Solubility and Diffusivity of Nitrous Oxide in Equimolar Potassium Carbonate–Potassium Bicarbonate Solutions at 25°C and 1 Atm

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Data are presented on the solubility and diffusivity of nitrous oxide in equimolar potassium carbonate–potassium bicarbonate solutions at 25°C and 1 atm. The relationship between the viscosity of the solution and the diffusivity of N_2O is obtained. Ways to estimate the solubility and diffusivity of carbon dioxide in the solutions from the data for N_2O are indicated.

Solutions of potassium carbonate–potassium bicarbonate are widely used in industry as absorbents for carbon dioxide. The knowledge of the solubility and the diffusivity of the gas in the absorbent is important in the design of absorption equipment. Carbon dioxide reacts in carbonate–bicarbonate solutions. This rules out the experimental determination of the solubility of CO_2 in these solutions by conventional means. We present data on the solubility and diffusivity of nitrous oxide in equimolar potassium carbonate–potassium bicarbonate solutions of various strengths. The solubilities and diffusivities of N_2O can be used to estimate fairly reliably the corresponding data for CO_2.

The solubility of N_2O was measured at constant atmospheric pressure, the diffusivity by means of a laminar jet apparatus.

THEORY

Solubility of Gases in Aqueous Electrolyte Solutions. The influence of the presence of electrolytes in a liquid on the solubility of a gas in that liquid can be expressed by the ratio He/He$_o$, where He$_o$ and He are the Henry coefficients of the gas in the pure liquid and in the electrolyte solution, respectively.

Most workers found a proportionality between log He/He$_o$, and the electrolyte concentration (*5*, *13*), and theories for the proportionality constant have been reviewed (*2*, *9*).

Van Krevelen and Hoftijzer (*14*) observed that the solubility of gas in electrolyte solutions is related to the ionic strength of the solution by

$$\log \frac{\text{He}}{\text{He}_o} = KI \tag{1}$$

and that the value of K is the sum of contributions referring to the species of positive and negative ions present and to the species of gas

$$K = K_+ + K_- + K_G \tag{2}$$

Barrett (*1*) compiled the value of K_+, K_-, and K_G for various ions and gases. These data are readily available in Danckwerts' book (*3*).

In mixed electrolyte solutions it may be supposed that the gas solubility is given by an expression of the form

$$\log \frac{\text{He}}{\text{He}_o} = \sum K_i I_i \tag{3}$$

where I_i is the ionic strength attributable to species i and K_i the value of K for that species. No previous experimental data seem to be available to test Equation 3.

Diffusion of Gases in Electrolyte Solutions. The prediction and correlation of diffusion coefficients of dissolved gases in liquids have been developed from either hydrodynamic or activated state theories. From simple hydrodynamic theory it follows that $D\eta$ equals a constant at constant temperature. The experimental results available usually fit better to an expression of the form

$$D\eta^\alpha = \text{constant} \tag{4}$$

In the activated state theories, diffusion (and also viscous flow) is supposed to occur by molecules jumping from one equilibrium position in the liquid lattice to an adjoining site, the move requiring a free energy of activation, ΔG. The presence of ions in the liquid causes changes in the activation energy. Ratcliff and Holdcroft (*11*) concluded that these changes are proportional to

$$y = \sum x_i/(1 - \sum x_i + \sum n_i x_i) \tag{5}$$

where x_i is the mole fraction of electrolyte i, which dissociates in solution into n_i particles.

Under some simplifying assumptions it can be deduced that the variation in diffusivity with y is given by

$$\frac{D}{D_o} = \exp(-Ay) \tag{6}$$

A similar expression is obtained for the viscosity of the solution

$$\frac{\eta_o}{\eta} = \exp(-By) \tag{7}$$

EXPERIMENTAL

The gas solubilities were determined in the same way as by Markham and Kobe (*10*). The accuracy of the experiments is probably better than 1.5%.

The diffusivities were determined in a laminar jet apparatus. The apparatus combined various features of the designs of Scriven and Pigford (*12*) and Kramers (*8*).

The composition of the potassium carbonate–bicarbonate solutions was determined by titration with hydrochloric acid. The first end point was determined by potentiometric titration, the second with methyl orange as an indicator.

RESULTS AND DISCUSSION

The procedure of determining the solubility of N_2O was checked by measuring the solubility of N_2O in pure water.

