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Physical Solubility of Hydrogen Sulfide in Aqueous Solutions of 2-(*tert*-Butylamino)ethanol

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The physical solubility of hydrogen sulfide in aqueous solutions of 2-(*tert*-butylamino)ethanol neutralized with hydrochloric acid was measured in this work. Measurements were made over the temperature range 25 °C to 40 °C and the amine concentration range 0 to 50 mass %. The solubility data exhibit a minimum in the solubility with amine concentration. The data were correlated using the van-Krevelen−Hoftijzer method for the “salting-out” effect up to the minimum solubility and by a new empirical method over the entire range of amine concentration.

Introduction

Sterically hindered amines have some advantages over nonhindered alkanolamines for acid gas removal from natural gas. Severely hindered amines cannot form stable carbamates on reaction with carbon dioxide but instead give bicarbonate as a reaction product. This results in a more favorable 1:1 stoichiometry for hindered amines compared to a 1:2 reaction stoichiometry for nonhindered primary and secondary amines. The reaction kinetics for the reaction between carbon dioxide and sterically hindered amines is generally slower than those for nonhindered primary and secondary amines. For this reason, hindered amines are attractive candidates for selective absorption of hydrogen sulfide from gases containing carbon dioxide.

The physical solubility of hydrogen sulfide is the key physical property needed to model absorption rates for this gas in aqueous amine solutions. Since H_2S reacts with the amines, the physical solubility cannot be measured directly. There does not appear to be an analogy gas for H_2S as is the case for CO_2 with the nitrous oxide analogy method (Clark).[1]

In the work reported here the physical solubility of H_2S was measured in aqueous solutions of 2-(*tert*-butylamino)ethanol (TBAE) neutralized by the addition of HCl. TBAE is a severely hindered amine that may be useful for selective absorption of H_2S in the presence of CO_2.

Experimental Apparatus and Procedure

For solvent preparation, TBAE was mixed with deionized water and protonated by titration with concentrated hydrochloric acid while stirring and cooling the solution until a pH of approximately 3.5 was reached. The amine can be considered to be completely protonated at this pH value due to the higher basicity of TBAE compared to that of water.

The solubility measurements were carried out in a modified Zipperclave reactor using a similar measuring method as previously described by Rinker and Sandall.[2] The main part of the apparatus consisted of a cylindrical one-liter Zipperclave reactor with an air driven magnetically coupled stirrer on the top, as schematically shown in Figure 1. An internal heating coil and external heating jackets were used to adjust and maintain the desired temperature. Additionally, an external gas tank was used to store a known volume of H_2S. The volume of tank and reactor was determined by measuring the mass of water displaced. The temperatures inside the absorption chamber and inside each gas tank were measured by thermocouples with an accuracy of 0.1 K, and the pressure, by pressure transducers with an accuracy of 0.14 kPa.

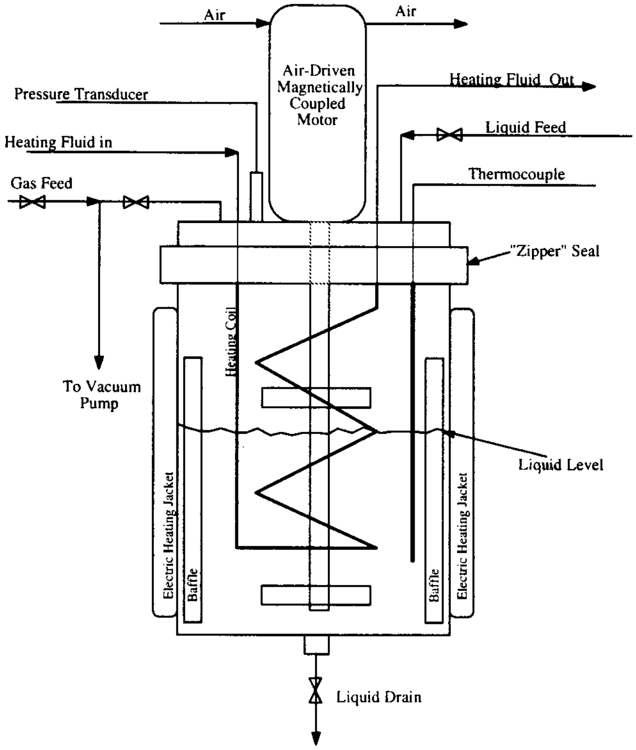

Figure 1. Modified Zipperclave reactor.

