

## SOLUBILITY OF CO<sub>2</sub> AND H<sub>2</sub>S IN A HINDERED AMINE SOLUTION

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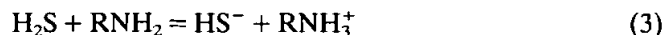
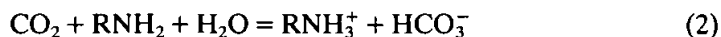
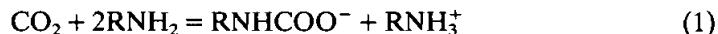
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The solubility of H<sub>2</sub>S and CO<sub>2</sub> in aqueous solutions of the sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP), was determined at 40 and 100°C. Partial pressures of CO<sub>2</sub> ranged from approximately 2 to 6000 kPa and of H<sub>2</sub>S from 2 to 2200 kPa. The solubility results were compared with previously reported acid gas solubilities in aqueous monoethanolamine (MEA) solutions.

**KEYWORDS** hydrogen sulphide carbon dioxide hindered amine solubility  
gas treating vapour-liquid equilibria

### INTRODUCTION

Acid gas impurities (CO<sub>2</sub> and H<sub>2</sub>S) are commonly removed from natural gas streams by countercurrent absorption into a liquid solvent. Low partial pressures of CO<sub>2</sub> and H<sub>2</sub>S in the treated gas are generally achieved through the use of chemical solvents which are characterized by liquid phase reactions between CO<sub>2</sub> and H<sub>2</sub>S and a reactive component. Aqueous solutions of alkanolamines are extensively employed in acid gas removal processes. The independent chemical reactions between an alkanolamine (RNH<sub>2</sub>) and CO<sub>2</sub> and H<sub>2</sub>S may be expressed as:



Stable carbamate ion (RNHCOO<sup>-</sup>) formation by reaction (1) limits the stoichiometric loading to 0.5 mol CO<sub>2</sub>/mol amine. Loadings greater than 0.5 mol CO<sub>2</sub>/mol amine can be achieved only at high CO<sub>2</sub> partial pressures. Tertiary amines such as methyldiethanolamine (MDEA) and triethanolamine (TEA) do not form stable carbamate species thus allowing loadings to reach 1.0 mol CO<sub>2</sub>/mol amine. The CO<sub>2</sub> absorption rates for tertiary amines are low, however, which tend to limit their industrial importance.

Sterically hindered amines are a new class of gas treating amines which exhibit a stoichiometric loading of  $\text{CO}_2$  of 1.0 mol/mol amine with absorption rates similar to those obtained with the primary and secondary amines (Sartori and Savage, 1983). The high thermodynamic capacity is achieved by destabilizing carbamate formation by placing bulky substituent groups next to the nitrogen site. Commercial application of hindered amines in gas treating processes has been described by Say *et al.* (1984) and Goldstein *et al.* (1984).

Accurate solubility data for  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in amine solutions are necessary for the design and operation of gas treating facilities. Solubility data for hindered amine solvents are generally lacking. In this study, the solubility of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in an aqueous solution of the hindered amine, 2-amino-2-methyl-1-propanol (AMP), was determined at 40 and 100°C over a wide range of acid gas partial pressures.

## EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental method is similar to that outlined by Jou *et al.* (1982). Full details on the experimental method are provided by Roberts (1983).

The experimental apparatus is shown in Figure 1. The liquid and vapor phases were brought to equilibrium in a windowed Jerguson cell. A 250 cm<sup>3</sup> cylindrical reservoir was attached to the top of the cell to increase the mass of vapor in equilibrium with the solvent. The vapor from the reservoir was recirculated through the solvent by a magnetically driven piston pump devised by Ruska *et al.* (1970). The cell and pump were enclosed in an electrically heated air bath