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Table I. Experimental Results

$[K_2CO_3]$ and $[KHCO_3]$, g-mol/l.	I, g-ion/l.	y	1/He, g-mol/cm³ atm × 10^5 ±1.5%	D_{N_2O}, cm²/sec × 10^5	η/η_o
0.000	0.00	0.00	2.44	1.92 ± 0.08	1.00
0.095	0.38	0.0034	2.21	1.88 ± 0.08	1.025
0.165	0.66	0.0059	2.06	1.84 ± 0.08	1.050
0.30	1.20	0.0109	1.82	1.77 ± 0.08	1.104
0.60	2.40	0.0216	1.37	1.55 ± 0.07	1.280
0.89	3.56	0.0325	1.00	1.37 ± 0.07	1.497
1.00	4.00	0.0370	0.93	1.33 ± 0.07	1.574
1.25	5.00	0.0464	0.75	1.18 ± 0.07	1.812

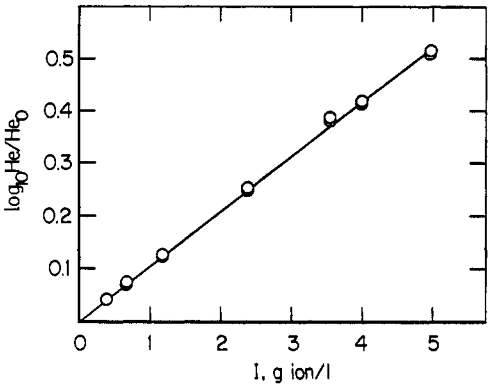

Figure 1. Salting-out of N_2O from equimolar potassium carbonate–bicarbonate solutions

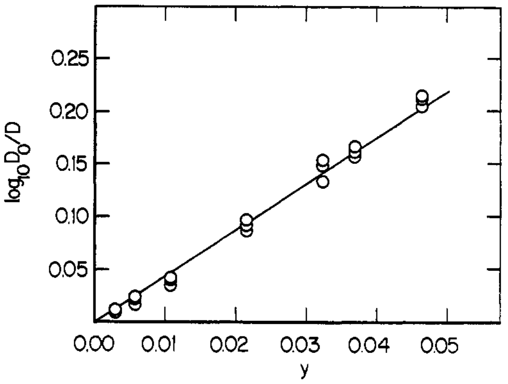

Figure 2. Dependence of $\log_{10} D_o/D$ on y

The results agreed within 0.5% with the result of Geffcken (*6*).

The results of the determinations of the solubility of N_2O in the equimolar potassium carbonate-bicarbonate solutions are given in Table I. A plot of log He/He$_o$ against the ionic strength of the solution gives a straight line of slope 0.105 ± 0.001 l./g-ion (Figure 1). When Barrett's (*1*) data are used and if we assume that Equation 3 is valid for mixed electrolyte solutions, the difference between the calculated and experimental value of He/He$_o$ is less than 2.5 I%. The accuracy in Barrett's data is 2 I%. The agreement between the observed and predicted values seems good enough to recommend Equation 3 for engineering purposes.

The ideality of the jet was tested by absorbing pure water-saturated CO_2 in water at 25°C. When we used the value of 3.39×10^{-5} g-mol/cm³ atm for the solubility of CO_2 in water (*11*), the experimental value of the diffusion coefficient of CO_2 was 1.92 ± 0.01 10^{-5} cm²/sec, which is in excellent agreement with the result of Davidson and Cullen (*4*). Thus the jet could be supposed to behave very close to ideal.

The experiments on the absorption of N_2O in the electrolyte solutions in the laminar jet give, together with the results of the solubility determinations, values for the diffusivity of nitrous oxide in the solutions. The results are reported in Table I, together with the viscosity of the solutions. The diffusivity of N_2O in water was 1.92 ± 0.08 × 10^{-5} cm²/sec. No data for the diffusion coefficient of N_2O in water at 25°C could be found in the literature.

The value of $\log_{10} D_o/D$ of the various solutions was plotted against the value of y. The data fall reasonably well on a straight line, of slope 4.40 ± 0.13; hence the value of A in Equation 6 is 10.1 ± 0.3 (Figure 2).

