The densities of binary mixtures were used to calculate the excess volumes of the two systems. Numerical values are listed in Table III and are shown in Figure 2. Excess volumes were also expressed by the right-hand side of Equation 5, and this equation was used to generate the solid lines in Figure 2. For the acetone-cyclohexane system, the constants C_1, C_2, and C_3 are 4.348 ± 0.009, −0.103 ± 0.024, and 0.623 ± 0.066, respectively, with a standard deviation of 0.005 $cm^3\ mol^{-1}$. The excess volume at $x_1 = 0.5$ is $V^E_{0.5} = 1.08\ cm^3\ mol^{-1}$. For the acetone-isopropanol system, only one constant was required. Here, $C_1 = 1.271 \pm 0.019$ with a standard deviation of 0.012 $cm^3\ mol^{-1}$. At $x_1 = 0.5$, $V^E_{0.5} = 0.32\ cm^3\ mol^{-1}$. The data for the acetone-isopropanol system are compared in Figure 2 with those calculated from the equation given by Thacker and Rowlinson (*12*).

Nomenclature

A, B, C = constants in Equation 1
B_{ii} = second virial coefficient of pure component i, $cm^3\ mol^{-1}$
B_{12} = cross virial coefficient, $cm^3\ mol^{-1}$
C_1, C_2, C_3 = coefficients in Redlich-Kister Equation 5, $J\ mol^{-1}$ for G^E and $cm^3\ mol^{-1}$ for V^E
G^E = molar excess Gibbs free energy, $J\ mol^{-1}$
P = total vapor pressure, mm Hg
P_i° = vapor pressure of pure component i, mm Hg
R = gas constant
T = absolute temperature, K
V^E = molar excess volume, $cm^3\ mol^{-1}$
v_i° = molar volume of pure component, $cm^3\ mol^{-1}$
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase

Greek Letters

γ_i = activity coefficient of component i in liquid phase
δ = difference of virial coefficients as defined by Equation 3, $cm^3\ mol^{-1}$
η_D = refractive index of the mixture
η_{D_i} = refractive index of pure component i

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Solubility of Nitrous Oxide in Sodium Carbonate-Sodium Bicarbonate Solutions at 25°C and 1 Atm

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Solubility of nitrous oxide in sodium carbonate-sodium bicarbonate solutions of various carbonation ratios and of various ionic strengths was measured at 25°C and 1 atm. The experimental results were analyzed on the basis of the method proposed by Danckwerts and Gillham for the solubility of the gas in mixed electrolyte solutions.

Aqueous solutions of alkali carbonate-bicarbonate are widely used in the chemical industry for the removal of the acid gases, such as carbon dioxide, hydrogen sulfide, sulfur dioxide, and chlorine. Therefore, knowledge of the gas solubility in these solutions is important in the rational design of absorption equipment. Since the acid gas reacts in carbonate-bicarbonate solutions, it is not possible to measure the gas solubility by conventional methods. However, in the case of electrolyte solutions, the solubility of the reacting gas can be estimated from that of the nonreacting gas in the same solutions by the method of van Krevelen and Hoftijzer (*10*). In this paper the data on the solubility of nitrous oxide in sodium carbonate-sodium bicarbonate solutions of various compositions and of various ionic strengths are reported.

Theory

The physical solubility of a gas in aqueous electrolyte solutions can be correlated by the following expression:

$$\log (A^*/A_w^*) = -k_s I \tag{1}$$

where A^* and A_w^* are the physical solubilities in the solution and in water, respectively, and I is the ionic strength of the solution defined by

$$I = \tfrac{1}{2}\Sigma c_i z_i^2 \tag{2}$$

c_i being the concentration of ions of valency z_i. The coefficient k_s is the salting-out parameter and is expressed as the sum of the contributions owing to the positive and negative ions present and the dissolved gas (*10*):

$$k_s = i_+ + i_- + i_g \tag{3}$$

The values of i for various ions and gases were reported by van Krevelen and Hoftijzer (*10*), Barrett (*1*), and Onda et al. (*8*). However, the value of i_- for bicarbonate ion has not been known.

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For estimating the gas solubility in mixed electrolyte solutions, Danckwerts and Gillham (3) have assumed that the following expressions may be used:

$$\log (A^*/A_w^*) = -K_s I \tag{4}$$

$$K_s I = k_{s1} I_1 + k_{s2} I_2 + \ldots \tag{5}$$

where I_1, I_2, etc., are the contributions to the ionic strength of the individual electrolytes; k_{s1}, k_{s2}, etc., are the values of k_s for that electrolyte; and K_s is the overall salting-out parameter for mixed electrolytes.

