Solubilities of Nitrogen and Oxygen in 1,2-Ethanediol + Water at 298.15 K and 101.33 kPa

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Solubilities of nitrogen and oxygen were determined on the 1,2-ethanediol + water solution over the full range of composition by a static method. The gas solubility was measured at 298.15 K and 101.33 kPa. Both the excess Ostwald coefficient and the excess volume of the mixed solvent showed similar dependencies on the volume fraction. The observed values of oxygen and nitrogen in 1,2-ethanediol + water were expressed by the Ostwald coefficient. From the result of the solubility of argon by Ben-Naim and our observed solubilities of nitrogen and oxygen, the order of gas solubility was argon > oxygen > nitrogen in the full range of composition. Furthermore, the excess Ostwald coefficients on the basis of the volume fraction which express the nonideality of gas solubility in nonideal solutions were defined, and excess Ostwald coefficients of these three solute gases in 1,2-ethanediol + water showed the same curve against the volume fraction of 1,2-ethanediol. This result means that the kind of solute gas had no effect on the excess Ostwald coefficient defined in this work. This property was identical with that for monoalcohol aqueous solutions.

Introduction

Gas solubilities in binary liquid mixtures having water as one component are very important for discussion about absorption equilibrium. However, the experimental data needed for investigation of its peculiar behavior were not sufficient, and the estimation and correlation method for these gas solubilities in the solvent mixture are regarded as very difficult at present.

Our previous work was the measurement of gas solubility in aqueous monoalcohol solutions (*16, 17, 19*). We have already presented one correlation on gas solubility in these aqueous solutions. That is, the relation between the excess volume calculated from the density for the solvent mixture and the excess solubilities for the solute gas in these solvent mixtures showed similarity (*18*). Excess Ostwald coefficients on the basis of the volume fraction which express the nonideality of gas solubility in nonideal solutions was defined (*14, 15*). For monoalcohol aqueous solutions, the excess Ostwald coefficient and the excess volume against volume fraction showed the same tendency. Especially, excess Ostwald coefficients against the composition of the volume fraction of the solvent mixture showed the same curve regardless of the solute gas (*15, 18*).

For the dihydric alcohol + water solution, Ben-Naim (*1*) measured the solubility of argon in 1,2-ethanediol + water over the full range of composition. In this work, in order to examine this property for dihydric alcohol + water solutions, the solubility measurements of nitrogen and oxygen in 1,2-ethanediol + water were carried out at a temperature of 298.15 K and at a pressure of 101.33 kPa. The excess Ostwald coefficients of nitrogen, oxygen, and argon (*1*) in 1,2-ethanediol + water were obtained. Furthermore, they were expressed by a polynomial equation of the Redlich–Kister type (*10*).

Experimental Apparatus and Procedure

The apparatus used in this experiment is shown in Figure 1. It was similar to the previously used method in refs 14–16 except for the use of an improved equilibrium cell, and it consisted of an equilibrium cell, a cylinder-type gas holder, and a digital pressure gauge. The equilibrium cell was made of Pyrex glass, and its volume was about 300 cm^3. The mass of the solvent mixture was measured from the weight difference of the equilibrium cell, and its accuracy for weight measurement was 1.0×10^{-3} g. The volumes of the equilibrium cell and stainless pipe line in Figure 1 was calibrated by means of pure water at 298.15 K prior to the experiment.

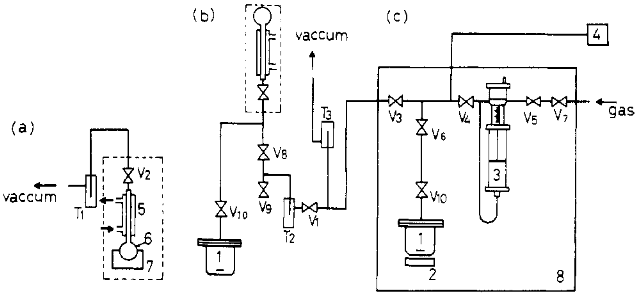

Figure 1. Schematic diagram of the experimental apparatus: (a) degassing unit, (b) solution sampling unit, (c) gas dissolving unit, (1) equilibrium cell, (2) magnetic stirrer, (3) cylinder-type gas holder, (4) digital pressure gauge, (5) condenser, (6) degassing flask, (7) mantle heater, (8) constant-temperature water bath, (T_1, T_2, T_3) cold traps, (V_1–V_6) bellows valves, (V_7) pressure regulator valve, (V_8–V_{11}) ball valves.

