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Solubilities of Gases in Aqueous Solutions of Amine

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Solubilities of nitrous oxide and ethylene were measured in aqueous solutions of diethanolamine, triethanolamine, and ethylenediamine at 25 °C and 1 atm. The data are useful to evaluate the solubilities of reacting gases in the amine solutions under consideration from the solubilities of the corresponding nonreacting gases, if the interaction parameters of the reacting gases are quite close to those of the nonreacting gases.

Solutions of amines are widely encountered in gas–liquid contact operations as absorbents of acidic gases. The rational design of the gas–liquid contactor requires a knowledge of the solubility as well as the diffusivity of the gas in these solutions. However, for the time being it is impossible to estimate the solubility of the reacting gas from that of the nonreacting gas in the same solutions except in the case of electrolyte solutions (*4*). Furthermore, for aqueous solutions of weak electrolytes such as amines and organic acids, it should be emphasized that there are few experimental data. In view of these facts, the solubilities of nitrous oxide and ethylene in aqueous monoethanolamine solutions were measured and the possibility of correlation for the prediction of solubility was discussed in a previous paper (*5*). In another paper (*6*), the data on the solubilities of carbon dioxide and nitrous oxide in aqueous solutions of weak acids were reported and correlated in terms of the hyperbolic equation proposed by Markham and Kobe (*3*).

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

Experimental Section

Aqueous solutions of amines were prepared from distilled water and reagent grade amines of guaranteed purity. The composition of the aqueous solutions of amine was determined by volumetric titration. The solutions were thoroughly degassed before being used in the experiment as described in a previous paper (*4*).

For gases, nitrous oxide and ethylene of high purity were supplied from commercial cylinders with minimum purities of 99.8 and 99.6%, respectively, and confirmed by analyzing by gas chromatograph.

The solubilities were measured with the same apparatus as described in our previous papers (*4–6*). The apparatus and technique employed were discussed in detail in an early paper (*4*). The reliability of the apparatus was checked by measuring the solubilities of nitrous oxide, ethylene, and carbon dioxide in pure water. These measured values (in pure water) were in excellent agreement with those reported in the literature. The accuracy of the experiments was within ±1.0%.

The working temperature was 25 ± 0.01 °C and kept constant by a water bath.

Results and Discussion

The vapor pressure of the amine–water solutions at 25 °C is required for the calculation of the solubility. The vapor pressure for amine–water solutions was calculated by assuming that the vapor phase was an ideal mixture.

The solubility data are shown in Table I for nitrous oxide and in Table II for ethylene. The solubilities are expressed in terms of the Bunsen coefficient. The Bunsen coefficient is defined as the volume of gas, reduced to 0 °C and 760 mm pressure of mercury, which is absorbed by the unit volume of solvent (at the temperature of the measurement) under a gas pressure of 760 mm.

For nitrous oxide–monoethanolamine and ethylene–monoethanolamine systems, Sada and Kito (*5*) presented the results in terms of $\log (\alpha/\alpha_w)$ vs. concentration (C), as in electrolyte solutions (*4*). For both systems, reasonable straight lines were found which held good up to a concentration of 3 M, and the contribution parameter for the amine was evaluated by a modified empirical Setschenow equation (*7*),

$$\log (\alpha/\alpha_w) = (x_a + x_g)C \qquad (1)$$

The results for the present systems are also shown in graphical form in Figure 1 in the same manner as in previous papers (*4–6*), to evaluate the contribution parameters for the amines, if possible. In this figure, the dependence of $\log (\alpha/\alpha_w)$ (the negative logarithm of the activity coefficient of the gaseous species) on the concentration of amine is given. As can be seen from the figure, these plots cannot be correlated by straight lines as in monoethanolamine systems, even in moderately dilute solutions of the amines. The results for the "salting out" of nitrous oxide by these amines differ markedly from those for the "salting in" of ethylene. It was found that salts of both large ions and large cations usually cause salting in and, in addition, the salting in is increased as the dipole moment of the molecule increases. Anyhow, at present, observed salt effects cannot be interpreted from existing knowledge on salt effects and are not in line with the above predictions. In general, the activity coefficient of any solute in solution is a function of all solute species present. At a given temperature $\log (\alpha/\alpha_w)$ can be expressed by a power series in the concentrations of all solute species (*2*). In reality, eq 1 is obtained by retaining only the first term in the power series. The results in Figure 1 may be fitted by the power series function with several terms, but the meanings of the coefficients in the correlation obtained thus are not clear. The

