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The Solubility of (Biphenyl, Naphthalene)-(Benzene, Cyclohexane, 1-Octanol) Binary Mixtures in Water

Isao SANEMASA,* Masaya KUMAMARU, Kazunari ISHIBASHI, and Toshio DEGUCHI
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860
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The solubility in water at 25 °C of binary mixed solutes, combinations of biphenyl and naphthalene with benzene, cyclohexane, and 1-octanol, was measured using a shake-flask method. As a function of biphenyl or naphthalene mole fraction, activity coefficients of biphenyl and naphthalene in benzene, cyclohexane, and 1-octanol, and those of benzene in biphenyl-benzene and naphthalene-benzene binary systems have been determined.

The solubility of hydrocarbons in water is still an important physicochemical property, and a large number of data have been accumulated. Most of the available data are concerned with the solubility of pure compounds, and there are only a few reports concerning the aqueous solubility of mixed solutes. For a better understanding of natural environment, it is essential to study mixed solute systems, since mixed organic compounds rather than a single solute is what we encounter in reality, e.g., spilled oil on water surface.

The study of aqueous solubility of binary organic solutes is also important in considering partition of an organic solute between aqueous and organic phases. The partition coefficient of a chemical is thought to be a measure of its relative hydrophobicity and considered to be a significant factor of bioaccumulation: the chemical with a large partition coefficient is likely to be accumulated into fish body.[1—3]

The object of this work is to determine activity coefficients of biphenyl and naphthalene in benzene, cyclohexane, 1-octanol, and water by measuring the solubility of these solid solutes in water.

Experimental

Materials. Deionized redistilled water was used throughout this work. Biphenyl, naphthalene, benzene, cyclohexane, and 1-octanol were of analytical reagent grade and used without further purification.

Apparatus and Procedures. Aqueous solutions saturated with binary solute mixtures were prepared in a glass vessel consisting of two parts. The upper part (300 cm^3 capacity) and the lower part (200 cm^3 capacity) were connected by a ground glass joint with stopcock. A side-arm with a stopcock was attached to the lower bottle at 2 cm above the bottom. The binary solute mixture (20—30 cm^3) was placed with 100 cm^3 of water in the lower bottle and the vessel was immersed up to above the stopcock of the joint in a water bath thermostated at 25.0±0.1 °C. The stopcock was closed and the contents were stirred for at least 24 h by a Teflon-coated magnet in the bottom. The vessel was then allowed to stand for at least 24 h without stirring and taken out of the bath. The upper part of the vessel was lightly evacuated through a stopcock attached to the top of the vessel. The top stopcock was closed, then the middle one with the joint was temporarily opened to reduce pressure inside the lower bottle, and air was carefully introduced into the bottle through the side arm by operating its stopcock to remove any solute droplets present inside the side arm. Then, the vessel was immersed again in the bath and stood for 24 h. A portion of the aqueous solution was withdrawn via the side arm, weighed, and extracted with cyclohexane.

The UV absorption of the extract was examined for biphenyl, naphthalene, and benzene at 247.5, 285, and 254 nm, respectively, on a Hitachi 100-50 spectrophotometer. The absorbance of benzene at 285 nm is practically negligible, while that of naphthalene at 254 nm cannot be neglected. Correction for naphthalene absorbance was made on benzene measurements; the contribution of naphthalene amounted to 3—20% depending on the relative concentration of naphthalene and benzene in the cyclohexane extract.

