

Solubility of Hydrogen Sulfide in Aqueous Solutions of Methyldiethanolamine and diethanolamine

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1. Introduction

Hydrogen sulfide is the most common sulfur-containing gas found in natural gas or synthetic natural gas. Since H₂S is both toxic and corrosive, it must be removed down to very low levels. H₂S is most often removed by absorption into a solvent in which it reacts. H₂S is then stripped from the solvent so that the solvent may be recycled to the absorber and the H₂S is reduced to elemental sulfur which is a useful commodity. The most common chemical solvents for H₂S removal are aqueous amine solutions with the tertiary amine, methyldiethanolamine, and the secondary amine, diethanolamine, being the amines most often used in practice.

The physical solubility of H₂S is a key parameter needed to model the absorption or stripping of the gas in solvents. However, when the gas reacts with the solvent, the physical solubility cannot be measured directly. In the case of carbon dioxide, another acid gas normally removed by amine treating, the "nitrous oxide analogy" method proposed by Clark (1964) is used to estimate the physical solubility of CO₂. This method works since CO₂ and N₂O have very similar molecular properties but N₂O does not react chemically with aqueous amines. Thus, measurement of the solubility of N₂O in an aqueous amine solution allows an estimation of the CO₂ solubility. There does not appear to be a similar analogy gas for H₂S.

2. Material and Methods

The solubility experiments were carried out in a modified ZipperclaveTM reactor shown schematically in Figure 1. Details regarding the solubility apparatus and its operation have been given by Rinker and Sandall (1996). The DEA used in these experiments was obtained from Fisher Scientific and had a minimum purity of 99 mass percent. The MDEA was donated by Union Carbide Corporation with a minimum purity of 99 mass percent. The H₂S used in the experiments was CP grade (>99.5 mol %) as obtained from Matheson. The water used in this work was

deionized. The concentration of the amine in solution was determined by titration with hydrochloric acid.

A weighed sample of approximately 400 g of test solution was injected into the $1.028 \times 10^{-3} \text{ m}^3$ (at 298 K) stainless steel chamber. The reactor was then sealed and heated or cooled to the desired temperature by two external electric heating jackets and by an internal heating/cooling coil through which an antifreeze/water solution was circulated by an external constant temperature circulator. The temperature was maintained to within $\pm 0.1 \text{ K}$, and the absorption chamber and tubing were insulated. The solution was degassed in the absorption chamber under vacuum while stirring with the attached Magnedrive packless stirrer. The vacuum was shut off after the pressure steadied, and the system was allowed to come to 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 and 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.

3. Results and Discussion

The system was allowed to reach vapor-liquid equilibrium at which point the final pressure (P_f) was measured and recorded. The final equilibrium pressure was generally achieved in less than 10 minutes. The Henry's law constant, H , was then calculated by the following equation:

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

$$P_A = HC_A$$

where V_l and V_g are the liquid and gas volumes, respectively, R is the ideal gas constant ($8.314 \times 10^{-3} \text{ MPa m}^3/\text{kmol K}$) and T is the absolute temperature (K). All pressures were measured with a pressure transducer to within $\pm 0.15 \times 10^{-3} \text{ MPa}$. The temperature dependence of the pressure transducer was compensated for by calibrating the transducer over the temperature range 20 to 100°C. The temperature was measured to within $\pm 0.1 \text{ K}$ with a type J thermocouple mounted in a stainless steel thermal well which was inserted into the absorption chamber. The protonated amine solutions were prepared by the addition of HCl to a pH of approximately 2.

Attempts were made to correlate the data shown for the protonated amine solutions according to the van Krevelen and Hofstijzer (1948) method for electrolyte solutions according to:

$$\log(H/H_0) = hI$$

where H_0 is the Henry's law constant for pure water, I is the ionic strength and h is the salting out factor with contributions due to the gas (h_g), the positive ion (h_+) and the negative ion (h_-).

$$h = h_g + h_+ + h_-$$

We found, however, that there is a simple empirical correlation of the gas solubility and the mole fraction of the solvent added to the water. The new proposed correlation is developed for Henry's law formulated in terms of the mole fraction of the solute gas in the liquid phase

$$p_A = H'x_A$$

where p_A is the partial pressure of H_2S (atm) and x_A is the mole fraction of H_2S . The correlation developed here for H_2S solubility in aqueous solutions was developed on a completely empirical basis and should be used with caution to predict H_2S physical solubility for conditions other than those for this study.

Literature Cited

Clark, J. K. A., Ind. Eng. Chem. Fundamentals 61, 668 (1964).

Rinker, E. B., and Sandall, O. C., Chem. Eng. Comm. 144, 85 (1996).