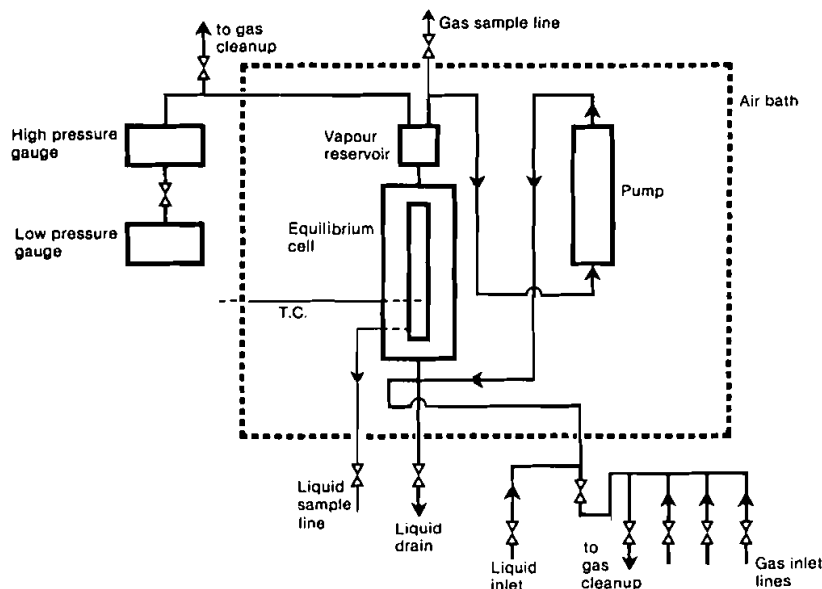


FIGURE 1 Experimental apparatus for the determination of acid gas solubility in gas treating solvents.

maintained at  $\pm 0.5^\circ\text{C}$  of the setpoint temperature. Fluid pressure was measured by a 0 to 1 000 and 0 to 10 000 kPa digital gauge. The accuracy of the gauges was rated at  $\pm 0.1\%$  of the full-scale span. The temperature of the fluid within the cell was monitored by a calibrated iron-constantan thermocouple.

Prior to introduction of the fluids, the apparatus was brought to the desired temperature and purged with nitrogen to remove traces of air. Approximately  $50\text{ cm}^3$  of the solvent was fed by gravity to the equilibrium cell. Hydrogen sulfide or carbon dioxide was added to the cell to an amount indicated by the pressure. The pump was started and the vapor recirculated through the solvent. Additional amounts of acid gas were added until the desired partial pressure had been approximately obtained. When necessary, nitrogen was added to maintain the system pressure above 350 kPa. At equilibrium, as established by a constant cell pressure, the pump was stopped and the phases analysed.

A portion of the vapor phase was released to a sample loop and analysed by gas chromatography. The water content of the vapor phase was estimated by assuming Raoult's law for the water-vapor equilibrium. A liquid sample was withdrawn from the equilibrium cell into a vessel containing 1 M sodium hydroxide, thus converting free dissolved acid gas into the involatile ionic species. The  $\text{CO}_2$  and  $\text{H}_2\text{S}$  content in the liquid sample were determined by wet chemical techniques. The experimental error in the solution loading (mol acid gas/mol amine) is estimated at 2–3% in the range studied.

## RESULTS AND DISCUSSION

The equilibrium solubility of  $\text{CO}_2$  in a 3.0 M aqueous AMP solution was measured at  $40^\circ\text{C}$  and  $\text{CO}_2$  partial pressures from approximately 1 to 400 kPa. The data, as expressed in terms of mol  $\text{CO}_2$ /mol AMP ( $\alpha$ ) at a specified partial pressure of  $\text{CO}_2$  (kPa), are outlined in Table I. The solubility values measured in this study are compared with measurements by Sartori and Savage (1983) in

TABLE I  
Solubility of  $\text{CO}_2$  in 3.0 M Aqueous AMP at  $40^\circ\text{C}$

| $\alpha$ (mol $\text{CO}_2$ /mol AMP) | P (kPa) |
|---------------------------------------|---------|
| 0.404                                 | 1.25    |
| 0.564                                 | 2.79    |
| 0.604                                 | 3.54    |
| 0.728                                 | 12.8    |
| 0.769                                 | 19.0    |
| 0.786                                 | 15.6    |
| 0.818                                 | 22.5    |
| 0.835                                 | 36.6    |
| 0.919                                 | 99.5    |
| 0.948                                 | 144.0   |
| 0.960                                 | 359.0   |
| 0.982                                 | 216.0   |