Because of a relatively high solubility of benzene in comparison with biphenyl, the absorbance of benzene at 247.5 nm is very strong, and hence, biphenyl cannot be determined directly on the cyclohexane extract. We overcame this problem by making use of the fact that in the presence of β-cyclodextrin the volatilization rate of benzene from aqueous into gaseous phase is much larger than that of biphenyl: Biphenyl forms more stable 1:1 complex with β-cyclodextrin than benzene does.[4] A 20 cm^3 portion of the aqueous solution containing biphenyl and benzene was taken into a cylindrical test tube (100 cm^3), to which 5 cm^3 of β-cyclodextrin (10^{-2} mol dm^{-3}) was added. The test tube was immersed in a water bath at 25.0±0.1 °C, and nitrogen was bubbled in the solution through a sintered glass ball at a rate of 500 cm^3 min^{-1} for 30 min. The content was diluted with water to 80 cm^3, and extracted with cyclohexane. Under the N_2 bubbling condition, 98.0% of benzene present initially was driven out of the solution, while 62.0% of biphenyl remained in the solution.

The absorbance of biphenyl at 254 nm cannot be neglected, and its correction was made on benzene measurements: the contribution of biphenyl was in 3—30% range.

Results and Discussion

Solubility in water of benzene, biphenyl, and naphthalene in binary mixtures was measured at 25 °C, but that of cyclohexane and 1-octanol was not measured. The results are shown in Figs. 1 and 2 as a function of biphenyl or naphthalene mole fraction. These solubility data were treated by the curve-fitting method as follows:

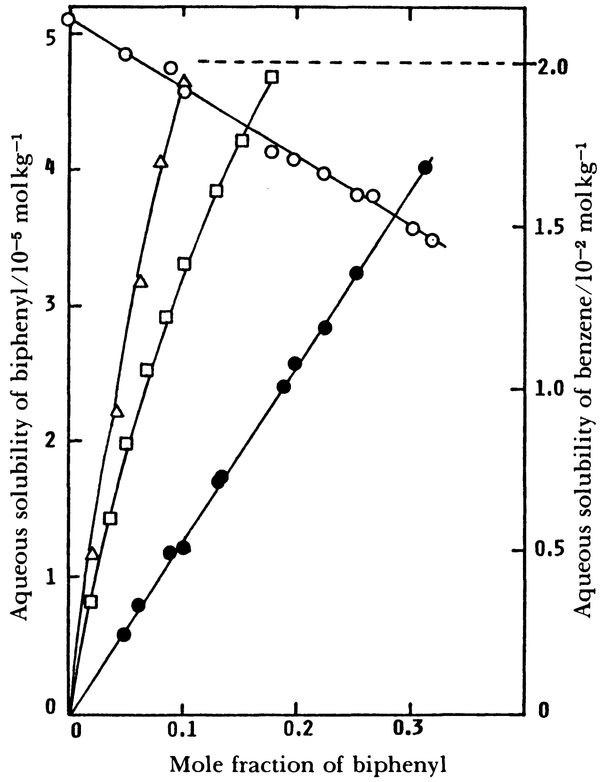

Fig. 1. Biphenyl-(benzene, cyclohexane, 1-octanol) binary systems at 25 °C. Aqueous solubility of biphenyl; ●: benzene system, □: cyclohexane system, △: 1-octanol system. Aqueous solubility of benzene; ○: biphenyl-benzene system. The dotted horizontal line shows the aqueous solubility of biphenyl determined at 25 °C for the solid solute.

