Glossary

C	concentration of species, mol/L
D	diffusivity, cm^2/s
α	Bunsen absorption coefficient, cm^3 of gas/cm^3 of solution
μ	viscosity of solution, g/(cm s)
κ	power in eq 1

Solubility of Hydrogen Sulfide and Carbon Dioxide in a Diglycolamine Solution

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The solubility of H$_2$S and CO$_2$ individually in an aqueous Diglycolamine solution (60 wt % DGA) has been measured at 50 and 100 °C. Partial pressures of H$_2$S ranged from 2.5 to 1890 kPa while partial pressures of CO$_2$ ranged from 1.6 to 5980 kPa.

A number of solvents are used for the removal of the acid gases (H$_2$S and CO$_2$) from natural and refinery gases by absorption. Most processes use an aqueous alkanolamine solution and Monoethanolamine (MEA) is the most commonly used amine. It has the advantages of low molecular weight and high reactivity. However, it reacts irreversibly with carbonyl sulfide and it has a relatively high vapor pressure, which leads to losses in the absorption process. The Fluor Corp. evaluated a number of chemicals for the purpose of acid gas removal and the use of Diglycolamine (DGA) was patented by Blohm and Riesenfeld (*1*). DGA is β,β'-hydroxyaminoethyl ether and has the same molecular weight as diethanolamine. However, it has the reactivity of primary amines with a much lower vapor pressure than MEA.

Little solubility data for the acid gases in DGA have been published. Operating details for plants have been provided (*2, 3, 8*) but only qualitative solubility data were presented. Physical properties of DGA solutions have been presented by Jefferson Chemical Co. (*4*) and these results are summarized in Kohl and Riesenfeld (*5*). This work was undertaken to provide equilibrium solubility data for CO$_2$ and H$_2$S in a typical DGA solution. These data may be useful in comparisons of alternate treating processes.

Experimental Section

The apparatus used in this study is the same as that used for previous studies of the H$_2$S–CO$_2$–Monoethanolamine system in this laboratory (*6, 7*). The equilibrium cell consisted of a Jerguson gauge and a gas reservoir (250-mL capacity) mounted at the top. A magnetic pump was used to circulate the gas phase from the reservoir to the bottom of the gauge. The temperature of the cell was measured by ten-junction copper–Constantan thermopiles which had been calibrated at the ice and steam points. The pressure of the cell was measured by a Heise bourdon tube gauge. The equilibrium cell was housed in a constant temperature air bath controlled within ±0.5 °C. The chromatograph used in this work had a 10 ft long, 0.25 in. o.d. column packed with Chromosorb 104. It was operated isothermally at 100 °C.

Table I. Experimental Data for the Solubility of CO$_2$ in 60% by Weight DGA

$T/°C$	P^a	α^b	$T/°C$	P^a	α^b
50	5980	0.798	100	5840	0.619
	4320	0.776		4940	0.613
	4230	0.774		4860	0.603
	4720	0.749		3570	0.592
	3180	0.740		3260	0.581
	1450	0.694		3830	0.579
	1470	0.653		2100	0.551
	1420	0.652		2980	0.536
	581	0.614		1249	0.524
	588	0.586		1620	0.522
	555	0.580		1124	0.521
	300	0.570		1020	0.494
	315	0.565		626	0.477
	316	0.554		764	0.466
	143	0.537		376	0.447
	69.1	0.511		302	0.445
	12.4	0.480		299	0.441
	2.28	0.439		108	0.423
	3.23	0.434		106	0.420
	1.58	0.400		51.5	0.375
				28.4	0.330
				14.6	0.270
				9.62	0.232
				6.44	0.195
				3.84	0.154
				2.49	0.129

^{a} Partial pressure of CO$_2$ in kPa. ^{b} Mole ratio in liquid, CO$_2$/DGA.

The Diglycolamine solution, composed of 60 wt % DGA and 40 wt % water, was charged to the cell and H$_2$S or CO$_2$ was added in amounts determined by observation of the pressure. This solution is 5.89 kmol m^{-3} and has a specific gravity of 1.058. The DGA was obtained from Jefferson Chemical Co. and had a minimum purity of 97 wt %. Nitrogen was added, when necessary, to ensure that the total pressure was always greater than 350 kPa. This was done to maintain smooth operation of the magnetic pump. The presence of nitrogen did not alter the solubility behavior, even at low partial pressures of H$_2$S or CO$_2$. The vapor was circulated through the liquid for at least 8 h to ensure that equilibrium had been reached.