The cylinder-type gas holder (3.27-cm i.d.) made of stainless steel was used for the measurement of the dissolved gas volume, and it was manufactured by Taika Kogyo Co., Ltd. The capacity of the gas holder was about 80 cm^3, and a gas piston of stainless steel in the cylinder had 25 turns with a 4-mm pitch. The dissolved gas volume was measured by the displacement of the plunger. The volume at each turn was calibrated by means of pure water at 298.15 K, and a linear relation between the volumes and the piston readings was observed. The accuracy of the measurement of the dissolved gas volume was 1.0×10^{-3} cm^3.

The digital pressure gauge, model DG-430K, has an accuracy of ±0.01% of full scale (0.2 MPa). This gauge was manufactured by Tokyo Aircraft Instrument Co., Ltd. It was immersed in the constant-temperature water bath, which was regulated within 298.15 ± 0.05 K by means of a PID controller. Densities of the solution ware measured by use of a density/specific gravity meter manufactured by Kyoto Electronics Manufacturing Co. Ltd., and the resolution for the density measurement was 1.0×10^{-5} g/cm^3.

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Table 1. Physical Properties of the Pure Solvents Used at 298.15 K

	ρ (kg m^{-3})		η		water content/ %	purity/ (mass %)
	exp	lit.[a]	exp	lit.[a]		
1,2-ethanediol	1109.86	1110.0	1.4305	1.430 6	0.0896	>99.99
water	997.06	997.05	1.3325	1.332 502 9		>99.99

[a] Riddick et al. (*11*).

The method of solubility measurement was similar to that previously used (*14*, *16*). It was carried out by the static method. The principle is as follows: a solvent mixture (1,2-ethanediol (2) + water (3)) was degassed using a vacuum pump with 2 h of heating by a mantle heater at 323 K (unit a in Figure 1). Then, the experimental apparatus was also evacuated by using the vacuum pump in order to remove moisture and air from the system. The degassed solvent was introduced into the equilibrium cell by the pressure difference between the degassing flask and equilibrium cell using unit b as shown in Figure 1. The volume of the mixed solvent was determined from the weight of the equilibrium cell and the density of the solvent mixture. The volume of the equilibrium cell was determined by pure water prior to the experiment. The accuracy of the volume measurement of the solvent was 1.0×10^{-3} cm^3. Then the temperature of the solution was kept at 298.15 K, and the vapor pressure (P_{sol}) of the solution was measured after the confirmation of equilibrium. It took about 1 or 2 h to reach the equilibrium state.

The cylinder-type gas holder and pipe arrangement for introduction of solute gas were also evacuated using the vacuum pump. Then, the solute gas (nitrogen or oxygen) was introduced into the parts. This operation was repeated two or three times. Impurity gas in the cylinder-type gas holder was replaced by solute gas. Finally, the volume of solute gas in the cylinder-type gas holder and its pressure were measured at 298.15 K. Then, the solute gas was contacted with degassed solvent while the pressure was kept constant at 101.33 kPa by regulating the gas piston and valve (V_{10}). The solution was slowly stirred until equilibrium was established. When no pressure lowering occurs after these operations, absorption equilibrium has been reached. After the valve (V_{10}) was closed, the level of the gas piston was read, and the volume of dissolved gas in the solution was determined by reading the scale on the cylinder-type gas holder. The total pressure under the equilibrium state was recorded at the same time. Furthermore, the density of the solvent mixture was measured for the determination of the solvent composition.

Materials

Nitrogen and oxygen gases were obtained from Seitetu Kagaku Co., Ltd., and their purity was 99.999% by the quality guaranty. They were used without further purification.