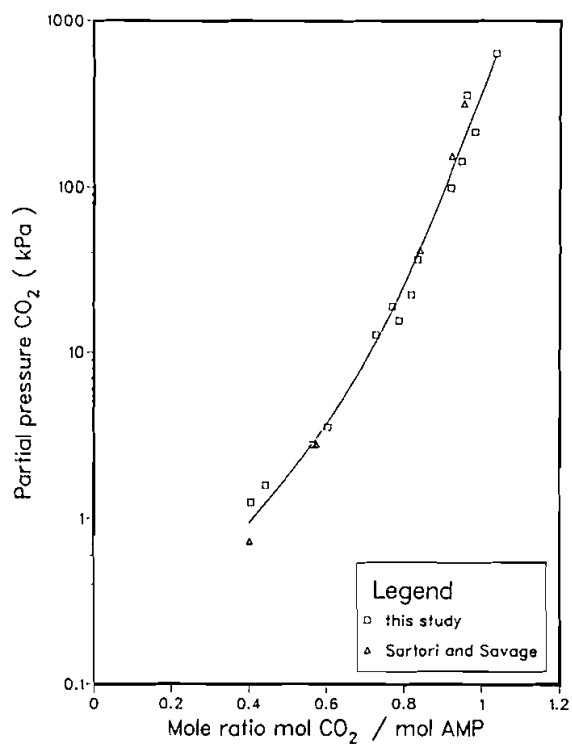
FIGURE 2 Solubility of CO<sub>2</sub> in 3.0 M aqueous AMP at 40°C.

TABLE II

Solubility of H<sub>2</sub>S at 40°C and 100°C in 2.0 M Aqueous AMP

| 40°C     |         | 100°C    |         |
|----------|---------|----------|---------|
| $\alpha$ | P (kPa) | $\alpha$ | P (kPa) |
| 0.618    | 2.69    | 0.140    | 2.26    |
| 0.630    | 2.93    | 0.203    | 5.51    |
| 0.726    | 5.46    | 0.256    | 9.40    |
| 0.793    | 9.79    | 0.400    | 23.9    |
| 0.794    | 8.82    | 0.506    | 31.8    |
| 0.834    | 13.1    | 0.529    | 51.8    |
| 0.904    | 30.3    | 0.750    | 148.0   |
| 0.970    | 68.8    | 0.786    | 187.0   |
| 1.021    | 178.0   | 0.979    | 466.0   |
| 1.109    | 380.0   | 1.126    | 947.0   |
| 1.175    | 566.0   | 1.278    | 1580.0  |
| 1.253    | 797.0   | 1.405    | 2010.0  |
| 1.441    | 1280.0  |          |         |
| 1.495    | 1470.0  |          |         |
| 1.715    | 2160.0  |          |         |

