Solubility of Helium in Methanol + Water, Ethanol + Water, 1-Propanol + Water, and 2-Propanol + Water Solutions at 25 °C

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The solubility of helium was measured in four aqueous alcohol solutions (methanol + water, ethanol + water, 1-propanol + water, and 2-propanol + water systems) over the full range of composition at 25 °C and 101.325 kPa. Both the excess quantity referring to the Ostwald coefficient and that referring to the excess volume show similar minima as a function of the volume fraction of alcohol.

Introduction

The solubilities of gas in binary liquid mixtures having water as one component and alcohols as the other exhibit peculiar behavior, and the present estimation method for these solubilities in mixed solvents is not good.

In this work, solubility measurements of helium in four mixed solvents (methanol + water, ethanol + water, 1-propanol + water, and 2-propanol + water systems) were made at a temperature of 25 °C and a pressure of 101.325 kPa. Furthermore, the correlation between the excess volume for mixed solvents and the excess solubility for the solute gas in these mixtures was examined.

Experimental Apparatus and Procedure

The apparatus used in this experiment is shown in Figure 1. It is similar to that used in a previous method (1, 2) except for the use of an improved equilibrium cell, and it consists of an equilibrium cell, a cylinder-type gas holder, and a digital pressure gauge. The equilibrium cell made of Pyrex glass has three graduated tubes of 0.211-cm i.d. The equilibrium cell volume below the zero mark of the three tubes is about 200 cm³, and the upper parts of these tubes have about 8 cm³. The cylinder-type gas holder made of stainless steel for measurement of the dissolved gas volume was manufactured by Taika Kogyou Co., Ltd., and the full volume is about 80 cm³. The dissolved gas volume was measured using the displacement of the plunger, keeping a constant pressure of 101.325 kPa. The digital pressure gauge, model DG-430K, has an accuracy of ±0.01% of full scale (2.0 MPa). This digital pressure gauge was manufactured by Tokyo Aircraft Instrument Co., Ltd. The main parts of this apparatus were immersed in the constant-temperature water bath, which was regulated within 25.0 ± 0.05 °C.

The method of gas solubility measurement was similar to the static method previously used (2). The principle is as follows; a mixed solvent (alcohol + water) was degassed using a vacuum pump for 2 h with heating by a mantle heater at 50 °C. Then, the experimental apparatus was evacuated by using a vacuum pump in order to remove the moisture from the system. The degassed solvent was introduced into the equilibrium cell by a pressure difference between the degassing flask and cell. The volume of the mixed solvent was measured by using a microscope. The volume of the equilibrium cell was determined by pure water previously. On the other hand, a measured volume of solute gas was introduced into the cylinder-type gas holder, and the solute gas was contacted with degassed solvent, keeping the pressure constant at 101.325 kPa. The solution was slowly stirred until equilibrium was established, and the volume of the remaining gas in the
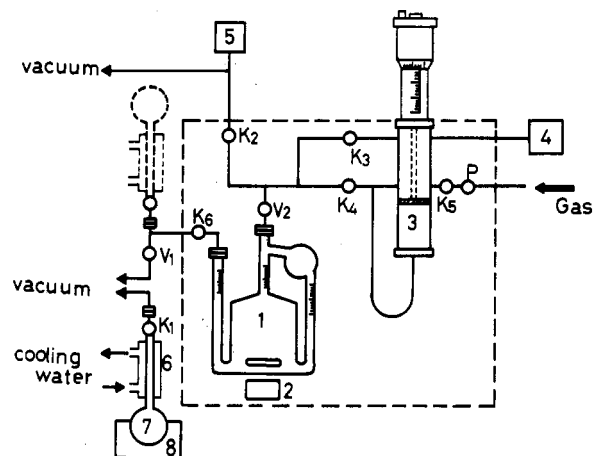

Figure 1. Schematic diagram of the experimental apparatus: (1) equilibrium cell, (2) magnetic stirrer, (3) cylinder-type gas holder, (4) digital pressure gauge, (5) manometer, (6) condenser, (7) degassing flask, (8) mantle heater, (9) constant-temperature water bath, (K₁–K₆) bellows valves, (P) pressure regulator valve, (V₁, V₂) ball valves.

Table 1. Density ρ and Refractive Index η for Pure Solvents at 25 °C

	$\rho/(\mathrm{kg \cdot m^{-3}})$		η		
	exp	lit.[a]	exp	lit.[a]	purity/%
methanol	786.20	786.74	1.3272	1.326 52	>99.98
ethanol	786.10	785.04	1.3597	1.359 41	>99.92
1-propanol	799.45	799.75	1.3830	1.383 70	>99.98
2-propanol	780.44	781.26	1.3753	1.375 2	>99.98
water	996.87	997.05	1.3326	1.332 50	>99.99

[a] Reference 7.

gas holder was measured. The density of the mixed solvent was measured using a 10 cm³ Ostwald-type pycnometer at 25 °C.

Materials

Helium gas was a high-purity gas, helium Zero-A, which was obtained from Seitets Kagaku Co., Ltd., and its purity was 99.995% by the quality guaranty.