Recent work of Onda et al. (9) on the solubilities of carbon dioxide, ethylene, and acetylene in mixed electrolyte solutions indicates that the measured values of the gas solubility agree well with the values predicted by using Equations 4 and 5. For the present system, Equation 5 can be written as:

$$K_s = \frac{k_{s1} R + 3\,k_{s2}}{R + 3} \tag{6}$$

where R is the carbonation ratio of the sodium carbonate-bicarbonate solution, i.e., the ratio of the concentration of bicarbonate ion to that of carbonate ion, and k_{s1} and k_{s2} are the values of k_s corresponding to sodium bicarbonate and sodium carbonate solutions, respectively. Thus, if Equation 6 is valid for the present system, a plot of the values of $K_s(R + 3)$ against the carbonation ratio of the solution, R, should give a straight line whose slope is k_{s1} and whose intercept at $R = 0$ is $3\,k_{s2}$.

Experimental

The gas solubility was measured by the gas volumetric method of Markham and Kobe (7). The apparatus was similar to that used by Onda et al. (8). Nitrous oxide was taken from a commercial cylinder, and its purity was above 99.8%. The sodium carbonate-bicarbonate solutions were prepared with analytical grade reagents and boiled distilled water. The composition of the solutions was determined by the chemical method used by Danckwerts and Kennedy (4). All the measurements were carried out at 25°C and atmospheric pressure.

Results and Discussion

The procedure of determining the gas solubility was checked by the measurement of the solubility of nitrous oxide in pure water. The measured value of the solubility agreed within 0.5% with the reported value in the literature (5).

The results on the solubility of nitrous oxide in sodium carbonate-bicarbonate solutions are given in Table I. Figure 1 shows a semilogarithmic plot of the ratio of the gas solubility in the solution to that in water, A^*/A_w^*, against the ionic strength I for each solution with a given value of the carbonation ratio R. Good straight lines are obtained, and this indicates that Equation 4 is satisfactory. The values of K_s were calculated from the slopes of the straight lines in this figure and are given in Table II.

Figure 2 shows a plot of the value of $K_s(R + 3)$ against the carbonation ratio, R, of the solution. Data points fall on a straight line (solid line), indicating that Equation 6 is valid for the present system. The values of k_{s1} and k_{s2} were calculated from the slope and the intercept of the straight line and were 0.214 and 0.112, respectively. From these values of k_{s1} and k_{s2}, the values of i_- for bicarbonate and carbonate ions were estimated as

$$i_-(HCO_3^-) = 0.119;\ i_-(CO_3^{2-}) = 0.017$$

by use of the values of $i_g(N_2O)$ and $i_+(Na^+)$ given by van Krevelen and Hoftijzer (10). The value of $i_-(CO_3^{2-})$ obtained in the present work is in reasonable agreement with van Krevelen and Hoftijzer's data (10).

The chain line in Figure 2 represents the predicted values of K_s calculated from Equation 6 by use of Barrett's data (1) for $i_g(N_2O)$, $i_+(Na^+)$, and $i_-(CO_3^{2-})$ and assuming that $i_-(HCO_3^-) = i_-(CO_3^{2-})$ as proposed by Danckwerts (2). The predicted values are in good agreement with the observed values at low carbonation ratios, but with the increasing of R, they become considerably lower than the observed values. The dotted line in Figure 2 shows the values of K_s predicted by using Onda et al.'s data (8) for $i_g(N_2O)$, $i_+(Na^+)$, and $i_-(CO_3^{2-})$ and the value of $i_-(HCO_3^-)$ estimated by Onda et al. (9). The agreement between the predicted and observed values of K_s is good at high values of R, but at lower values of R,

Table I. Solubility of N_2O in Aqueous Na_2CO_3–$NaHCO_3$ Solutions at 25°C and 1 Atm

