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Solubility and Diffusivity of Gases in Aqueous Solutions of Amines

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Solubilities of N_2O, C_2H_4, and C_2H_2 and diffusivity of N_2O in various aqueous solutions of amines (MEA, DEA, TEA, MIPA, DIPA, and EDA) were measured at 25 °C and 1 atm of pressure. For these present systems, solubility and diffusivity data could not be correlated by suitable correlations. The best ways to estimate solubility and diffusivity of CO_2 in aqueous solutions of amines may be $\log (\alpha/\alpha_w)_{CO_2} = \log (\alpha/\alpha_w)_{N_2O}$ and $(D/D_w)_{CO_2} = (D/D_w)_{N_2O}$, respectively, using the corresponding data for N_2O.

Aqueous solutions of amines are widely used in gas–liquid contact operations for the removal of acidic gases. The solubility and the diffusivity of the acidic gas in these solutions are fundamental physicochemical properties necessitated in the design of gas–liquid contactors. These properties, however, cannot be conventionally measured because of the presence of chemical reaction and, hence, must be estimated by the corresponding data for nonreacting gases. For the time being, no correlation has been developed on the solubility and the diffusivity of gases in amine solutions. It is rather essential to systematically accumulate data on solubility and diffusivity.

The previous paper (*2*) reported that the solubility of CO_2 in aqueous amine (monoethanolamine, diethanolamine, triethanolamine, or ethylenediamine) solution may be reliably estimated from the corresponding values of N_2O by $\log (\alpha/\alpha_w)_{CO_2} = \log (\alpha/\alpha_w)_{N_2O}$. Such a correlation is considered to be applicable to estimate the diffusivity of CO_2.

In view of these facts, the solubility of N_2O, C_2H_4, or C_2H_2 in aqueous solutions of amines was measured by a volumetric method and the diffusivity of N_2O by means of a laminar liquid-jet apparatus.

Experimental Section

Aqueous solutions of amines (monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), mono(isopropyl alcohol)amine (MIPA), di(isopropyl alcohol)amine (DIPA), and ethylenediamine (EDA)) were prepared from distilled water and reagent grade amines of guranteed purity. The solution was degassed by refluxing it for a sufficient length of time before being used in the solubility experiment. The composition of the solution was determined by volumetric titration.

For gases, N_2O, C_2H_4, and C_2H_2 were supplied from commercial cylinders with minimum purities 99.8, 99.6, and 99.9%, respectively, and confirmed by analyzing by gas chromatography.

The gas solubilities were measured by a volumetric technique. Systems studied were N_2O–MIPA and –DIPA, C_2H_4–MIPA and –DIPA, and C_2H_2–MEA, –DEA, –TEA, –MIPA, –DIPA, and –EDA. The apparatus and operating method were essentially the same as those employed in our previous study (*2*). Briefly, the principle of the apparatus used is that a measured volume of solute gas is brought in contact with a measured quantity of gas-free liquid, equilibrium is established by agitation, and the remaining volume of gas (undissolved) is measured. The change in the gas volume gives the amount dissolved in the liquid. Further details of solubility apparatus, procedure, and experimental conditions may be found in ref 2.

Table I. Solubility of Nitrous Oxide in Aqueous Solutions of Amines at 25 °C and 1 Atm of Pressure

Amine	*C*, mol/L	α
Mono(isopropyl alcohol)amine	0.0	0.5512
	0.255	0.5470
	0.501	0.5353
	0.761	0.5340
	1.194	0.5296
	1.695	0.5219
	2.282	0.4960
	2.928	0.4754
	3.400	0.4576
	3.736	0.4387
Di(isopropyl alcohol)amine	0.255	0.5386
	0.486	0.5330
	0.915	0.5145
	1.356	0.4968
	1.584	0.4775
	1.950	0.4512
	2.379	0.4144
	2.528	0.4091
	2.619	0.3883
	2.918	0.2947

Table II. Solubility of Ethylene in Aqueous Solutions of Amines at 25 °C and 1 Atm of Pressure

Amine	*C*, mol/L	α
Mono(isopropyl alcohol)amine	0.0	0.1111
	0.279	0.1145
	0.819	0.1155
	1.319	0.1145
	2.175	0.1124
	2.301	0.1123
	2.802	0.1122
	3.240	0.1100
Di(isopropyl alcohol)amine	0.236	0.1131
	0.290	0.1125
	0.550	0.1120
	1.048	0.1105
	1.467	0.1077
	2.127	0.1030
	2.982	0.1001

The diffusivity of N_2O in various aqueous solutions of amines (MEA, DEA, TEA, MIPA, DIPA, and EDA) was measured in a laminar liquid-jet apparatus. The laminar liquid-jet apparatus was the one which was previously described (*3*). The gas–liquid contact time ranged from 0.002 to 0.02 s by varying the jet length but keeping the liquid flow rate constant.

The viscosities of various aqueous solutions of amines were determined with the standard Ostwald viscometer with efflux time in excess of 100 s. Based on the viscosity of distilled water, the maximum error in the viscosity measurements was about 0.5%.

All the experiments were carried out at a constant temperature of 25 °C and 1 atm of pressure.

