

Solubility of Hydrogen Sulfide in Aqueous Solutions of Methyldiethanolamine and diethanolamine

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The solubility of H₂S is an important parameter for modeling H₂S absorption. Since the direct measurement of H₂S solubility in aqueous amine solutions is impossible, this work initially attempted to develop an H₂S analogy method, however, this was unsuccessful. Consequently, H₂S solubilities were measured in aqueous amines which were completely protonated with HCl over a temperature range of 25-60°C. The solvents investigated in this work included 0-50% aqueous solutions of methyldiethanolamine and diethanolamine. Thereafter, a new empirical correlation was developed that can predict Henry's constant for H₂S using only the solubility of H₂S in water and the molecular weight of the aqueous solvent.

Key words : solubility, H₂S analogy method, methyldiethanolamine and diethanolamine.

1. Introduction

Aqueous solutions of methyldiethanolamine (MDEA) and diethanolamine (DEA) are attractive solvents for the selective removal of H₂S from process streams containing CO₂ and hydrocarbons. The first description of the use of MDEA in a process to selectively remove H₂S in the presence of CO₂ is given in the publications of Frazier and Kohl (1950) and Miller and Kohl (1953) which describe the results of laboratory, pilot plant, and commercial plant studies carried out by the Fluor Corporation during the late 1940's and early 1950's. MDEA is currently used in a number of treating plants plus it is evident that the number of applications for MDEA and DEA processing technologies will continue to increase including the enrichment of the H₂S content in the acid gas fed to Claus sulfur recovery plants and used in the synthesis of sulfur derivatives, the removal of H₂S for recycling in a sulfur plant, and the recovery of CO₂ and removal of H₂S from gases rich in CO₂. The removal of H₂S from gases

produced from gasifying coke and coal is another probable area of application. In this case, the removal of large quantities of CO₂ may not be economically justified. A number of companies have reported on results from a pilot plant and commercial scale testing [Pearce and Brownlie (1976); Pearce (1978); Vidaurri and Kahre (1977); Johnson and Say (1979); Blanc et al. (1980)]. Suggestions for processing schemes that employ the use of MDEA treating have also been presented by Goar (1980).

In this work, the solubility of H₂S was measured in various aqueous solutions in which H₂S does not react. The solutions investigated were aqueous solutions of methyldiethanolamine (MDEA) and diethanolamine (DEA) that had been neutralized by the addition of HCl. The data was found to correlate fairly well with the use of a relatively simple empirical formula. Accordingly, due to a lack of alternative information, it is proposed that this correlation be used to estimate the solubility of H₂S in aqueous amine solutions.

2. Materials and Methods

2.1. H₂S Solubility in Aqueous Protonated Amines

Since no appropriate analogy method for H₂S has been currently developed, this paper proposes an alternative technique. The physical solubility of H₂S was measured in aqueous MDEA and DEA solutions that were protonated with HCl in order to suppress the chemical reactions between H₂S and the amines. Since the reactions between H₂S and MDEA and DEA were essentially instantaneous, almost all the amines at the gas-liquid interface were protonated. It then follows that the physical solubility of H₂S in protonated amine solutions can be used to model the H₂S absorption into aqueous amine solutions. Amines protonated by HCl contain the Cl⁻ ion, whereas amine solutions reacted with H₂S contain the HS⁻ ion. Accordingly, it was initially proposed that the effect of the Cl⁻ ion could be quantified by correlating the solubility data according to the van Krevelen and Hoftijzer (1948) approach. According to Danckwerts (1970), Henry's law constant for a gas in an aqueous solution can be correlated according to the following expression:

$$\log_{10} \left(\frac{H}{H^0} \right) = hI \quad (1)$$

where I is the ionic strength of the solution, $h = (h^+ + h^- + h_g)$ is the salting-out factor, h^+ , h^- , and h_g are the salting-out factors due to the positive ions, negative ions and gas, respectively, and H^0 and H are Henry's law constants for the gas in pure water and in an aqueous electrolyte solution, respectively. The values of h^+ and h^- for several different ions are given by Danckwerts (1970). It is assumed that only h_g is a function of temperature. The temperature dependence of h_g for H₂S is unknown, yet it can be easily determined by measuring the H₂S solubilities in aqueous NaCl solutions over the temperature range of interest with various ionic strengths. The values of h^+ for MDEAH⁺ and DEAH⁺ are also unknown, however, these can be determined from the H₂S solubility data in the protonated amine solutions because h_g and h are known. When H₂S reacts with amines, the products are MDEAH⁺

and/or DEAH⁺ and HS⁻. The value of h^- for HS⁻ has not been previously reported, yet the published data of h^- for OH⁻ is probably a good estimate.

