Solubility of N_2O in Aqueous Solutions of Diethanolamine at Different Temperatures

Noman M. Haimour

Department of Chemical Engineering, Faculty of Engineering and Technology, University of Jordan, Amman, Jordan

Solubilities of nitrous oxide were measured in aqueous solutions of diethanolamine (DEA) at 15, 20, 25, and 30 °C under atmospheric pressure. The data could be used to evaluate the solubility of CO_2 gas into DEA solutions with N_2O–CO_2 analogy.

Introduction

Solutions of amines are used extensively for acid-gas removal in gas sweetening processes (*1*). Among the most important amines used is diethanolamine (DEA). DEA has a wide application for refinery gases sweetening processes (*1*). Physical properties such as solubility and diffusivity of acid gases in amines are required in order to simulate acid-gas absorption in amines. The total solubilities of CO_2 in DEA solutions could be measured directly. However, it is the free-gas solubility that is needed to model the rate of absorption. The free-gas solubility cannot be measured directly because of the chemical reaction between CO_2 and DEA. For the time being, theoretical models cannot be used to predict the solubility of CO_2 into amines with reasonable accuracy. Since acid gases react chemically with amines in general, nonreacting gases with similar interaction parameters are used to determine such physical properties. Nitrous oxide was suggested by Clarke (*2*) to be used instead of CO_2 for determining solubility in amines. In view of the similarities of N_2O and CO_2 with regard to configuration, molecular volume, and electronic structure, Laddha et al. (*3*) examined the ratios of the solubility of N_2O and CO_2 in different alcohols that are somewhat similar in structure to DEA. Laddha et al. (*3*) found that the solubilities of CO_2 and N_2O in the different solutions examined have a constant ratio of 1.37. The N_2O analogy was used thereafter by many researchers (*4-7*) to predict the solubility of CO_2 in amine solutions.

Experimental solubility data for N_2O into different amines such as monoethanolamine (MEA), DEA, triethanolamine (TEA), and some less important amines are available at 25 °C only. In industry, the temperature in CO_2-amine absorber changes along with the absorber (*1*). In view of these facts, the solubilities of N_2O into DEA solutions over a range of temperature were measured.

In the present work, the solubilities of nitrous oxide in aqueous solutions of diethanolamine were measured by a volumetric method at 15, 20, 25, and 30 °C under atmospheric pressure.

Experimental Section

Aqueous diethanolamine solutions of different concentrations were prepared from distilled water and reagent-grade amine of purity >99%. The distilled water was degassed by boiling. The mixture was then kept in a tightly closed volumetric flask. The composition of the aqueous solutions was determined by volumetric titration with 0.5 N HCl aqueous solution and methyl orange as an indicator.

Nitrous oxide, for commercial use, was supplied from commercial cylinders with a minimum purity of 99.6%.

Table I. Solubility of N_2O in DEA Solutions at Different Temperatures

T, °C	concn, g-mol/L	C^*, g-mol/L	H, (L atm)/g-mol	α	L
15	0.0	0.0320	31.3	0.717	0.756
20	0.0	0.0290	34.6	0.647	0.695
25	0.0	0.0255	39.3	0.570	0.622
30	0.0	0.0230	43.5	0.513	0.569
15	1.039	0.0308	32.5	0.689	0.727
20	1.039	0.0282	35.5	0.632	0.678
25	1.039	0.0241	41.5	0.540	0.590
30	1.039	0.0202	49.5	0.453	0.503
15	2.077	0.0283	35.3	0.633	0.668
20	2.077	0.0268	37.3	0.601	0.645
25	2.077	0.0225	44.4	0.505	0.551
30	2.077	0.0174	57.5	0.390	0.432
15	3.116	0.0255	39.2	0.571	0.603
20	3.116	0.0246	40.7	0.550	0.591
25	3.116	0.0200	50.1	0.447	0.488
30	3.116	0.0143	70.1	0.320	0.355

The solubilities were measured with the apparatus shown schematically in Figure 1. The principle of the apparatus used is to bring a measured volume of solution in contact with a gas. Equilibrium is attained by stirring until no change in the volume of the gas is noticed. The change in the volume of the gas at constant temperature and pressure is equal to the volume of the gas absorbed. The apparatus is similar to that used by Haimour and Sandall (*7*) with the following modifications. Mixing was performed with use of a magnetic stirrer. The temperature of the whole unit was kept constant within 0.1 °C by a constant-temperature water bath with water circulating through a jacket enclosing the measuring branches. The system was first purged with saturated N_2O gas for a few minutes at constant temperature. Then, the inlet and outlet valves were closed. A degassed sample of DEA solution was injected into the absorption flask. After the solution was stirred for about 20 min, the levels of the mercury in the three branches were made equal and the change in the mercury level in the measuring branch was measured. This measured volume change is equal to the volume of the sample minus the volume of gas absorbed. The reliability of the apparatus was checked by measuring the solubilities of nitrous oxide in pure water. The results were in good agreement with those reported in the literature. The estimated maximum experimental error in the measured gas solubility is about ±2%.