Results and Discussion

Tables I, II, and III present solubility data for N_2O–MIPA and –DIPA, C_2H_4–MIPA and –DIPA, and C_2H_2–MEA, –DEA, –TEA, –MIPA, –DIPA, and –EDA, respectively. Solubility data for

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Table III. Solubility of Acetylene in Aqueous Solutions of Amines at 25 °C and 1 Atm of Pressure

Amine	C, mol/L	α
Monoethanolamine	0.0	0.9413
	0.317	0.9608
	0.870	0.9677
	1.362	0.9735
	1.834	0.9770
	2.557	0.9802
	3.165	0.9812
Diethanolamine	0.445	0.9554
	0.975	0.9519
	1.478	0.9470
	1.813	0.9402
	2.238	0.9213
	2.898	0.9075
Triethanolamine	0.272	0.9645
	0.508	0.9574
	0.990	0.9419
	1.703	0.9334
	2.211	0.9264
	2.515	0.9226
	2.924	0.9127
Mono(isopropyl alcohol)amine	0.309	0.9661
	0.744	0.9541
	1.341	0.9503
	1.792	0.9417
	2.243	0.9347
	2.761	0.9267
	3.212	0.9195
Di(isopropyl alcohol)amine	0.283	0.9530
	0.555	0.9318
	0.985	0.8998
	1.383	0.8622
	1.844	0.8362
	2.494	0.8144
	3.223	0.7974
Ethylenediamine	0.495	0.9772
	0.833	0.9915
	1.315	1.0001
	1.886	0.9992
	2.355	1.0110
	2.450	1.0088
	3.271	1.0079

Table IV. Diffusivity of Nitrous Oxide in Aqueous Solutions of Amines at 25 °C

Amine	C, mol/L	10^5D, cm^2/s	μ/μ_w
Monoethanolamine	0.0	1.78	1.0
	0.731	1.74	1.12
	1.364	1.63	1.27
	2.023	1.46	1.46
	2.766	1.24	1.70
	3.361	1.15	1.92
Diethanolamine	0.498	1.66	1.23
	0.981	1.56	1.42
	1.922	1.40	2.10
	2.808	1.26	3.15
	3.457	1.04	4.31
Triethanolamine	0.497	1.70	1.24
	1.048	1.44	1.61
	1.596	1.23	2.16
	1.921	0.91	2.59
Mono(isopropyl alcohol)amine	0.477	1.54	1.14
	0.990	1.44	1.30
	1.467	1.34	1.51
	2.012	1.12	1.83
	2.746	1.07	2.40
Di(isopropyl alcohol)amine	0.396	1.54	1.20
	0.830	1.41	1.65
	1.107	1.20	1.99
	1.410	0.90	2.41
	1.663	0.77	2.83
Ethylenediamine	0.618	1.91	1.11
	1.373	1.67	1.31
	1.821	1.44	1.46
	2.350	1.30	1.63
	3.369	1.09	2.01

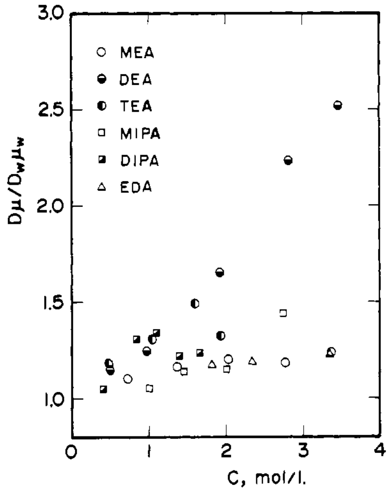

Figure 1. Dependence of $D\mu/D_w\mu_w$ on C.

N_2O-MEA, -DEA, -TEA, and -EDA, and C_2H_4-MEA, -DEA, -TEA, and -EDA were reported in our previous work (*2*). These results are given in terms of the Bunsen absorption coefficient. For the evaluation of the Bunsen absorption coefficient, the vapor pressure of amine-water solution at 25 °C is required. The vapor pressure for aqueous solution of amine under consideration was calculated by assuming that the vapor phase was an ideal mixture. For such amine concentrations, the estimated values of vapor pressure were very low as compared with the total pressure. Therefore, the uncertainty in vapor pressure is believed to have a negligible effect on gas solubility.

It was discussed in our previous work (*2*) for the solubility of N_2O and C_2H_4 in various aqueous solutions of amines (MEA, DEA, TEA and EDA) that the solubility data could not be correlated by some suitable correlations as for electrolyte solutions. For the present systems the solubility data also showed the same trends as that in previous work (*2*), i.e., "the salting out" of nitrous oxide by these amines differs from those for "the salting in" of ethylene and acetylene. Therefore, for the present systems too, the solubility data could not be expressed by some suitable equation. However, as suggested previously (*2*), the data as such are useful for evaluating the solubility of reacting gas through measurements with nonreacting gas, if the interaction parameters of reacting and nonreacting gases are almost the same.

The experiments on the absorption of N_2O in aqueous solutions of amines in the laminar liquid-jet apparatus give values for the liquid-phase diffusivity of N_2O. In the calculation of diffusivities, experimentally determined solubilities of N_2O in the same solutions were used. The results were listed in Table IV together with the viscosity of the solutions. The value of $D\mu/D_w\mu_w$ for various amine solutions was plotted against the amine concentration in Figure 1. The relationship between these two factors depends on the species of amine. Also, when the results for diffusivity were plotted as log (D/D_w) vs. log (μ_w/μ), these did not give a straight line. That is, the experimental results could not be correlated by an expression of the form of

$$D\mu^K = \text{constant} \tag{1}$$

The better way to estimate the diffusivity of CO_2 in aqueous solutions of amines may be

$$(D/D_w)_{CO_2} = (D/D_w)_{N_2O} \tag{2}$$

using the data for N_2O, as suggested by Joosten and Danckwerts (*1*).

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

Subscript

w	water

Literature Cited

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Solubility of Hydrogen Sulfide and Carbon Dioxide in a Diglycolamine Solution

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The solubility of H_2S and CO_2 individually in an aqueous Diglycolamine solution (60 wt % DGA) has been measured at 50 and 100 °C. Partial pressures of H_2S 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_2S 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_2S 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_2S–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_2S 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_2S 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_2S was calculated from the analysis

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