

SOLUBILITIES OF ARGON, OXYGEN AND NITROGEN IN 1,2-PROPANEDIOL+WATER MIXED SOLVENT AT 298.15 K AND 101.33 kPa

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Solubilities of argon, oxygen and nitrogen were determined in 1,2-propanediol+water mixed solvent over the full range of composition by a static method. Gas solubility measurements were carried out at a temperature of 298.15 K and pressure of 101.33 kPa. Both the excess quantity referring to the Ostwald coefficient and to the excess volume of solvent mixture showed similar relation having minima against the volume fraction composition of 1,2-propanediol.

The order of gas solubility expressed by the Ostwald coefficient in 1,2-propanediol+water mixed solvent was argon > oxygen > nitrogen in full range of composition. Furthermore, the excess Ostwald coefficients on the basis of volume fraction which express the non-ideality of gas solubility in non-ideal solutions were defined, and excess Ostwald coefficient of these three solute gases in 1,2-propanediol+water mixed solvent showed one parabolic curve against volume fraction of 1,2-propanediol. This result means that excess Ostwald coefficients of these gases do not depend on the type of solute gas, but on solvent. This property was similar to that of monoalcohol aqueous solutions.

Introduction

Gas solubilities in binary liquid mixtures having water as one component are very important for discussion about absorption equilibrium. However, a few experimental data needed for investigation of its peculiar behavior were reported, and the estimation for these solubilities in mixed solvent was very difficult at present. Furthermore no correlation method of gas solubility for non-ideal solutions like an aqueous alcohol solutions was developed.

Our previous work was the measurement of gas solubility in the aqueous monoalcohol solutions^{14, 15, 16, 18}. We have already presented some correlation on gas solubility in these aqueous solutions. That is, the excess quantity of solubility of solute gas in a mixed solvent has closely been correlated to the excess volume calculated from its density^{15, 17}. Furthermore excess Ostwald coefficients on the basis of volume fraction which express the non-ideality of gas solubility in non-ideal solutions were defined. For the monoalcohol aqueous solutions, excess Ostwald coefficient and excess volume of solvent mixture against volume fraction showed the same tendency. The relation between excess Ostwald coefficient and volume fraction showed the same curve independently of solute gas^{14, 18, 20}.

On the other hand, a few experimental gas solubility data have been reported for dihydric alcohol+water solution. Ben-Naim¹ measured the solubility of argon in 1,2-ethanediol+water mixed solvent over the full range of

composition. In other works, in order to examine the above stated properties for dihydric alcohol+water solutions, the solubility measurements for oxygen and nitrogen in 1,2-ethanediol+water mixed solvents were carried out at temperature of 298.15 K and pressure of 101.33 kPa, and similar tendencies for the excess Ostwald coefficient of argon, oxygen and nitrogen in 1,2-ethanediol+water mixed solvent were obtained²⁰.

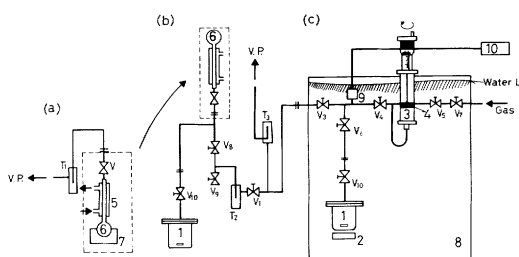
In this work, the solubility of argon, oxygen and nitrogen in 1,2-propanediol+water mixed solvent was measured at a temperature of 298.15 K and pressure of 101.33 kPa. The excess Ostwald coefficients of argon, oxygen and nitrogen in 1,2-propanediol+water mixed solvent were evaluated for discussion about non-ideality of gas solubility, and the excess volume of solvent mixture against volume fraction was also evaluated for comparison with these excess quantities. Furthermore, the excess Ostwald coefficients on the basis of volume fraction which express the non-ideality of gas solubility in non-ideal solutions were also defined, and they were expressed by polynomial equation of Redlich-Kister type¹¹.