Methanol, ethanol, 1-propanol, and 2-propanol were guaranteed reagents from Wako Pure Chemical Industry. These reagents were distilled in a fractionating column manufactured by Taika Kogyo Co., Ltd., and used for this work.

Water was purified by automatic distillation equipment and ion exchanger. The physical properties and overall accuracy of these solvents are shown in Table 1.

Table 2. Comparison of the Ostwald Coefficient L of Helium in Pure Solvents with Literature Values at 25 °C

| | L^c | | | |
	exp	lit.	$\delta^c/\%$	$\epsilon^c/\%$
water	0.0097	0.0095[a]	2.11	±2.06
methanol	0.0344	0.0357[b]	-3.64	±1.60
ethanol	0.0305	0.0321[b]	-4.98	±1.64
1-propanol	0.0264			±1.14
2-propanol	0.0315			±0.63

[a] Reference 8. [b] Reference 9. [c] $\delta = 100\{(L_{exp} - L_{lit.})/L_{lit.}\}$. $\epsilon = \pm(1/2)\cdot100\cdot\{(L_{max} - L_{min})/L_{av}\}$. $L_{av} = (1/n)\sum_{i=0}^{n} L_{exp,i}$.

Table 3. Ostwald Coefficient L of Helium in Methanol (2) + Water (3) Mixed Solvent at 25 °C and 101.325 kPa

ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L	ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L
0	996.87	0.0097	0.6931	881.40	0.0146
0.0758	986.74	0.0106	0.8741	830.50	0.0230
0.1724	974.77	0.0114	0.9394	808.47	0.0267
0.2011	970.99	0.0111	0.9561	802.48	0.0287
0.2034	970.67	0.0108	0.9666	798.62	0.0292
0.4449	933.33	0.0114	1	786.20	0.0344

The composition of mixed solvent used in each experiment was determined from its density. The densities of degassed solvent were determined using a 10 cm³ Ostwald-type pycnometer. The density data for methanol + water and ethanol + water were taken from the literature (3, 4), and for 1-propanol + water and 2-propanol + water, the values were measured in our laboratory previously.

Calculation of Gas Solubilities

The gas solubilities were expressed in terms of the Ostwald coefficient:

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

where V_{dis} is the volume of the dissolved gas and V_{sol} is the volume of the mixed solvent. For calculation of the Ostwald coefficient, the observed volume of the solute gas was converted into the value under the partial pressure of the solute gas at 101.325 kPa using eq 2, where Henry's law was assumed to apply at pressures near atmospheric. The partial pressure of solute gas, P_g, was found from eq 3, where π is the

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

assumed to apply at pressures near atmospheric. The partial pressure of solute gas, P_g, was found from eq 3, where π is the

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

total pressure at which absorption equilibrium was established and P_{sol} is the vapor pressure of mixed solvents.

The vapor pressures, P_{sol}, for methanol + water and ethanol + water were obtained from Katayama (5) and Dornte (6), respectively, and for 1-propanol + water and 2-propanol + water, they were measured in this work.

Results and Discussion

The solubilities of helium in the five pure solvents at 25 °C are given in Table 2. The reproducibilities of the solubilities were within ±2.1%, and the deviations from literature values were within ±5%, except for 1-propanol and 2-propanol for which no data were available.

The solubilities of helium in four systems of alcohol (2) + water (3) at 25 °C are given in Tables 3–6. Except for the ethanol solutions, the maximum and minimum values on the solubility curves were found in the range of volume fraction
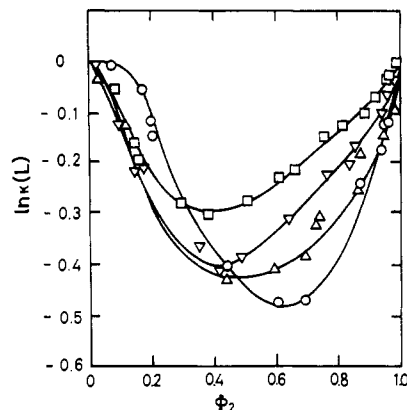

Figure 2. Experimental values of ln $\kappa(L)$ and best fit lines of eq 5 for helium in four aqueous alcohol solutions at 25 °C: (O) methanol + water; (△) ethanol + water; (□) 1-propanol + water; (▽) 2-propanol + water.

Table 4. Ostwald Coefficient L of Helium in Ethanol (2) + Water (3) Mixed Solvent at 25 °C and 101.325 kPa

ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L	ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L
0	996.87	0.0097	0.7416	865.92	0.0167
0.0233	995.37	0.0096	0.8660	829.96	0.0203
0.1115	984.67	0.0097	0.8706	828.54	0.0219
0.4434	933.37	0.0105	0.9462	804.31	0.0248
0.5976	901.60	0.0128	0.9837	791.70	0.0273
0.6975	877.50	0.0147	1	786.10	0.0305

Table 5. Ostwald Coefficient L of Helium in 1-Propanol (2) + Water (3) Mixed Solvent at 25 °C and 101.325 kPa

ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L	ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L
0	996.87	0.0097	0.7566	863.88	0.0178
0.0852	988.37	0.0100	0.8196	848.13	0.0194
0.1434	980.85	0.0095	0.8908	830.39	0.0213
0.1574	978.97	0.0093	0.9257	821.64	0.0228
0.2949	958.81	0.0098	0.9594	812.77	0.0245
0.3842	943.89	0.0105	0.9765	807.75	0.0251
0.5065	920.82	0.0122	0.9920	802.64	0.0261
0.6074	899.33	0.0141	1	799.45	0.0264
0.6613	886.95	0.0151			

Table 6. Ostwald Coefficient L of Helium in 2-Propanol (2) + Water (3) Mixed Solvent at 25 °C and 101.325 kPa

ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L	ϕ_2	$\rho_{23}/(\text{kg·m}^{-3})$	L
0	996.87	0.0097	0.7609	851.46	0.0189
0.0172	994.66	0.0098	0.8309	832.04	0.0209
0.0882	985.74	0.0095	0.8501	826.60	0.0222
0.1437	978.25	0.0092	0.9424	800.20	0.0265
0.1740	973.96	0.0096	0.9577	795.55	0.0280
0.3543	944.88	0.0102	0.9804	788.08	0.0297
0.4175	933.08	0.0105	0.9939	783.02	0.0306
0.4858	919.26	0.0117	1	780.44	0.0315

of $\phi_2 < 0.3$. For the aqueous ethanol system, these extreme values did not explicitly appear. The solubilities in these mixed solvents increased monotonously with increasing alcohol volume fraction over the composition range of about $0.3 < \phi_2 \leq 1.0$.

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

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

The observed excess values calculated by use of eq 4 are plotted for four aqueous alcohol solutions in Figure 2, and these values were fitted by the following polynomial expression

Table 7. Constants in Equation 5 and Average Deviations between the Observed Values and the Value Calculated from Equation 5

	A	B	C	D	$\delta_{av}{}^a$
methanol + water	0.684 116	-9.322 21	11.9942	-6.376 47	1.62
ethanol + water	-0.638 925	-8.005 08	17.4683	-11.605 7	2.20
1-propanol + water	-0.794 434	-5.100 86	13.0075	-8.431 58	0.90
2-propanol + water	-1.126 66	-5.043 82	12.8093	-8.699 23	1.12

$$^a \, \delta_{av} = (1/n)100\sum_{i=1}^{n}\{(|\ln \kappa(L_{cal})-\ln \kappa(L_{exp})|)/\ln \kappa(L_{exp})\}.$$
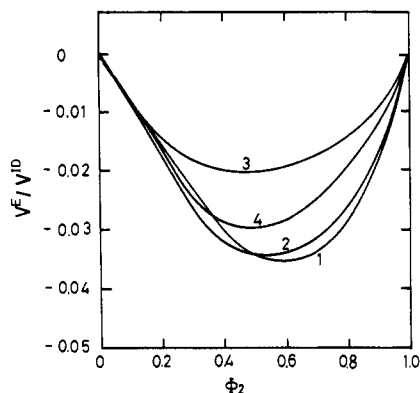
Figure 3. Ratio of the excess molar volume to the volume of an ideal mixture for aqueous alcohol solutions at 25 °C: (1) methanol + water, (2) ethanol + water (3) 1-propanol + water (4) 2-propanol + water.

of the Redlich–Kister type:

$$\ln \kappa(L) = \phi_2\phi_3(A + B\phi_2 + C\phi_2{}^2 + D\phi_2{}^3) \tag{5}$$

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 7.

The values of ln $\kappa(L)$ were given by peculiar concave curves for each system (Figure 2), and these curves had minimum values at the particular composition of mixed solvents. The minimum values of ln $\kappa(L)$ for four systems increased in the following order: 1-propanol < 2-propanol < ethanol < methanol.

On the other hand, for the nonideality of mixed solvents, the ratio of excess molar volume to the volume of an ideal mixture as expressed by eq 6 was used.

$$V^E/V^{ID} = V^E/\sum_{i=2}^{3}x_iV_i \tag{6}$$

The values of V^E/V^{ID} were calculated from the density data at 25 °C. The relation between V^E/V^{ID} and alcohol composition in aqueous alcohol solutions is shown in Figure 3. In this figure, the shape of these curves and alcohol concentration showing the minimum excess quantities are similar to those in Figure 2.

For solubilities of nitrogen, oxygen, and carbon dioxide in the same aqueous alcohol solution, this similarity has been found in previous work (2).

The agreement between the experimental solubilities in this work and the ones estimated from eqs 4 and 5 using constants reported in this paper was satisfactory, and the average deviations in the excess quantities were within 3.0%.

Glossary

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 points
P	pressure
V	molar volume or volume
x	mole fraction
δ	deviation
ϵ	reproducibility
η	refractive index
κ	excess quantity defined by eq 4
ρ	density
ϕ	volume fraction

Subscripts

1	solute gas
2	alcohol
3	water
av	average of experimental data
dis	dissolve
exp	experimental value
lit.	literature value
max	maximum value
min	minimum value
sol	solution

Superscripts

E	excess
ID	ideal

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