Samples of the vapor were withdrawn from the top of the cell and passed to the gas chromatograph for analysis. The partial pressure of CO$_2$ or H$_2$S was calculated from the analysis

Table II. Experimental Data for the Solubility of H_2S in 60% by Weight DGA

$T/°C$	P^a	α^b	$T/°C$	P^a	α^b
50	1730	1.091	100	1890	0.909
	1490	1.068		1660	0.849
	1730	1.052		1460	0.806
	1480	1.043		987	0.712
	1140	1.001		662	0.640
	679	0.929		620	0.639
	414	0.877		509	0.571
	217	0.778		396	0.522
	121	0.711		273	0.456
	121	0.699		126	0.316
	86.1	0.657		65.3	0.217
	72.9	0.654		55.1	0.210
	63.1	0.608		48.2	0.182
	46.2	0.577		17.5	0.116
	53.1	0.543		16.5	0.100
	28.3	0.508		13.4	0.095
	18.9	0.452		9.29	0.071
	11.5	0.381		4.87	0.057
	8.87	0.344			
	5.36	0.291			
	3.91	0.262			
	2.52	0.221			

^{a} Partial pressure of H_2S in kPa. ^{b} Mole ratio in liquid, H_2S/DGA.

and a consideration of the gauge, barometric, and vapor pressures. The latter was taken from the Jefferson Chemical data bulletin (*4*).

Liquid samples were withdrawn from the bottom of the cell and passed into a sample bottle containing 7 M H_2SO_4. Upon contact with the H_2SO_4, the acid gas evolved and was collected in a burette of 250 mL capacity. To ensure more complete evolution of the acid gas, the sample bottle was then heated to 100 °C. The pressure of the evolved gases was adjusted to atmospheric and their temperature was measured. From the P–V–T data the amount of gas which evolved was determined and the ratio of CO_2 or H_2S to DGA in the liquid phase was calculated. The data are estimated to be accurate to about 0.02 mol acid gas/mol of DGA or 4%, whichever is larger, in liquid concentration at a given partial pressure of acid gas.

Results and Discussion

Experimental measurements of the solubility of CO_2 and H_2S in a DGA solution have been made at 50 and 100 °C. Partial pressures of CO_2 ranged from 1.6 to 5980 kPa while partial pressures of H_2S ranged from 2.5 to 1890 kPa. The results are presented in Tables I and II for CO_2 and H_2S, respectively. No comparisons with data from the literature are possible for this solution, but comparisons with a 2.5 kmol m^{-3} MEA solution (15.3 wt % MEA) are shown in Figures 1 and 2 for H_2S and CO_2, respectively. The values for CO_2 and H_2S in a 2.5 kmol m^{-3} MEA solution at 50 and 100 °C were taken from ref 6 and 7.

It can be seen that the solubility of H_2S is much lower in the DGA solutions than in the MEA solution. The effect is not as large as it may appear from the figure since the amine concentration in the DGA solution is over twice that in the MEA solution. Since the acid gases react with the amines on an
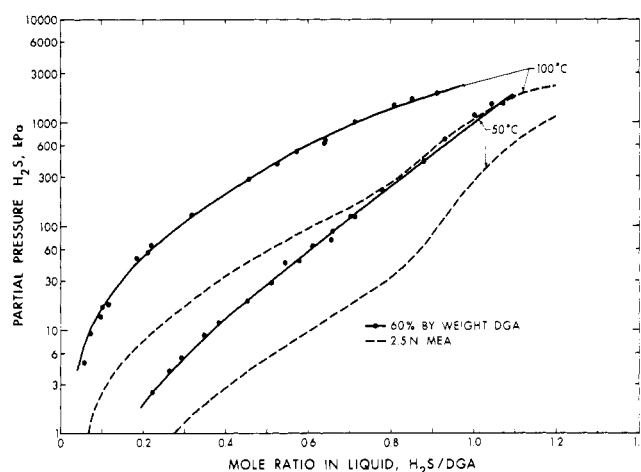
Figure 1. Solubility of H_2S in DGA and MEA solutions.
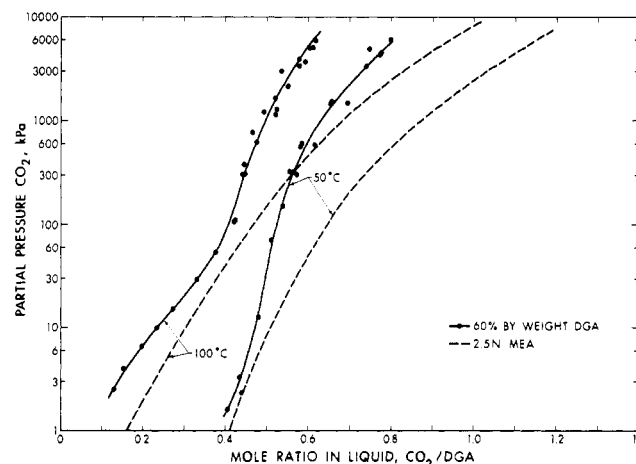
Figure 2. Solubility of CO_2 in DGA and MEA solutions.

equivalent rather than a weight basis, it is advantageous to use as high a concentration of amine in solution as possible, subject to other constraints such as corrosion or excessively high viscosities. For CO_2 the solubilities are comparable at low partial pressures; hence the circulation rate with DGA need only be about half that required with the MEA solution. It is this feature which has led to the changeover of plants from MEA to DGA solvent (*8*).

Literature Cited

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