1,2-Ethanediol was a guaranteed reagent from Wako Chemical Industries. Water was purified by use of a Milli-Q Labo manufactured by Millipore Ltd., after distillation and ion exchange.

The physical properties of these solvents are shown in Table 1. For the determination of the solvent composition, the densities of the solvent mixture were measured by use of the density/specific gravity meter. The densities of 1,2-ethanediol aqueous solutions were measured in our laboratory. The measured densities are listed in Table 2. and satisfactory agreement with those of Nakanishi (*9*) was obtained. The composition of the solvent mixture was determined from the observed density.

Table 2. Density of the 1,2-Ethanediol (2) + Water (3) Solution at 298.15 K

x_2	$\rho_{2,3}$/(kg m^{-3})	x_2	$\rho_{2,3}$/(kg m^{-3})	x_2	$\rho_{2,3}$/(kg m^{-3})
0	997.06	0.3989	1085.25	0.7815	1103.15
0.1121	1034.56	0.5125	1094.24	0.8897	1105.74
0.1980	1054.96	0.6002	1098.47	0.9568	1107.94
0.3012	1073.21	0.6985	1101.45	1	1109.86

Calculation of Gas Solubilities

The solubilities were expressed in terms of the Ostwald coefficient, which is defined as the ratio of the volume of the gas (V_{dis}) absorbed to the volume (V_{sol}) of the absorbing liquid, that is,

$$L = V_{dis}/V_{sol} \qquad (1)$$

For calculation of the Ostwald coefficient, the observed volume of the solute gas (V_{dis}^{exp}) dissolved in the solution was converted into the value under the partial pressure of the solute gas at 101.325 kPa by use of eq 2, where Henry's law

$$L = \left(\frac{V_{dis}^{exp}}{V_{sol}^{exp}}\right)\left(\frac{101.325}{P_g}\right) \qquad (2)$$

was assumed to apply at near atmospheric pressure. The volume of solution (V_{sol}^{exp}) was calculated from the weight and its density.

The partial pressure of the solute gas, P_g, was found from

$$P_g = \pi - P_{sol} \qquad (3)$$

where π is the total pressure with absorption equilibrium established and P_{sol} is the vapor pressure of the solution. Observed π and P_{sol} were used for the calculation of the partial pressure (P_g).

Results and Discussion

Observed solubilities of nitrogen and oxygen in two pure solvents at 298.15 K and 101.33 kPa are listed in Table 3. Reproducibilities of the experimental values were within ±1.5%, and the maximum deviations from literature values were within 5.6% for 1,2-ethanediol and 2.6% for water, respectively. For the 1,2-ethanediol + water solution, the reproducibility of the experimental solubilities was within ±1.5% in this work. The experimental solubilities of nitrogen and oxygen in the 1,2-ethanediol + water solution are given in Tables 4 and 5. These are shown graphically in Figure 2.

In this figure, the solubilities of argon by Ben-Naim (*1*) in 1,2-ethanediol + water solution were added for comparison. For the three curves in Figure 2, the minimum values on each solubility curve were found for the composition of about $x_2 = 0.3$. And the solubilities in the mixed solvent increased monotonously with increasing alcohol mole fraction over the composition range of about $0.3 < x_2 < 1.0$. The order of gas solubility in the 1,2-ethanediol + water solution was argon > oxygen > nitrogen in the full composition range.

The excess Ostwald coefficient on the basis of the volume fraction (ϕ_2) which expresses the nonideality of gas solubility in nonideal solutions is defined by

$$\ln \kappa(L) = \ln L_{1,23} - \sum_{i=2}^{3} (\phi_i \ln L_{1,i}) \qquad (4)$$

where the subscripts 1, 2, and 3 denote the solute gas, alcohol, and water, respectively. The observed excess values calculated by use of eq 4 were plotted against the volume fraction of 1,2-ethanediol in Figure 3. The calculated excess Ostwald coefficient ($\ln \kappa(L)$) was fitted by the following polynomial