1. Experimental Section

1.1 Experimental apparatus

The apparatus used in this experiment is shown in Fig. 1. It is similar to the apparatus used previously^{9, 17, 18} except an improved equilibrium cell, which consists of an

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(a): degassing unit, (b): mixed solvent sampling unit, (c): gas dissolving unit 1: equilibrium cell, 2: magnetic stirrer, 3: cylinder type gas holder, 4: piston, 5: condenser, 6: degassing flask, 7: mantle heater, 8: constant temperature water bath, 9: pressure sensing quartz, 10: digital pressure gauge, T_1, T_2, T_3 : cold trap, V_1 - V_6 : bellows valve, V_7 : pressure regulator valve, V_8 - V_{10} : ball valve

Fig. 1 Schematic diagram of the experimental apparatus

equilibrium cell, a cylindrical type gas holder, and a digital pressure gauge. The equilibrium cell is made of Pyrex glass and its volume is about 300 cm³. Mass of mixed solvent was determined by measuring weight difference of equilibrium cell; the accuracy for weight measurement was 1.0×10^{-3} g. The volume of equilibrium cell and stainless pipe line shown in Fig. 1 was calibrated by means of pure water of 298.15 K previously.

A cylindrical type gas holder (3.27 cm ID) made of stainless steel was used for measurement of the dissolved gas volume, manufactured by Taika Kogyo Co., Ltd. A gas piston of stainless steel has 25 turns with 4 mm a pitch; the full volume of gas holder is about 80 cm³. The dissolved gas volume was measured by using the displacement of the plunger. The volume at each turn was calibrated by means of pure water at 298.15 K; a linear relation between the volumes and the piston readings was observed. The accuracy of the measurement of dissolved gas volume was 1.0×10^{-3} cm³.

A digital pressure gauge manufactured by Tokyo Aircraft Instrument Co., Ltd. Model DG-430 K has an accuracy of ± 0.01 % of full scale (0.2 MPa). This digital gauge was immersed in the constant temperature water bath, which was regulated within 298.15 K ± 0.05 K by means of PID controller.

The density of a solution was measured by use of a Density/Specific Gravity Meter manufactured by Kyoto Electronics Manufacturing Co. Ltd., and its digital resolution for density measurement was 1.0×10^{-5} g/cm³.

1.2 Experimental procedure

The method of gas solubility measurement is similar to that of previously used¹⁶⁻¹⁸, which is classified to the static method. The procedure of a gas solubility measurement is as follows; a mixed solvent (1,2-propanediol (2) + water (3)) was degassed by using a vacuum pump for 2 hours with heating by mantle heater at 323 K using the unit (a) in Fig. 1. Then, the experimental apparatus was evacuated by using a vacuum pump in order to remove moisture and air from the system. The degassed solvent was introduced into the equilibrium cell by pressure difference

Table 1. Physical Properties of Pure Solvent used at 298.15 K

	Density ρ		Refractive Index η		Water Content [wt%]	Purity [%]
	Exp	Lit. ¹²⁾	Exp	Lit. ¹²⁾		
1,2-propanediol	1032.53	1032.80	1.4315	1.4314	0.1973	>99.80
Water	997.06	997.05	1.3325	1.3325029	-	>99.99

between degassing flask and equilibrium cell showing at unit (b) in Fig. 1. The volume of mixed solvent was determined from weight difference of the equilibrium cell and the density of the mixed solvent. The accuracy of the measurement of volume of the mixed solvent was 1.0×10^{-3} cm³. The temperature of the mixed solvent was then kept at 298.15 K, and the vapor pressure (P_{sol}) of the mixed solvent was measured after the confirmation of equilibrium. It took about one to one and a half hour to reach the equilibrium state.

On the other hand, the cylinder type gas holder and pipe arrangement for introduction of solute gas were also evacuated using a vacuum pump. The solute gas (argon, nitrogen or oxygen) was then 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 gas holder and its pressure were measured at 298.15 K. The solute gas was contacted with degassed solvent keeping the pressure at 101.33 kPa by regulating the gas piston and valve (V_{10}). The mixed solvent was slowly stirred using a magnetic stirrer until absorption equilibrium was established. When no pressure lowering occurs after these operations, equilibrium is reached. It took one or two hours after solution had started. After the valve (V_{10}) is closed, the level of gas piston is read, and the volume of dissolved gas into the mixed solvent was determined by reading the scale on the cylinder type gas holder. The total pressure (π) under the equilibrium state was recorded at the same time. Furthermore, the density of the mixed solvent was measured for the determination of the solvent composition.

1.3 Materials

Argon, oxygen and nitrogen were high purity of super pure gas, which were obtained from Seitetu Kagaku Co. Ltd. The purity of these gases was 99.999 % according to the quality guaranty, and was used without further purification.

1,2-propanediol was guaranteed reagent from Wako Pure Chemical Ind. Water was purified using Milli-Q Labo manufactured by Millipore Ltd., after distillation and ion exchange.