$[Na_2CO_3]$, g-mol/l.	$[NaHCO_3]$, g-mol/l.	R	I, g-ion/l.	$A^* \times 10^2$, g-mol/l.
0	0	...	0	2.356
0.329	0	0	0.987	1.753
0.661	0	0	1.98	1.296
0.992	0	0	2.98	1.064
1.33	0	0	3.98	0.7750
1.66	0	0	4.97	0.6404
0.309	0.0630	0.204	0.990	1.729
0.621	0.125	0.201	1.99	1.389
0.927	0.183	0.197	2.96	1.036
1.24	0.249	0.201	3.97	0.7923
1.54	0.310	0.201	4.93	0.6314
0.198	0.200	1.01	0.794	1.777
0.395	0.398	1.01	1.58	1.429
0.600	0.587	0.978	2.39	1.180
0.783	0.755	0.964	3.10	0.9568
0.0990	0.199	2.01	0.496	1.917
0.197	0.402	2.04	0.993	1.668
0.301	0.593	1.97	1.50	1.441
0.395	0.801	2.03	1.99	1.186
0.0374	0.187	5.00	0.299	2.024
0.0740	0.373	5.04	0.595	1.807
0.113	0.553	4.89	0.892	1.665
0.151	0.736	4.87	1.19	1.439
0.190	0.927	4.88	1.50	1.267

Table II. Overall Salting-Out Parameter for Solubility of N_2O in Aqueous Na_2CO_3–$NaHCO_3$ Solutions at 25°C and 1 Atm

R	K_s, l./g-ion
0	0.118
0.2	0.118
1	0.129
2	0.149
5	0.181

Table III. Values of i_+, i_-, and i_g at 25°C Used for Prediction of A^*/A_w^* Values in Figures 3 and 4

Positive ion	i_+, l./g-ion	Negative ion	i_-, l./g-ion	Solute gas	i_g, l./g-mol
Na^+	0.094[a]	HCO_3^-	0.119[b]	N_2O	0.001[a]
K^+	0.071[a]	CO_3^{2-}	0.017[b]	C_2H_4	0.016[c]

[a] (10). [b] Present work. [c] (9).

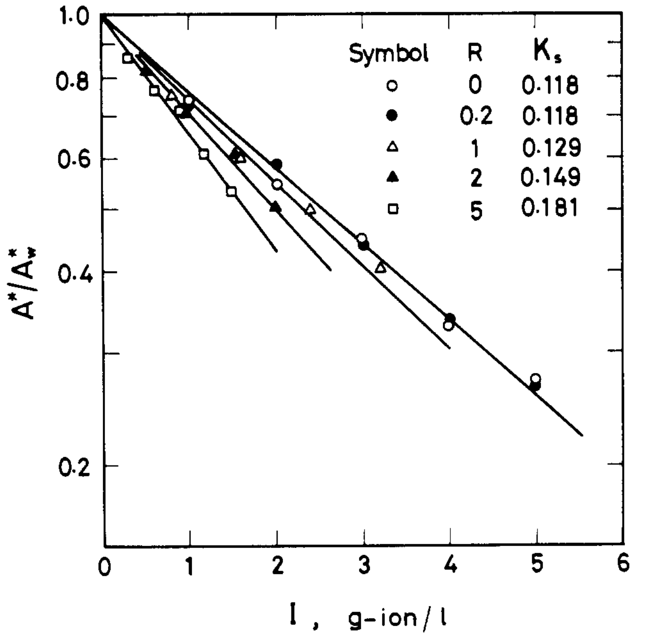

Figure 1. Solubility of N_2O in Na_2CO_3-$NaHCO_3$ solutions at 25°C and 1 atm

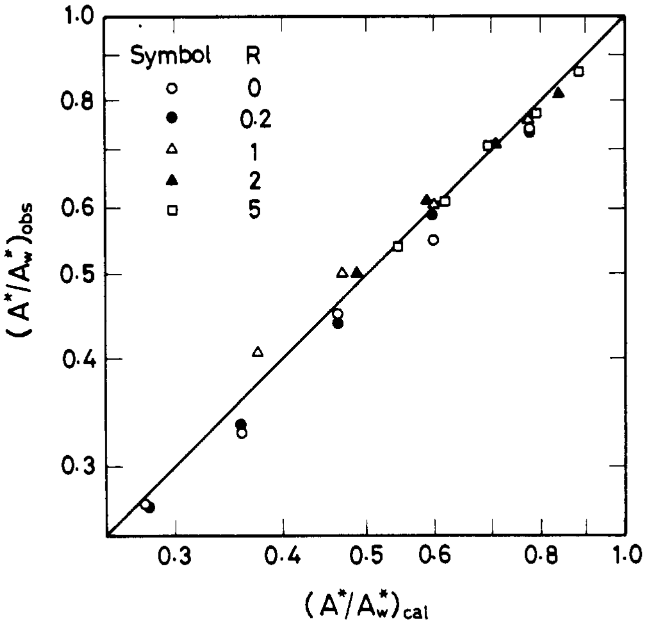

Figure 3. Comparison of observed and calculated solubilities (present data)