A plot of log D/D_o vs. log η_o/η resulted in a reasonably straight line of slope 0.82. Hence the value of α in Equation 4 is 0.82. Ratcliff and Holdcroft (*11*) analyzed their own data and data from the literature and found a value of 0.637 for α. However, their value of α was an average of the value of α for various electrolytes. The activated state theory predictions for D/D_o and η_o/η are given by Equations 6 and 7. It is clear that the slope of a log D/D_o vs. log η_o/η plot is the same for all electrolytes only if invariably $A = B$—i.e., if all electrolytes influence the free energy of activation for diffusion and viscous flow to the same extent. The change in free energy of activation for diffusion owing to the presence of electrolyte is related to the difference between the ion-solute and water-solute interactions and for viscous flow to the difference in ion-water and water-water interactions. The differences in slope of plots of log D/D_o vs. log η_o/η for various electrolytes are therefore not surprising. The value of α probably has to be determined for each electrolyte separately. For the particular electrolyte mixture used in this work the best value of α is 0.82. The available data on the diffusivity of gases in electrolyte solutions show that α is smaller than unity for almost all electrolytes tested. The perturbation, due to the presence of electrolyte, of the free energy of activation for viscous flow is apparently larger than that for diffusion.

Prediction of Solubility and Diffusivity of CO_2 from the N_2O Data. The solubility of CO_2 in the solutions can be found using the values of K_G for CO_2 and N_2O at 25°C given by Danckwerts (*3*) and the experimental slope of the $\log_{10}$ He/He$_o$ vs. I plot for N_2O (Figure 1). The CO_2 solubility in the solutions is then given by

$$\log \frac{\text{He}}{\text{He}_o} = (0.105 - K_{N_2O} + K_{CO_2})I = 0.086\, I$$

Gubbins et al. (*7*) found that the change in D/D_o produced by a given electrolyte is little affected by the species of diffusant. Consequently, the diffusivity of CO_2 in a particular solution can be estimated from

$$\left[\frac{D_{\text{soln}}}{D_o}\right]_{N_2O} = \left[\frac{D_{\text{soln}}}{D_o}\right]_{CO_2}$$

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NOMENCLATURE

A = constant in Equation 6
B = constant in Equation 7
D = diffusion coefficient, cm^2/sec
ΔG = free energy of activation, cal/g-mol
He = Henry coefficient, cm^3 atm/g-mol
I = ionic strength, g-ion/l.
K = salting-out parameter, l./g-ion
x = mole fraction
y = variable defined in Equation 5

Greek Letters

α = power in Equation 4
η = viscosity, g/cm sec

Subscripts

o = pure water
i = species i

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Isothermal Vapor-Liquid Equilibria in Binary Mixtures Containing Alkanes and Ethers

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Vapor-liquid equilibrium data were determined at 90°C for the binary systems di-*n*-propyl ether/*n*-octane, di-*n*-propyl ether/*n*-nonane, and di-*n*-butyl ether/*n*-heptane using a modified Gillespie still. These systems all exhibit nearly ideal behavior.

Experimental vapor-liquid equilibria were determined at 90°C for three binary mixtures containing ethers and alkanes using a modified Gillespie still. The still and experimental technique have been described elsewhere (*3*).

n-Heptane supplied by Eastman Organic Chemicals was further purified by redistilling in a packed column and collecting a fraction with physical properties reproducing literature values. Research-grade *n*-octane and *n*-nonane supplied by the Phillips Petroleum Co. and ethers from Aldrich Chemicals, were directly used without further purification. The physical properties of the chemicals used are listed in Table I.

Temperature was measured by a copper-constantan thermocouple and a Leeds and Northrup type K3 potentiometer and is believed accurate to ±0.05°C. Pressure was measured by a mercury manometer and cathetometer, and was controlled by a Cartesian manostat to within about 0.2% of the still pressure. Mixture compositions were determined by refractive index using a Carl Zeiss refractometer. The refractive index was measured against sodium light, and the temperature of the prisms was maintained at 25 ± 0.02°C by water circulated from a constant-temperature bath. A typical refractive index–composition plot is shown in Figure 1; the full calibration data are available elsewhere (*2*).

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Table I. Physical Properties of Pure Compounds at 25°C

Compound	Refractive index		Density		Normal boiling point, °C	
	This work	Lit.	This work	Lit.	This work	Lit.
n-Heptane (*1*)	1.3850	1.3851	0.6792	0.6795	98.4	98.4
n-Octane (*1*)	1.3949	1.3950	0.6982	0.6982	125.4	125.6
n-Nonane (*1*)	1.4028	1.4030	0.7132	0.7138	151.0	150.8
Di-*n*-propyl ether (*4*)	1.3775	[a]	0.7375/30°C	0.7373/30°C	91.0	90.5
Di-*n*-butyl ether (*4*)	1.3960	[a]	0.7600/30°C	0.7597/30°C	141.5	142.4

Numbers in parentheses give references for literature values.
[a] Not available at a suitable temperature.