2.2. Experimental

Protonated aqueous solutions of DEA and MDEA were made with deionized water and concentrated HCl. The amines were mixed with the appropriate amount of deionized water, thereafter the appropriate amount of concentrated HCl was added dropwise while stirring and cooling the aqueous amine mixture.

The solubility measurements were carried out in a modified Zipperclave reactor, shown schematically in Figure 1. The experimental procedure was identical to that used to measure N₂O solubilities except that the entire apparatus was operated in a fume hood and all gases released from the reactor were vented through Mallcosorb (a granular acid gas absorbent) to limit any contact with the highly toxic H₂S gas.

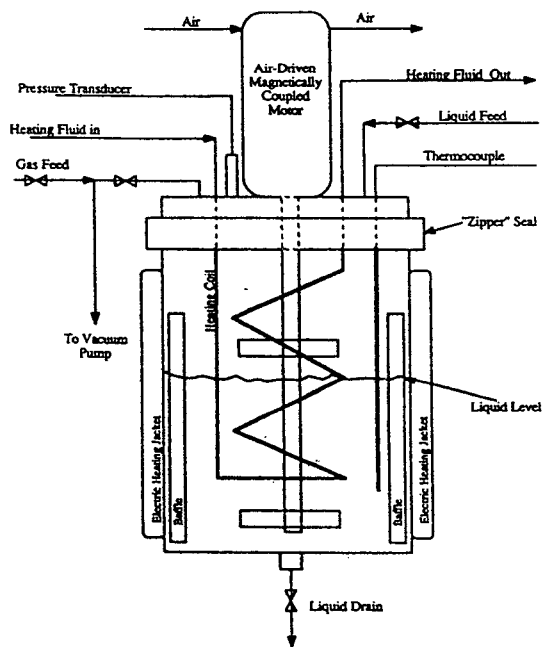


Fig. 1. Schematic diagram of modified Zipperclave reactor.

A weighed sample of approximately 400 g of the test solution was injected into the 1.028×10^{-3} m³ (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 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 ± 0.1 K, and the absorption chamber and tubing were insulated. The solution was degassed in the absorption chamber under a vacuum while stirring with the attached Magnedrive packless stirrer. The vacuum was shut off after the pressure steadied, and the system was then 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 then 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.

The system was allowed to reach a 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:

$$H = \frac{(P_f - P_v) V_l}{(P_i - P_f) V_g} RT \quad (2)$$

$$P_A = H C_A \quad (3)$$

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

3. Results and Discussion

The Henry's law constants for H_2S in 10wt% - 50wt% aqueous protonated MDEA solutions were measured at 25°C, 40°C, and 60°C and the data are listed in Table 1 and plotted in Figure 2. The solubilities of H_2S in 10wt% - 50wt% aqueous

protonated DEA solutions were measured at 25°C, 40°C, and 60°C and the data are listed in Table 2 and plotted in Figure 3. The solubilities of H_2S in aqueous NaCl solutions were measured at 25°C and 40°C and the data are listed in Table 3 and plotted in Figure 4. Clearly, the maxima in Figures 2 and 3 cannot be accounted for by correlating the data according to the van Krevelen and Hofstijzer approach. One possible reason for the odd maxima in Figures 2 and 3 is that the MDEAH^+ and DEAH^+ ions are relatively large ions which may allow for some delocalization of their charge.

Since the van Krevelen and Hofstijzer approach is clearly ineffective for correlating H_2S solubility in aqueous protonated amine solutions, a new correlation method is postulated which uses the following definition of Henry's law.

$$P_A = H_A x_A \quad (4)$$

where H_A is the Henry's law constant for solute A in units of atm, P_A is the partial pressure of solute A in atmosphere, and x_A is the mole fraction of solute A in solution. In all previous work, Henry's law constants were reported in units of (atm l)/mol. To convert from units of (atm l)/mol to units of atm, the following equation is used.