Table 3. Comparison of the Experimental Solubilities of Nitrogen and Oxygen in Pure Solvents with Literature Values at 298.15 K[h]

gas	solvent	Ostwald Coefficient L_{exp}	Ostwald Coefficient $L_{lit.}$	deviation (100 δ)	reproducibility (100 ϵ)
nitrogen	1,2-ethanediol	0.015 84	0.015 00[a] (298.16 K)	5.6	±1.3
			0.015 59[a] (298.17 K)	1.6	
	water	0.016 02	0.016 0[b]	0.1	±0.8
			0.015 9[c]	−0.8	
oxygen	1,2-ethanediol	0.030 25			±1.1
	water	0.031 61	0.030 80[d]	2.6	±1.5
			0.031 20[e]	1.3	
			0.031 00[f]	2.0	
			0.031 08[g]	1.7	

[a] Gjaldaek and Niemann (5). [b] Clever and Battino (2). [c] Cosgrove and Walkley (3). [d] Geffecken (4). [e] Livingston (7). [f] Shchukarev and Toimacheva (13). [g] Novak and Conway (8). [h] These solubility data were placed on the list in the IUPAC Solubility Data Series, nitrogen, oxygen, 1980. $\delta = \{(L_{exp} - L_{lit.})/L_{lit.}\}$. $\epsilon = \pm(1/2)\{(L_{max} - L_{min})/L_{av}\}$. $L_{av} = (1/n)\sum_{i=1}^{n} L_{exp,i}$.

Table 4. Oswald Coefficients L of Nitrogen in 1,2-Ethanediol (2) + Water (3) at 298.15 K at 101.33 kPa

x_2	ϕ_2[a]	$\rho_{2,3}$/(kg m^{-3})	L
0	0	997.06	0.016 02
0.0085	0.0237	1000.85	0.015 70
0.0326	0.1026	1010.62	0.014 75
0.1146	0.3052	1037.67	0.012 50
0.1852	0.4310	1053.98	0.011 48
0.2444	0.5233	1065.80	0.011 27
0.3130	0.6072	1075.71	0.011 24
0.4197	0.7105	1086.36	0.011 59
0.7333	0.9032	1103.56	0.013 82
1	1	1109.86	0.015 84

[a] Calculated from $\phi_2 = x_2v_2/[x_2v_2 + (1 - x_2)v_3]$.

Table 5. Ostwald Coefficients L of Oxygen in 1,2-Ethanediol (2) + Water (3) at 298.15 K and 101.33 kPa

x_2	ϕ_2[a]	$\rho_{2,3}$/(kg m^{-3})	L
0	0	997.06	0.031 61
0.0354	0.1180	1011.64	0.029 12
0.0775	0.2219	1025.98	0.026 26
0.1185	0.3133	1038.76	0.024 35
0.1795	0.4261	1053.35	0.022 45
0.3234	0.6186	1076.98	0.020 87
0.4242	0.7143	1086.72	0.021 51
0.5404	0.7996	1094.42	0.023 30
0.7337	0.9034	1103.63	0.025 59
1	1	1109.86	0.030 25

[a] Calculated from $\phi_2 = x_2v_2/[x_2v_2 + (1 - x_2)v_3]$.

Table 6. Constants in Eq 5 and Average Deviation between Observed and Calculated Solubilities

gas	constants A	constants B	constants C	constants D	deviation (100δ)[a]
nitrogen	−1.380 749	−0.174 770	0.253 210	0.164 155	0.28
oxygen	−1.451 859	−0.841 821	0.219 642	−0.434 316	0.80

[a] $\delta = (1/n)\sum_{i=0}^{n}|\ln \kappa(L)_{cal} - \ln \kappa(L)_{obs}|$.

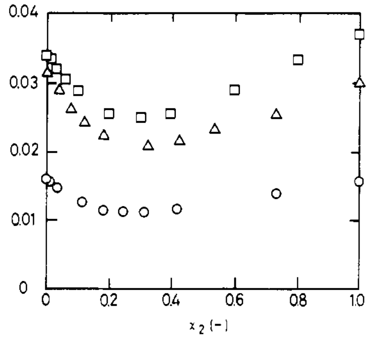

Figure 2. Ostwald coefficient L of argon (1), nitrogen (1), and oxygen (1) in 1,2-ethanediol (2) + water (3) mixed solvent at 298.15 K and 101.33 kPa: △, oxygen; ○, nitrogen; □, argon.