A weighed quantity of approximately 400 g of protonated amine solution was injected into the absorption chamber. The reactor was then sealed and adjusted to the desired temperature, and a vacuum was applied. To degas the solvent, the liquid was stirred under vacuum for several

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Table 1. Henry's Constant for H_2S in Pure Water, H/MPa·m^3·kmol^{-1}

t/°C	this work	Rinker and Sandall[2]	Perry et al.[5]
25	1.083	1.073	0.996
40	1.400	1.480	1.369

minutes. After the vacuum pump was shut off, the system reached vapor−liquid equilibrium and the pressure was recorded at this point as vapor pressure, p_v, of the solvent. H_2S was then allowed to flow into the absorption chamber. The amount of injected H_2S, n_t, was determined by measuring temperature and pressure in the external gas storage tank before (1) and after (2) the gas transfer, taking into consideration the nonideality of H_2S:

$$n_t = \left(\frac{p_1}{Z_1T_1} - \frac{p_2}{Z_2T_2}\right)\frac{V_{GT}}{R} \tag{1}$$

V_{GT} is the volume of the gas storage tank, and Z_1 and Z_2 are the compressibility factors.

The system reached equilibrium while stirring for about 20 min. The final pressure, p_f, was measured at this point to determine the H_2S equilibrium partial pressure and the concentration of dissolved H_2S from the difference in transferred, n_t, and remaining moles of H_2S, n_r:

$$n_r = \left(\frac{p_f}{Z_f} - \frac{p_v}{Z_v}\right)\frac{V_G}{RT} \tag{2}$$

V_G is the gas-phase volume in the absorption chamber. Z_v is the compressibility factor of the vapor, and Z_f is that of the final gas mixture in the equilibrium cell, which consisted mainly of water and H_2S. All compressibility factors were determined according to the Redlich−Kwong equation for pure and mixed solvents as given by Tester and Model.[3]

Henry's constant for H_2S is then calculated from the equation

$$H_{H_2S} = \frac{(p_f - p_v)V_l}{n_t - n_r} \tag{3}$$

The density of aqueous TBAE solution as a function of temperature and concentration, which was needed to determine the liquid volume, V_l, in the equilibrium cell, was measured in a previous work.[4] The quantity of injected H_2S was chosen so as to have a final partial pressure of H_2S close to 1 atm.

For safety, the apparatus was operated in a fume hood. After finishing an experimental run, the dissolved H_2S was stripped off by bubbling an air stream through the solution for several minutes. All gases released from the reactor were vented through a sodium hydroxide solution to chemically absorb the H_2S and to avoid release of the highly toxic gas into the environment.

The hydrogen sulfide used in this work was CP grade with a minimum purity of 99.5% as obtained from Matheson. The TBAE was delivered by Aldrich Chemicals and was of stated minimum purity of 99 mass %. The hydrochloric acid was 37 mass % delivered by Fischer Chemicals.

Results and Correlation

For testing the accuracy of the measuring method and the proper operation of the apparatus, the solubility of H_2S in pure water was measured. The results are listed in Table 1 along with data found in the literature. The values are in good agreement with an average deviation of 3% from the values reported by Rinker and Sandall[2] and 5% from the values reported by Perry et al.[5]

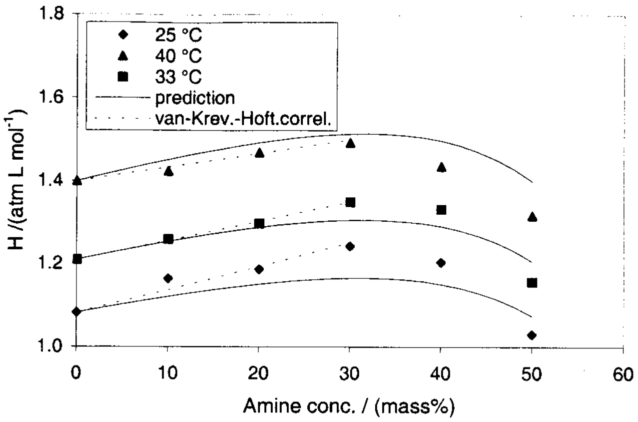

Figure 2. Henry's constant in aqueous protonated TBAE solutions.

Table 2. Henry's Constant for H_2S in Aqueous Protonated TBAE Solutions

TBAE conc	t	H_{H_2S}	σ	H_{H_2S}'
mass %	°C	MPa·m^3·kmol^{-1}	MPa ·m^3·kmol^{-1}	MPa
10	25	1.165	0.0211	58.87
	33	1.260	0.0041	63.51
	40	1.423	0.0027	71.47
20	25	1.187	0.0105	53.98
	33	1.298	0.0042	58.85
	40	1.468	0.0164	66.52
30	25	1.244	0.0001	50.83
	33	1.350	0.0033	54.93
	40	1.493	0.0067	60.44
40	25	1.205	0.0268	43.31
	33	1.332	0.0167	47.67
	40	1.435	0.0029	51.02
50	25	1.030	0.0048	32.06
	33	1.158	0.0079	35.86
	40	1.317	0.0033	40.49

The Henry's constants for H_2S in protonated amine solution as measured in this work are summarized in Table 2 and plotted in Figure 2. Each value reported in Table 2 is the average of at least two measurements. The standard deviation between experimental runs as listed in the table indicates that the error is between 1 and 3%, while the maximum experimental error was estimated to be approximately 7−10%. The shape of the H_2S solubility plots in Figure 2 is in agreement with results observed by Rinker and Sandall,[2] who conducted solubility measurements in protonated MDEA and DEA solutions.