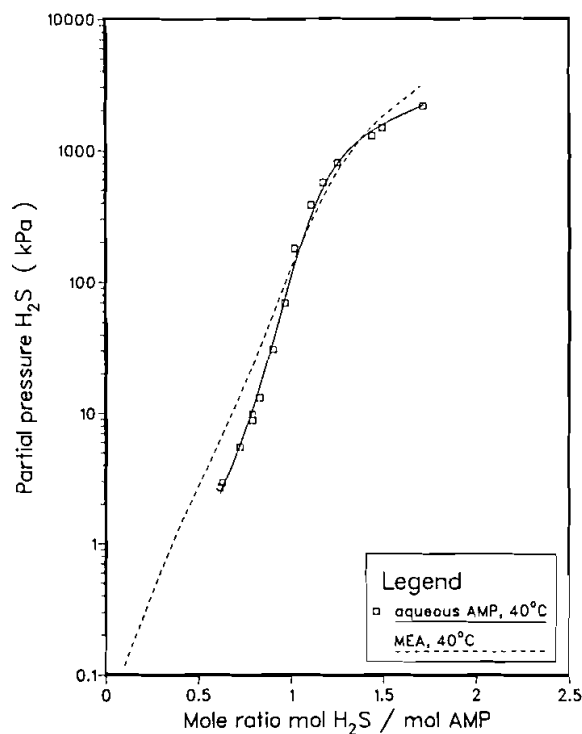
TABLE III

Solubility of CO<sub>2</sub> at 40°C and 100°C in 2.0 M Aqueous AMP

| 40°C     |         | 100°C    |         |
|----------|---------|----------|---------|
| $\alpha$ | P (kPa) | $\alpha$ | P (kPa) |
| 0.493    | 2.17    | 0.136    | 8.53    |
| 0.732    | 9.58    | 0.193    | 16.2    |
| 0.742    | 10.6    | 0.292    | 35.3    |
| 0.916    | 44.5    | 0.414    | 73.2    |
| 0.952    | 95.4    | 0.583    | 172.0   |
| 1.008    | 266.0   | 0.776    | 466.0   |
| 1.042    | 640.0   | 0.832    | 551.0   |
| 1.059    | 653.0   | 0.896    | 886.0   |
| 1.084    | 1140.0  | 0.998    | 1330.0  |
| 1.128    | 1800.0  | 1.033    | 1960.0  |
| 1.190    | 2680.0  | 1.162    | 3530.0  |
| 1.325    | 5740.0  | 1.275    | 5870.0  |

Figure 2 under similar equilibrium conditions; an excellent agreement between the studies is indicated.

The equilibrium solubility of H<sub>2</sub>S and CO<sub>2</sub> in a 2.0 M aqueous AMP solution was measured at 40 and 100°C. The results are presented in Tables II and III. A comparison between the solubility of H<sub>2</sub>S and CO<sub>2</sub> in the 2.0 M aqueous AMP solution and in a 2.0 M aqueous MEA solution at 40°C is shown in Figures 3 and

FIGURE 3 Solubility of H<sub>2</sub>S in 2.0 M aqueous AMP at 40°C.

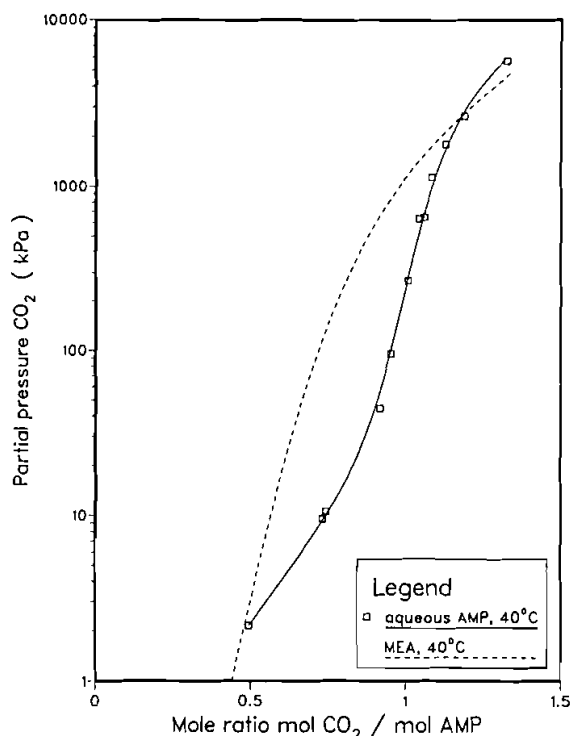


FIGURE 4 Solubility of CO<sub>2</sub> in 2.0 M aqueous AMP at 40°C.

4. The acid gas solubilities in the MEA solution are smoothed values as calculated through the use of the Kent-Eisenberg thermodynamic model (Kent and Eisenberg, 1976) which was fitted to experimental data.

The solubility of H<sub>2</sub>S is slightly higher in the aqueous AMP solution than in the MEA solution. The higher solubility in the AMP solution may be attributed to the slightly higher basicity for AMP (pK<sub>a</sub> = 9.7 for AMP versus 9.5 for MEA (Sartori and Savage, 1983)).

The solubility of CO<sub>2</sub> is much greater in the aqueous AMP solution than in the MEA solution at loadings between 0.5 and 1.0 mol CO<sub>2</sub>/mol amine. This difference in solubility cannot be attributed solely to the difference in amine basicity. The lower solubility in the aqueous MEA solution is a result of stable carbamate formation which, as previously noted, tends to limit the stoichiometric loading to 0.5 mol CO<sub>2</sub>/mol amine. The formation of the carbamate ion by reaction of AMP with CO<sub>2</sub> is negligible (Sartori and Savage (1983), Chakraborty *et al.* (1986)) and thus a solution loading of 1.0 mol CO<sub>2</sub>/mol amine may be more easily attained.

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