Physical properties and purity of 1,2-propanediol and water are shown in Table 1. For the determination of mixed solvent composition, the density of mixed solvent was measured by use of Density/Specific Gravity Meter. For the determination of relationship between a composition and its density, the density of 1,2-propanediol+water mixed solvent was measured under the various compositions at

Table 2. Density of 1,2-Propanediol (2) + Water (3) Mixed Solvent at 298.15 K

Mole fraction x_2 [-]	Density ρ_{23} [kg·m ⁻³]
0	997.06
0.0913	1020.88
0.1982	1035.01
0.3003	1039.75
0.4031	1040.42
0.5002	1039.60
0.5999	1038.36
0.7036	1036.97
0.8022	1035.47
0.9012	1033.81
1	1032.53

Table 3. Comparison of Experimental Solubilities of Argon, Oxygen and Nitrogen in Pure Solvents with Literature Values at 298.15 K

Gas	Solvent	Ostwald Coefficient L_{ext} [-]	Deviation* ¹ L_{lit} [-]	Reproducibility* ² δ [%]	ϵ [%]
Argon	1,2-propanediol	0.06592	-	-	±1.4
	water	0.03410	0.03408 ¹⁾	+0.1	±1.4
			0.03415 ⁷⁾	-0.1	
Oxygen	1,2-propanediol	0.05816	-	-	±0.7
	water	0.03161	0.03080 ⁴⁾	2.6	±1.5
			0.03120 ⁶⁾	1.3	
			0.03100 ¹³⁾	2.0	
			0.03108 ¹⁰⁾	1.7	
Nitrogen	1,2-propanediol	0.02756	-	-	±1.1
	water	0.01602	0.01602 ²⁾	0.1	±0.8
			0.01593 ³⁾	0.8	

*¹ $\delta = \{(L_{exp} - L_{lit})/L_{lit}\} \cdot 100$

*² $\epsilon = \pm(1/2) \{(L_{max} - L_{min})/L_{ave}\} \cdot 100$

$$L_{ave} = (1/n) \cdot \sum_{i=1}^n L_{exp,i}$$

298.15 K previously. These measured densities were listed in **Table 2**, and satisfactory agreement with Nakanishi⁸⁾ was obtained.

2. Calculation of Gas Solubility

The solubilities were expressed in terms of the Ostwald coefficient, which was defined as “the ratio of volume of gas absorbed to the volume of the absorbing liquid” that is

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

For the calculation of Ostwald coefficient, the observed volume of solute gas under the partial pressure of solute gas was converted into the value at 101.325 kPa by use of Eq. (2), where Henry’s law was assumed to apply at pressure near atmospheric.

$$L = (V_{dis} / V_{sol}) (101.325 / P_g) \quad (2)$$

The partial pressure of solute gas, P_g , was found from Eq. (3).

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

where P_{sol} is observed vapor pressure of the mixed

Table 4. Ostwald Coefficients of Argon in 1,2-Propanediol (2) + Water (3) Mixed Solvent at 298.15 K and 101.33 kPa

Mole fraction x_2 [-]	Volume fraction Φ_2^* [-]	Ostwald coefficient L [-]
0	0	0.03410
0.0267	0.1006	0.03251
0.0605	0.2080	0.03005
0.0977	0.3063	0.02751
0.1437	0.4063	0.02508
0.2659	0.5963	0.02761
0.3841	0.7178	0.03349
0.4901	0.7967	0.04067
0.6976	0.9039	0.05277
1	1	0.06592

* was calculated from $\Phi_2 = x_2 v_2 / [x_2 v_2 + (1 - x_2) v_3]$

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

Mole fraction x_2 [-]	Volume fraction Φ_2^* [-]	Ostwald coefficient L [-]
0	0	0.03161
0.0290	0.1086	0.02911
0.0606	0.2083	0.02700
0.0961	0.3024	0.02443
0.1398	0.3986	0.02341
0.1996	0.5042	0.02364
0.2702	0.6016	0.02575
0.3784	0.7128	0.02977
0.4991	0.8025	0.03585
0.6854	0.8988	0.04694
1	1	0.05816

* was calculated from $\Phi_2 = x_2 v_2 / [x_2 v_2 + (1 - x_2) v_3]$

Table 6. Ostwald Coefficients of Nitrogen in 1,2-Propanediol (2) + Water (3) Mixed Solvent at 298.15 K and 101.33 kPa

Mole fraction x_2 [-]	Volume fraction Φ_2^* [-]	Ostwald coefficient L [-]
0	0	0.01602
0.0284	0.1065	0.01518
0.0582	0.2013	0.01330
0.0940	0.2973	0.01153
0.1387	0.3964	0.01135
0.2007	0.5059	0.01136
0.2725	0.6043	0.01255
0.3611	0.6974	0.01470
0.5136	0.8115	0.01849
0.6988	0.9044	0.02168
1	1	0.02756

* was calculated from $\Phi_2 = x_2 v_2 / [x_2 v_2 + (1 - x_2) v_3]$

solvent at 298.15 K, and π is the total pressure which absorption equilibrium is established. Observed π and P_{sol} were used for the calculation of partial pressure (P_g) of solute gas.