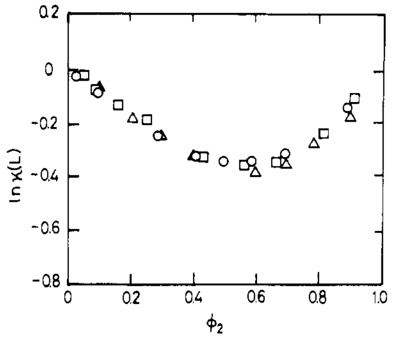

Figure 3. Relation between excess quantities ln $\kappa(L)$ and volume fraction ϕ_2 at 298.15 K and 101.33 kPa: △, oxygen; ○, nitrogen; □, argon.

expression of the Redlich–Kister type (10):

$$\ln \kappa(L) = \phi_2\phi_3[A + B(\phi_2 - \phi_3) + C(\phi_2 - \phi_3)^2 + D(\phi_2 - \phi_3)^3] \quad (5)$$

The constants in eq 5 were determined by the least-squares procedure from the observed values. These constants and the average deviations between the observed Ostwald coefficients and calculated ones from eq 5 are given in Table 4.

The values of ln $\kappa(L)$ were given by peculiar concave curves for each system, and the excess Ostwald coefficients for these three solute gases were approximately plotted on an identical curve (Figure 3). This curve had minimum values at the particular composition of mixed solvents. The minimum value of ln $\kappa(L)$ for three gases for the 1,2-ethanediol + water mixed solvent appeared at nearly the same composition. And this result meant that the excess Ostwald coefficient is not affected by the solute gas, but by the solvent. This property was similar to that for monoalcohol aqueous solutions presented by us previously (15).

On the other hand, for the nonideality of mixed solvents, the ratio of the excess molar volume to that of the ideal mixture was used. It was expressed by

$$v^E/v^{ID} = v^E/\sum_{i=2}^{3}(x_iv_i) \quad (6)$$

$$v^E = v - \sum_{i=2}^{3}(x_iv_i) \quad (7)$$

The values of v^E/v^{ID} were calculated from the density data at 298.15 K. The relation of v^E/v^{ID} to composition in 1,2-

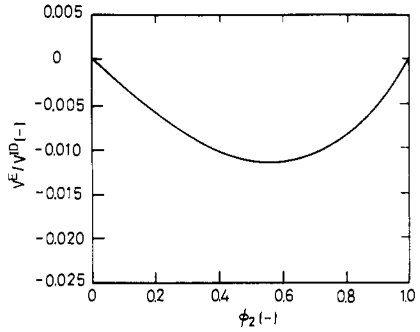

Figure 4. Relation between excess quantities v^E/v^{ID} and volume fraction ϕ_2 at 298.15 K.

ethanediol + water is shown in Figure 4. In this figure, the 1,2-ethanediol composition showing the minimum excess quantities exactly corresponds to that in Figure 3.

For the solubilities of argon, nitrogen, and oxygen in the aqueous acetone solution, these correlations were obtained in a previous work (*16*).

Conclusion

The solubilities of nitrogen and oxygen were determined in the 1,2-ethanediol + water solution over the full range of composition of 1,2-ethanediol using the static method. The excess Ostwald coefficient of these solute gases in this solution showed the same curve against the volume fraction of 1,2-ethanediol. The excess Ostwald coefficient calculated from solubility data of argon in 1,2-ethanediol + water reported by Ben-Naim showed the same tendency as that in this work. Furthermore, the relation between the excess volume quantity (v^E/v^{ID}) and volume fraction of 1,2-ethanediol (ϕ_2) is similar to that for the excess Ostwald coefficient ($\ln \kappa(L)$) and volume fraction. This correlation for the dihydric alcohol + water solvent mixture agrees with that for the monoalcohol + water mixture.

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