The commonly used method to describe the effect of ionic strength on gas solubility is the empirical van-Krevelen−Hoftijzer approach as reported by Danckwerts[6]

$$\log\left(\frac{H}{H^*}\right) = \sum_j (k_+ + k_- + k_g)_j I \tag{4}$$

The parameters k_+, k_-, and k_g (van-Krevelen coefficients) in eq 4 are specific to the cations, the anions, and the gas, respectively, and are assumed to be ion concentration independent. The superscript * refers to unloaded amine solution.

However, the maxima exhibited in Figure 2 cannot be accounted for by the monotonically increasing function according to the van-Krevelen−Hoftijzer equation. Only in the range of low ionic strength for initial amine concentra-

Table 3. Van-Krevelen Coefficients for H_2S and the Ions Present in Protonated TBAE Solution

ion	k_i/L· mol^{-1}	H_2S	k_{H_2S}/L·mol^{-1}
H_3O^+	0[a]	at 25 °C	−0.027
Cl^-	0.021[a]	at 33 °C	−0.033
$R_2NH_2^+$	0.031	at 40 °C	−0.040

[a] Taken from ref 5.

tions of less than 30 mass % can eq 4 be applied to correlate the solubility data.

To implement eq 4, the ionic strength of the solution was calculated assuming complete protonation of TBAE and a pH of approximately 3.5. The van-Krevelen coefficients for Cl^- and H_3O^+ ions are given by Danckwerts,[6] and the coefficient for protonated TBAE was determined by additional nitrous oxide solubility measurements in partially protonated amine solutions as proposed by Browning and Weiland.[7] The only unknown parameter, k_{H_2S} for hydrogen sulfide, was estimated by least-squares fits of the experimental solubility data at each temperature investigated according to the model equation (eq 4). The coefficients for protonated TBAE, H_3O^+, and Cl^- were held constant in the fitting procedure, as is proposed by Danckwerts.[6] All coefficients and results are summarized in Table 3, and the best fits are shown in Figure 2.

Recently, Rinker and Sandall[2] suggested another empirical correlation to describe the H_2S solubility over the entire range of amine concentration investigated. Using Henry's law formulated as a relationship between partial pressure, p_1, and mole fraction, x_1, of dissolved H_2S,

$$p_1 = H_1'x_1 \tag{5}$$

they found the following simple equation representing the H_2S solubility data,

$$\frac{H_1'}{H_1^{0\prime}} = 1 - \beta_A x_A \tag{6}$$

where x_A is the mole fraction of protonated amine in solution, β_A is the empirical parameter to be obtained by fitting the experimental data, and the superscript ^{0} refers to the solubility in pure water. The $H_1^{0\prime}$ in eq 6 is the value in pure water. If the reference value for water with HCl added to give a pH of 3.5 were used, the $H_1^{0\prime}$ values would be about 10% higher. The experimentally determined Henry's constant, H/MPa·m^3·kmol^{-1}, can be converted into H'/MPa, as used in eqs 5 and 6, by

$$H_1' = H\rho \sum_i \frac{w_i}{M_i} \tag{7}$$

where ρ is the solution density, w_i is the mass fraction, and M_i is the molecular weight of the solvent species i, amine and water, respectively. The mass fraction is calculated on an HCl-free basis. Table 2 lists these values of H_1'. Figure 3 shows the converted Henry's constant as measured in this work plotted versus the TBAE mole fraction in solution. From the slope of the linear plot a value for the fitting parameter β_A of 3.35 was found which appears to be independent of temperature over the investigated range of 25 °C to 40 °C. Rinker and Sandall[2] found that β_A could be simply correlated with the molecular weight of the solvent as given by eq 8.

$$\beta_A = 0.0334M_A - 0.917 \tag{8}$$

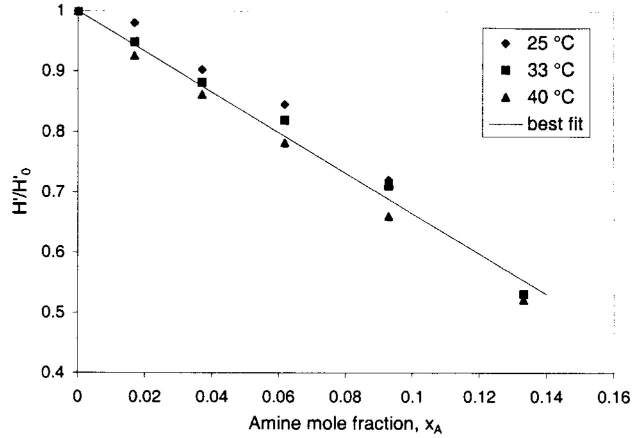

Figure 3. H_2S solubility correlation in aqueous protonated TBAE solutions.