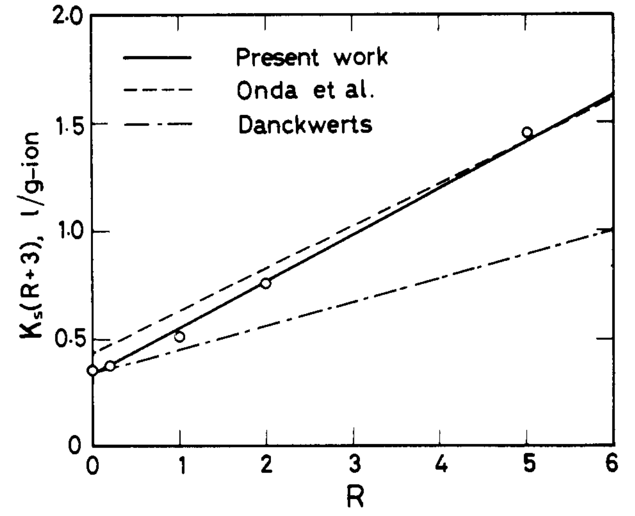

Figure 2. Effect of carbonation ratio of solution on overall salting-out parameter

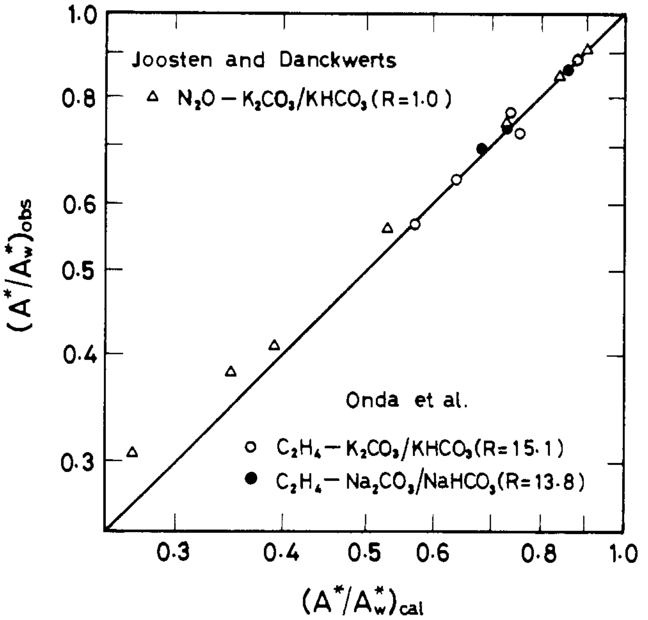

Figure 4. Comparison of observed and calculated solubilities [data of Onda et al. (*9*) and Joosten and Danckwerts (*6*)]

the predicted values are slightly higher than the observed values.

In Figure 3 the predicted and observed values of A^*/A_w^* are plotted and compared. The predicted values were calculated from Equation 6 by use of the values of $i_-(CO_3{}^{2-})$ and $i_-(HCO_3{}^-)$ obtained in this work and van Krevelen and Hoftijzer's data (*10*) which are given in Table III. As can be seen in Figure 3, the observed values are in good agreement with the predicted values, the average deviation being 4.0%.

Figure 4 shows the comparison of the observed values of A^*/A_w^* for the systems ethylene-sodium carbonate-bicarbonate (R = 13.8) and ethylene-potassium carbonate-bicarbonate (R = 15.1) obtained by Onda et al. (*9*) and that for the system nitrous oxide-potassium carbonate-bicarbonate (R = 1) obtained by Joosten and Danckwerts (*6*) with the predicted values. In calculating the predicted values, the present values of $i_-(CO_3{}^{2-})$ and $i_-(HCO_3{}^-)$, Onda et al.'s value (*9*) of $i_g(C_2H_4)$, and van Krevelen and Hoftijzer's values (*10*) of $i_g(N_2O)$, $i_+(Na^+)$, and $i_+(K^+)$ were used. These values of i_+, i_-, and i_g are also shown in Table III. The agreement between the predicted and observed values is good, the average deviations of Onda et al.'s data for ethylene and Joosten and Danckwerts' data for nitrous oxide being 1.8 and 4.9%, respectively.