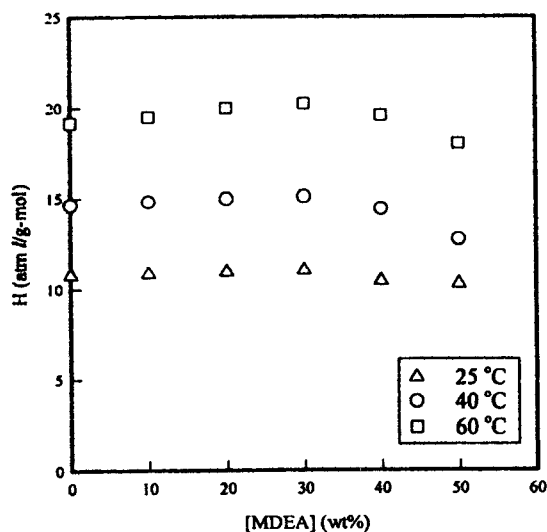


Fig. 2. Solubility of H_2S in Aqueous MDEA Solutions.

Table 1. Solubility of H₂S in Aqueous MDEA Solutions

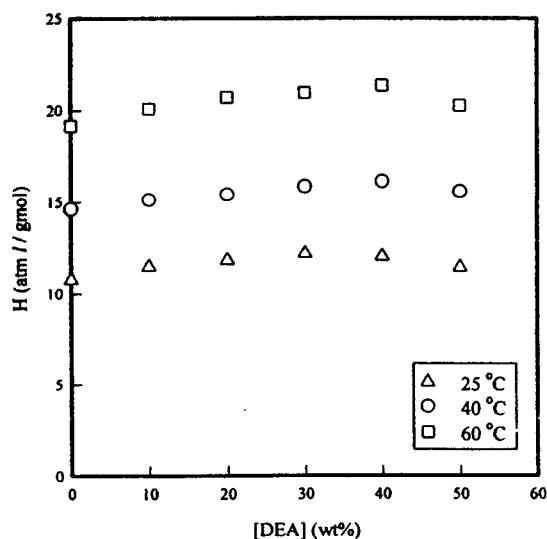
Temp. (°C)	[MDEA] (wt%)	H _{H₂S} (atm l/gmol)	H _A /H _A ^o
25	0	10.77	1.0
	10	10.83	0.93
	20	10.94	0.857
	30	11.01	0.770
	40	10.42	0.644
	50	10.25	0.54
40	0	14.62	1.0
	10	14.79	0.94
	20	14.95	0.862
	30	15.08	0.777
	40	14.40	0.656
	50	12.73	0.504
60	0	19.17	1.0
	10	19.50	0.993
	20	20.00	0.894
	30	20.24	0.794
	40	19.59	0.679
	50	18.03	0.533

Table 2. Solubility of H₂S in Aqueous DEA Solutions

Temp. (°C)	[DEA] (wt%)	H _{H₂S} (atm l/gmol)	H _A /H _A ^o
25	0	10.77	1.000
	10	11.47	0.991
	20	11.82	0.936
	30	12.18	0.872
	40	12.02	0.760
	50	11.43	0.619
40	0	14.62	1.000
	10	15.12	0.964
	20	15.42	0.901
	30	15.87	0.838
	40	16.13	0.751
	50	15.59	0.622
60	0	19.17	1.000
	10	20.08	0.974
	20	20.70	0.920
	30	20.95	0.841
	40	21.35	0.756
	50	20.26	0.615

Table 3. Solubility of H₂S in Aqueous NaCl Solutions

Temp. (°C)	[NaCl] (gmol/l)	H _{H₂S} (atm l/gmol)	H _A /H _A ^o
25	0	10.77	1.00
	0.171	10.96	1.02
	0.511	11.75	1.09
	1.042	12.68	1.18
	2.171	15.20	1.41
	3.392	18.34	1.70
40	0	14.61	1.00
	1.040	17.12	1.17
	2.166	20.47	1.40
	3.382	24.49	1.68

Fig. 3. Solubility of H₂S in Aqueous DEA Solutions.

$$H_A(\text{atm}) = H_A\left(\frac{\text{atm} \cdot \text{l}}{\text{mol}}\right) \rho \sum_i \frac{w_i}{M_i} \quad (5)$$

where ρ is the solution density in units of g/l, w_i is the mass fraction of solvent species i (i.e., water, MDEA, DEA), M_i is the molecular weight of solvent species i in units of g/mol. By plotting H_A/H_A^o versus the mole fraction of solvent x_i (i.e. MDEA, DEA, etc.), a straight line is produced with an H_A/H_A^o unity intercept. (H_A^o is the solubility of species A in pure water). Thus the

data can be correlated according to the following equation:

$$\frac{H_A}{H_A^0} = 1 - \beta x_i \quad (6)$$

The slope of this line, β , is the fitting parameter which apparently depends on the solvent properties. Figures 5 and 6 present the transformed data for the solubilities of H_2S in aqueous protonated