3. Results and Discussion

Observed solubilities of argon, oxygen and nitrogen in two pure solvents at 298.15 K are listed in **Table 3**.

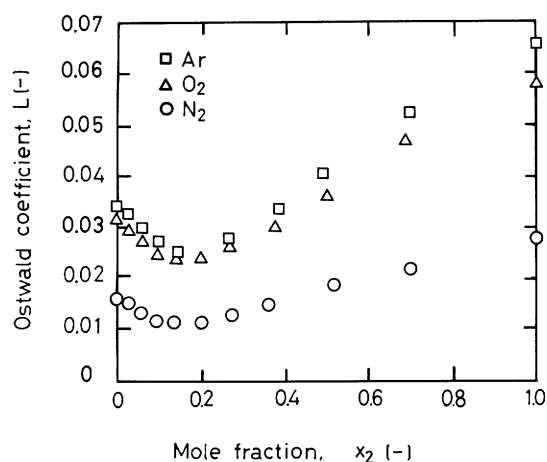


Fig. 2 Gas solubility of argon, nitrogen and oxygen in 1,2-propanediol + water mixed solvent at 298.15 K and 101.33 kPa

Reproducibility of the experimental solubilities was within ± 1.0 %, and the maximum deviations from literature values were within 2.6 %. Experimental solubilities expressed by Ostwald coefficient of argon, oxygen and nitrogen in 1,2-propanediol+water mixed solvent at 298.15 K are given in **Tables 4, 5 and 6**. These are shown graphically in **Fig. 2**.

For aqueous alcohol solutions, the reproducibility of the experimental solubilities was within ± 1.5 % in this work. For the three curves in **Fig. 2**, a minimum point on each solubility curve was found in the composition about $x_2 = 0.18$. The solubility in the mixed solvent increased monotonically with an increase in alcohol mole fraction in the composition range of $0.18 < x_2 < 1.0$. The order of gas solubilities in 1,2-propanediol+water mixed solvent was argon > oxygen > nitrogen in the full composition range. The excess Ostwald coefficient on the basis of volume fraction (ϕ_2), which express the non-ideality of gas solubility in aqueous alcohol solutions was defined by Eq. (4).

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

The observed excess values calculated by use of Eq. (4) were plotted against volume fraction of 1,2-propanediol in **Fig. 3**.

The calculated excess Ostwald coefficients ($\ln \kappa(L)$) were fitted by the following polynomial expression of the Redlich-Kister type¹¹⁾:

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

The constants in Eq. (5) were determined by the least square 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 7**.

The values of $\ln \kappa(L)$ were given by peculiar concave curves for each system (**Fig. 3**) and these curves had minimum values at the particular composition of mixed solvents. The values of $\ln \kappa(L)$ for three gases for 1,2-

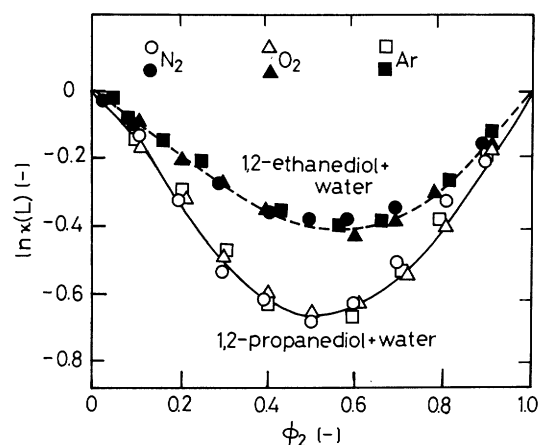


Fig. 3 Relation between excess quantities $\ln \kappa(L)$ and volume fraction ϕ_2 of 1,2-propanediol at 298.15 K; (the dotted line shows the correlated values by Eq. (5) for the excess Ostwald coefficient of Ar, N₂ and O₂ in 1,2-ethanediol + water mixed solvent at 298.15 K and 101.33 kPa^{1, 20)})

propanediol+water mixed solvent were shown by the same curve, and the minimum excess Ostwald coefficient for these three solute gases showed same value. This result meant that excess Ostwald coefficient do not depend on solute gas, but on the solvent. This relation was similar to that of monoalcohol aqueous solutions presented by us previously^{17, 18)}.