Nomenclature

A^* = solubility of gas in electrolyte solution, g-mol/l.
A_w^* = solubility of gas in water, g-mol/l.
c_i = concentration of ions in solution, g-ion/l.
i_+, i_-, i_g = contributions of positive ion, negative ion, and dissolved gas, l./g-ion or l./g-mol
I = ionic strength of solution defined by Equation 2, g-ion/l.
k_s = salting-out parameter for single electrolyte, l./g-ion
K_s = overall salting-out parameter for mixed electrolytes, l./g-ion
R = carbonation ratio, ratio of concentration of bicarbonate ion to that of carbonate ion in solution
z_i = valency of ions

Subscripts

1 = electrolyte 1 ($NaHCO_3$)
2 = electrolyte 2 (Na_2CO_3)

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Phase-Equilibria Behavior of System Carbon Dioxide-*n*-Decane at Low Temperatures

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Pressure, composition, and molar volume data of the two coexisting liquid phases for the system CO_2-*n*-decane are presented as a function of temperature along the three-phase (L_1-L_2-V) curve. Also, pressure, composition, and molar volume data on the S_1-L_1-V curve and the *P-T* profile of the S_1-L_2-V curve are presented. The termination points of these loci are located and characterized.

Although extensive vapor-liquid equilibria information is available on the binary system CO_2-*n*-decane as reported by Reamer and Sage (*7*), to our knowledge no information is available on its partial miscibility behavior. For this reason, a study has been completed of the above system describing the partial miscibility regimes. Our study of the system CO_2-*n*-decane involves the P-$\bar{V}$-T-X equilibrium data on the S_1-L_1-V and L_1-L_2-V loci, *P-T* profile of the S_1-L_2-V locus, and the invariant points such as the *Q*-points, as well as the upper critical solution temperature of L_1 and L_2.

The partial miscibility of various CO_2-normal alkane binary systems has been studied by several different workers: Im and Kurata (*5*), CO_2-*n*-heptane; Stewart and Nielsen (*9*), CO_2-*n*-tetradecane and CO_2-*n*-hexadecane; Schneider (*8*), CO_2-*n*-octane, CO_2-*n*-undecane, CO_2-*n*-tridecane, and CO_2-*n*-hexadecane; Francis (*2*), CO_2-*n*-tetradecane, CO_2-*n*-hexadecane, CO_2-*n*-octadecane, and CO_2-*n*-eicosane; Huie (*3*) and Huie et al. (*4*) CO_2-*n*-eicosane. However, only Huie has reported detailed P-$\bar{V}$-T-X information over the entire immiscibility range for the system he studied. Kurata has reported *P-T-X* information over the entire immiscibility range for CO_2-*n*-heptane. The Kurata study would seem to indicate that CO_2 is partially miscible with all normal alkanes from *n*-heptane up to the high-molecular-weight alkanes. Francis has reported L_1-L_2 compositions at room temperature on the systems he studied. Only *P-T* projections of loci are reported by Schneider.

The authors feel that an extensive study of CO_2-*n*-decane partial miscibility phenomena, along with previously cited detailed studies, would lead to further insight into the partial miscibility behavior of CO_2 mixtures with normal alkanes, as a family, when considered in concert with the studies cited earlier. Furthermore, economically attractive methods of separation along the solid-liquid-vapor and liquid-liquid-vapor three-phase surfaces are presently being developed requiring detailed data of this nature for design purposes.

Experimental

A detailed description of the experimental equipment and procedure is given elsewhere (*3, 4, 6*). Briefly, a known amount of *n*-decane was placed in a 10-cc glass equilibrium cell. During the experimental runs, measured amounts of pure CO_2 gas were added to the thermostated equilibrium cell from a high-pressure bomb, through use of a positive displacement mercury pump. By a mass balance, the moles of CO_2 added to the liquid phase or phases were then determined. In the case of the L_1-L_2-V runs, the moles of CO_2 in the individual liquid phases were determined by making separate runs in which one or the other of the two phases is present in a trace amount.

In the case of the S_1-L_1-V system, S_1 crystals (assumed to be pure n-decane) were maintained in trace amounts; hence, composition in the liquid phase is easily calculated. However, this technique of determining com-

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