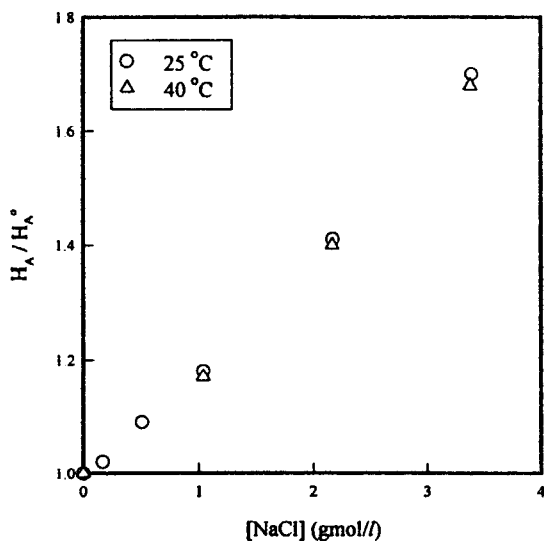


Fig. 4. Solubility of H_2S in Aqueous NaCl Solutions.

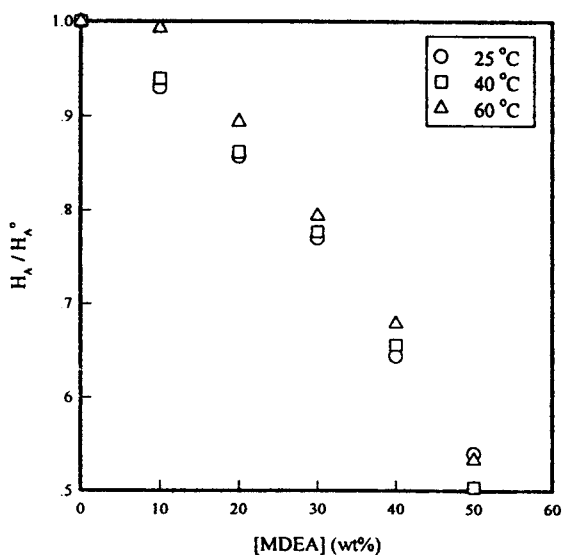


Fig. 5. Correlation of H_2S Solubility in Aqueous MDEA.

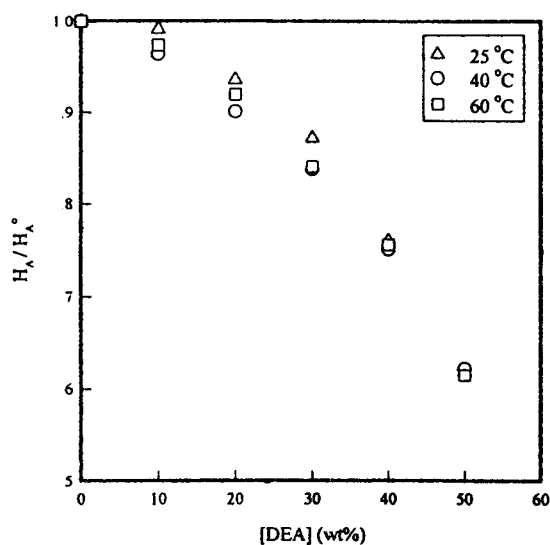


Fig. 6. Correlation of H_2S Solubility in Aqueous DEA.

MDEA and aqueous protonated DEA, respectively. The data in Figures 5 and 6 appear to be independent of temperature over the temperature range of 25-60°C.

4. Conclusion

Henry's law constants for H_2S in aqueous protonated MDEA, aqueous protonated DEA, and aqueous NaCl solutions were measured in a modified Zipperclave reactor. The experimental procedure was the same as that used to measure Henry's law constants for nitrous oxide in aqueous amine solutions. The plots of Henry's law constants for H_2S in aqueous protonated MDEA and DEA vs. wt% amine exhibited maxima, whereas Henry's law constants for H_2S in aqueous NaCl solutions monotonically increased with an increasing salt concentration. Accordingly, the fitted slope and Henry's law constant of H_2S in pure water are the only parameters needed to generate the curves shown in Figures 2 and 3. This method of correlation is fairly simple and can capture the maxima observed in Figures 2 and 3.

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