On the other hand, for the non-ideality of mixed solvents, the ratio of excess molar volume to the volume of ideal mixture was used and expressed by Eqs. (6), (7).

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

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

The values of v^E/v^{ID} were calculated from the density data at 298.15 K. The relation between v^E/v^{ID} and volume fraction in 1,2-propanediol+water mixed solvent is shown in **Fig. 4**. In this figure, 1,2-propanediol composition showing the minimum excess quantities coincided with those in **Fig. 3**. For comparison, the dotted line in **Fig. 3** shows the correlated values for the excess Ostwald coefficient of argon, nitrogen and oxygen in 1,2-ethanediol+water mixed solvent by Eq. (5), and **Fig. 4** shows the relation between ratio of excess molar volume to the ideal solvent mixture and volume fraction of 1,2-ethanediol at 298.15 K^{1, 20)}.

Conclusion

Solubilities of argon, nitrogen and oxygen were determined in 1,2-propanediol+water mixed solvent over the full range of composition using static method. Excess Ostwald coefficient of these solute gases in 1,2-propanediol+water mixed solvent was shown by the same curve against volume fraction of 1,2-propanediol. The kind of solute gas has no effect on the excess Ostwald coefficient defined in this work. Furthermore, the relation between excess quan-

Table 7. Constants in Eq. (5) and Average Deviation between Observed Solubility and Calculated One

Gas	A	B	Constants C	Deviation* D	[%]
argon	-2.697101	-0.533120	1.645005	0.212219	0.80
oxygen	-2.579922	-0.484285	1.128900	0.457457	0.97
nitrogen	-2.599212	0.317568	1.382471	-1.298809	1.06

* was calculated from $(1/n) \cdot \sum_{i=1}^n |\ln \kappa(L)_{cal} - \ln \kappa(L)_{obs}| \times 100$

tity (v^E/v^{ID}) and volume fraction of 1,2-propanediol (ϕ_2) was similar to that for the excess Ostwald coefficient ($\ln \kappa(L)$) and volume fraction. This correlation for dihydric alcohol+water mixed solvent was similar to that for monoalcohol aqueous solutions.

Nomenclature

A	=	constant in Eq. (5)	[-]
B	=	constant in Eq. (5)	[-]
C	=	constant in Eq. (5)	[-]
D	=	constant in Eq. (5)	[-]
L	=	Ostwald coefficient	[-]
n	=	number of data point	[-]
P	=	pressure	[kPa]
v	=	molar volume or volume	[cm ³ /mol] [cm ³]
x	=	mole fraction	[-]
δ	=	deviation	[%]
ϵ	=	reproducibility	[%]
η	=	refractive index	[-]
κ	=	excess quantity defined by Eq. (4)	[-]
ρ	=	density	[kg/m ³]
ϕ	=	volume fraction	[-]

<Subscripts>

1	=	solute gas
2	=	1,2-propanediol
3	=	water
ave	=	average of observed data
dis	=	dissolve
exp	=	experimental value
lit.	=	data from literature
max	=	maximum
min	=	minimum
sol	=	solvent

<Superscripts>

E	=	excess
ID	=	ideal

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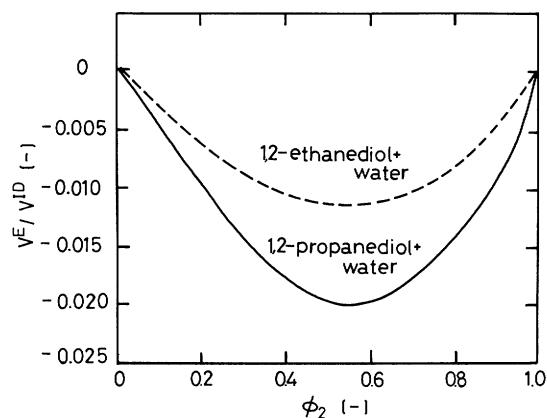


Fig. 4 Relation between excess quantities v^E/v^{ID} and volume fraction ϕ_2 at 298.15 K; (the dotted line shows the same relationship for 1,2-ethanediol+water mixed solvent at 298.15 K⁽²⁰⁾)

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