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

Amine	C (mol L^{-1})	α (-)
Diethanolamine (DEA)	0.0	0.5512
	0.449	0.5480
	0.996	0.5406
	2.026	0.5205
	2.313	0.5114
	3.081	0.4918
Triethanolamine (TEA)	0.628	0.4997
	0.874	0.4774
	1.293	0.4327
	2.160	0.3825
	2.912	0.3170
Ethylenediamine (EDA)	0.805	0.5276
	1.473	0.5106
	1.871	0.4936
	2.267	0.4728
	2.371	0.4687
	2.738	0.4415
	3.133	0.4211

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

Amine	C (mol L^{-1})	α (-)
Diethanolamine (DEA)	0.0	0.1111
	0.949	0.1131
	1.540	0.1141
	2.038	0.1156
	2.442	0.1136
	2.895	0.1121
	2.977	0.1115
	3.123	0.1104
Triethanolamine (TEA)	0.193	0.1131
	0.443	0.1138
	0.599	0.1156
	0.707	0.1161
	0.889	0.1165
	1.148	0.1163
	1.557	0.1150
	2.277	0.1100
	2.624	0.1053
Ethylenediamine (EDA)	0.561	0.1153
	1.049	0.1184
	1.596	0.1196
	2.023	0.1187
	2.091	0.1199
	2.890	0.1186
	2.929	0.1185
	3.464	0.1145
	3.683	0.1124

solubility of other gases in the same solutions cannot be predicted by this correlation. However, the data as such are useful to evaluate the solubilities of the reacting gases from the corresponding nonreacting gases in the amine solution under consideration, if the reacting gas has almost the same interaction parameters as suggested by Clarke (*1*). For instance, solubility of carbon dioxide in aqueous amine solution may be evaluated from the corresponding values of nitrous oxide by the following relationship,

$$\log (\alpha/\alpha_w)_{CO_2} = \log (\alpha/\alpha_w)_{N_2O} \qquad (2)$$

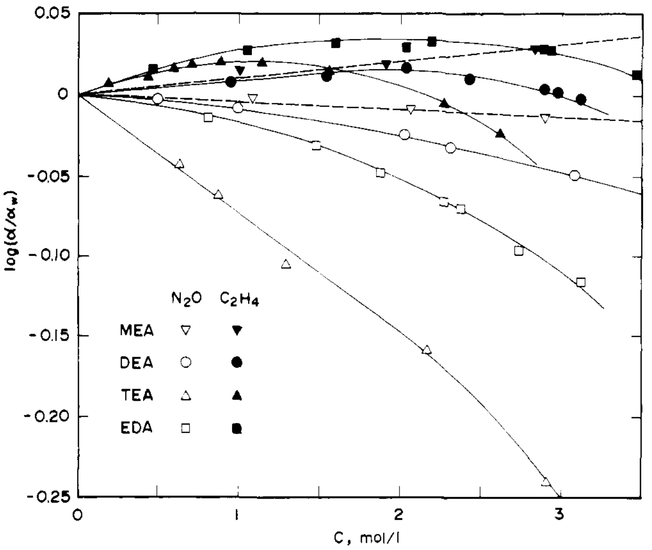

Figure 1. Solubilities of N_2O and C_2H_4 in aqueous solutions of amines at 25 °C and 1 atm. Broken straight lines represent MEA and are taken from previous work (*5*).

Glossary

C	concentration of species, mol L^{-1}
α	Bunsen absorption coefficient, cm^3 of gas/cm^3 of solution

Subscripts

a	amine
g	gas
w	water

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