392			30	6376
		40	7765			40	7588			40	7178
		50	8860			50	8524			50	7911
		60	9911			60	9314			60	8574
15	15	20	5239	25	15	20	5345	40	10	10	4855
		30	6759			30	6465			20	5718
		40	8446			40	7494			30	6461
		50	10162			50	8398			40	7213
		60	12206			60	9163			50	7869
20	30	10	4465	25	20	10	4388			60	8412
		20	5530			20	5448	50	0	10	4625
		30	6318			30	6519			20	5478
		40	7249			40	7497			30	6002
		50	7978			50	8244			40	6667
		60	8968			60	9043			50	7187
										60	7743

Table 4. Henry's Constant for N_2O Solubility in 50 mass % MDEA in H_2O at 25 °C

H/($Pa \cdot m^3 \cdot mol^{-1}$)	ref
5400	Haimour and Sandall (1984)
5229	Al-Ghawas et al. (1989)
5850	Browning and Weiland (1994)
5740	this work (interpolated value)

perature. Our results for N_2O solubility in aqueous blends of AMP and MDEA are listed in Table 3. The maximum error in these results for solubility was estimated to be ±3%.

Our values for N_2O solubility in aqueous 50 mass % MDEA agree with the trends for increasing MDEA composition of Li and Lai (1995) and Rinker et al. (1995). The results for N_2O solubility in aqueous 50 mass % MDEA at 25 °C agree with those reported by Browning and Weiland (1994), Haimour and Sandall (1984), and Al-Ghawas et al. (1989), listed in Table 4. Interpolated values for Henry's constants were found by a linear least squares fit of the results to an Arrhenius function of temperature as predicted by the Clausius−Clapeyron equation (Astarita et al., 1983):

$$\ln(H) = a + b/T \tag{7}$$

Our results for the solubility of N_2O in aqueous 50 mass % AMP are consistent with the trend of decreasing solubility with increasing AMP composition at low temperatures (10−30 °C) as reported by Bosch et al. (1990), Xu et al. (1991), Littel et al. (1992), Saha et al. (1993), and Li and Lai (1995). However, at higher temperatures, our results indicate an increase in N_2O solubility with increasing AMP concentration when compared with the data of Xu et al. (1991) and Li and Lai (1995). If the water vapor pressure correction of eq 2 is ignored, there appears to be closer agreement over the entire range of temperatures, indicating a possible disparity between the methods used to account for water in the gas phase at equilibrium. Interpolated values from this work for N_2O solubility in AMP + MDEA + H_2O blends at 25 °C are consistent with the experimental results of Wang et al. (1992), as shown in Figure 2.

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