Results and Discussion

The solubility was calculated in terms of the Bunsen coefficient α, Ostwald coefficient L, Henry's law constant H, and solubility C^*. The vapor pressure of the amine aqueous solutions was calculated assuming ideal mixtures. The vapor pressure of pure DEA at different temperatures was taken to be 0.01 mmHg (*1*). The vapor pressure of pure water at different temperatures was calculated with the Antoine equation given by (*8*)

$$\log P = A - B/(T + C)$$

with $A = 8.107\,65$, $B = 1750.286$, and $C = 235.0$. The experimental data are shown in Table I and Figure 2. Figure 2

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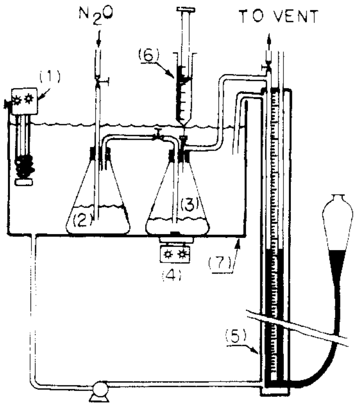

Figure 1. Solubility apparatus: (1) heater circulator; (2) saturation flask; (3) absorption flask; (4) magnetic stirrer; (5) measuring branches; (6) liquid sample injection; (7) water bath.

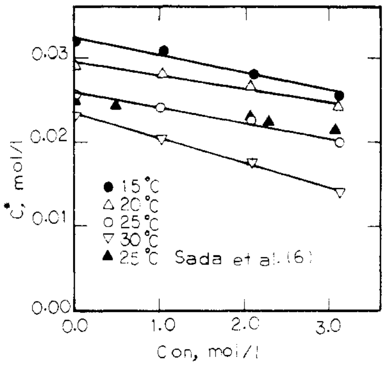

Figure 2. Solubility data plotted as C^* versus DEA concentration at different temperatures.

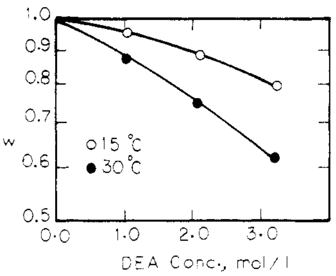

Figure 3. Effect of DEA concentration on solubility.

shows also data obtained by Sada et al. (*6*). The results are in good agreement with the results obtained in the work. The solubility changes linearly with amine concentration for the ranges of DEA concentration for the ranges of DEA concentration and temperatures studied. Table II shows the data obtained for N_2O in DEA at 25 °C by different authors (*1,5–7,9–11*). Good agreement is found. Figure 3 shows the data as log (α/α_w) versus C^* for 15 and 30 °C. The effect of temperature on the solubility is shown in Figure 4 as an Arrhenius type of plot. The results deviate from a linear relation for amine concentration greater than 2 g-mol/L. The solubility decreases with increasing temperature to a minimum value and then increases again. This trend was found by Hayduck and Laudie (*12*) for the solubilities of different gases in polar solvents. Hayduck and Laudie attributed that to the effect of association or hydrogen bonding in the solution. The data are useful for evaluating the solubility of CO_2 in DEA aqueous solutions at the temperature range examined with use of the N_2O analogy.

Table II. Solubility of N_2O in DEA Solutions at 25 °C

author	DEA concn, mol/L	H, (L atm)/mol
Yasunishi et al. (*9*)	0.0	41.2
Sada et al. (*6*)	0.0	40.6
Joosten and Danckwerts (*5*)	0.0	41.0
Sada and Kito (*10*)	0.0	41.2
Markham and Kobe (*11*)	0.0	41.6
Haimour and Sandall (*7*)	0.0	41.1
this work	0.0	39.3
Laddha et al. (*3*)	1.0	42.0
Sada et al. (*6*)	0.996	41.4
this work	1.04	41.5
Laddha et al. (*3*)	2.0	43.7
Sada et al. (*6*)	2.026	43.0
this work	2.077	44.4
Sada et al. (*6*)	3.081	45.6
this work	3.116	50.1

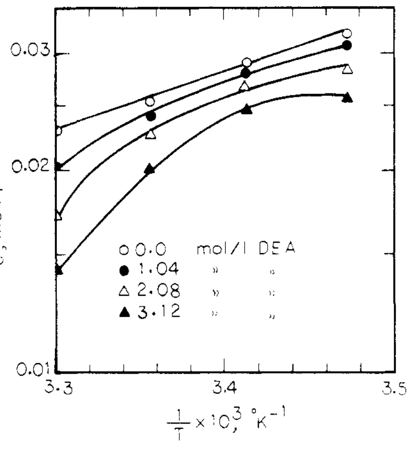

Figure 4. Solubility data plotted as ln C^* vs $1/T$.

Glossary

A	constant in Antoine equation
B	constant in Antoine equation
C	constant in Antoine equation
C^*	solubility of N_2O, g-mol/L
H	Henry's law constant, (L atm)/g-mol
L	Ostwald coefficient
α	Bunsen coefficient

Subscript

w	water

Registry No. DEA, 111-42-2; N_2O, 10024-97-2; CO_2, 124-38-9.

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