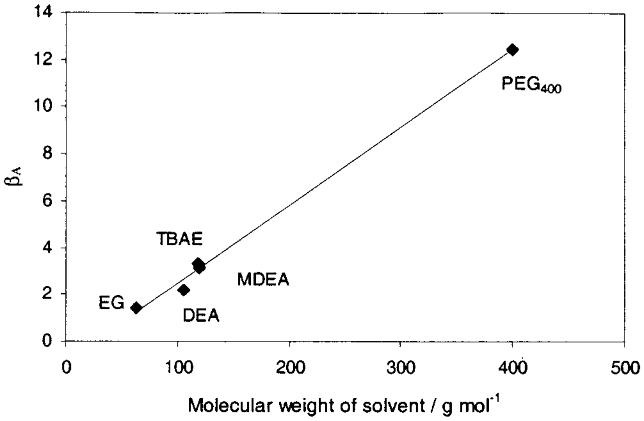

Figure 4. Relation between β_A and molecular weight of the solvent.

Table 4. Molecular Weight and Values for β_A of Different Solvents

solvent	molecular weight/g·mol^{-1}	β_A
EG (ethylene glycol)	62.07	1.42[a]
DEA	105.14	2.19[a]
TBAE	117.19	3.35
MDEA	119.16	3.17[a]
PEG_{400} (poly(ethylene glycol))	400	12.47[a]

[a] Taken from ref 1.

The value of β_A calculated from the correlation, eq 8, for TBAE is 3.00, compared to the best fit value of 3.35. Table 4 shows the values for β_A and the molecular weight of the solvents investigated by Rinker and Sandall,[2] as plotted in Figure 4. The molecular weight in eq 8 is the molecular weight of the solvent added to the water.

Equations 6 and 7 were used to generate the correlation curves shown in Figure 2. The measured data fit the correlation within an average deviation of 2.7%, and the method is able to capture the maximum of Henry's constant. With the knowledge of only the molecular weight of solvent mixed with water and the physical solubility in pure water, the hydrogen sulfide solubility can be interpolated within the experimental range. However, since this method is empirical, the correlation cannot be extended to other solvents and conditions other than those for this study.

Nomenclature

Latin Letters

H = Henry's constant, MPa·m^3·kmol^{-1}
H' = Henry's constant, MPa
I = ionic strength, mol·L^{-1}
k = van-Krevelen coefficients, L·mol^{-1}
M = molecular weight, g·mol^{-1}
n = mole number, mol
p = pressure, MPa
R = general gas constant, 8.314 × 10^{-3} MPa·m^3·kmol^{-1}·K^{-1}
T = temperature, °C
V = volume, cm^3
w = mass fraction
x = mole fraction
Z = compressibility factor

Greek Letters

ρ = solvent density, g·cm^{-3}
β = constant for solvent

Subscripts

A = amine
f = final
g, G = gas phase
GT = gas tank
l = liquid phase
r = remaining in gas phase
t = transferred
v = equilibrium vapor pressure

Superscripts

0 = property in pure water

Literature Cited

(1) Clarke, J. K. A. Kinetics of Absorption of Carbon Dioxide in Monoethanolamine solutions at short contact times. *Ind. Eng. Chem. Fundam.* **1964**, *3* (3), 239−245.
(2) Rinker, E. B.; Sandall, O. C. Physical Solubility of Hydrogen Sulfide in Several Aqueous Solvents. *Can. J. Chem. Eng.* **2000**, *78*, 232−236.
(3) Tester, J. W.; Modell, M. *Thermodynamics and Its Applications*, 3rd ed.; Prentice-Hall: Upper Saddle River, NJ, 1997.
(4) Kraehnert, R. *Experimental investigation of the absorption system carbon dioxide − 2(tert*-butylamino)-ethanol. Diploma Thesis TU Clausthal, UCSB, Santa Barbara, 1999.
(5) Perry, R. H.; et al. *Chemical Engineers' Handbook*, 5th ed.; McGraw-Hill Book Company: New York, 1973.
(6) Danckwerts, P. V. *Gas Liquid Reactions*; McGraw-Hill: New York, 1970.
(7) Browning, G. J.; Weiland, R. H. Physical Solubility of Carbon Dioxide in Aqueous Alkanolamines via Nitrous Oxide Analogy. *J. Chem. Eng. Data* **1994**, *39*, 817−822.

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