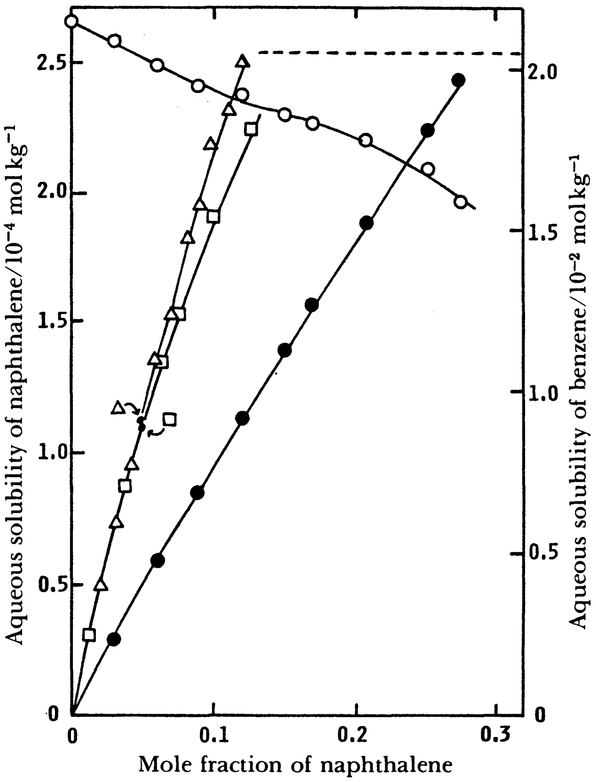

Fig. 2. Naphthalene-(benzene, cyclohexane, 1-octanol) binary systems at 25 °C. Aqueous solubility of naphthalene; ●: benzene system, □: cyclohexane system, △: 1-octanol system. Aqueous solubility of benzene; ○: naphthalene-benzene system. The dotted horizontal line shows the aqueous solubility of naphthalene determined at 25 °C for the solid solute.

benzene solubility;

$5.55\times10^{3}X_{w}=-2.15X_{o}+2.14$
(biphenyl-benzene system),

biphenyl solubility;

$5.55\times10^{6}X_{w}=12.8X_{o}-0.015$
(biphenyl-benzene system),
$5.55\times10^{6}X_{w}=-90.44X_{o}^{2}+41.45X_{o}+0.07327$
(biphenyl-cyclohexane system),
$5.55\times10^{6}X_{w}=-150.4X_{o}^{2}+60.98X_{o}-0.007946$
(biphenyl-1-octanol system),

naphthalene solubility;

$5.55\times10^{5}X_{w}=-3.812X_{o}^{2}+9.884X_{o}-0.0001182$
(naphthalene-benzene system),
$5.55\times10^{5}X_{w}=-57.10X_{o}^{2}+24.92X_{o}+0.001489$
(naphthalene-cyclohexane system),
$5.55\times10^{5}X_{w}=-33.27X_{o}^{2}+24.90X_{o}+0.0003351$
(naphthalene-1-octanol system),

where X_w is the aqueous solubility in mole fraction and X_o is mole fraction of biphenyl or naphthalene in the binary system. The results are summarized in Tables 1 and 2.

From equilibrium thermodynamics, the activity of a given solute is equal in both phases, then,

$$X_{w}\gamma_{w}=X_{o}\gamma_{o}, \tag{1}$$

where γ_w and γ_o are activity coefficients of a solute in the aqueous and the organic solvent phases, respectively. According to the literature,[5–8] the biphenyl-benzene system shows very small positive deviation from Raoult's law. It is, however, difficult to discriminate this small deviation from solubility measurements, because a relatively large error is unavoidable in solubility measurements. The X_w vs. X_o plots being linear, we assume this system as an ideal one: the γ_o values for benzene and biphenyl in the binary system are taken to be unity. From the reciprocal slope of the straight line, activity coefficients of biphenyl and benzene in water at 25 °C are evaluated to be 4.33×10^{5} and 2.58×10^{3}, respectively. Using these values as γ_w, the activity coefficient of biphenyl in the binary system with cyclohexane or 1-octanol and that of benzene in the binary system with naphthalene can be determined at any composition, X_o, with the aid of Eq. 1. The results are given in Table 2.

On the other hand, though there is a report from vapor pressure measurements of benzene to support that naphthalene forms an ideal solution with benzene,[9] it seems reasonable to consider from the data on the solubility of naphthalene in benzene[10,11] that this system is not ideal, but exhibits more positive deviation from Raoult's law in comparison with the biphenyl-benzene system. We, therefore, determined γ_w for naphthalene from the equation,[12]

$$\ln(X_w\gamma_w)=\ln(f_s/f_l)=\Delta H_f(T_m^{-1}-T^{-1})R^{-1}, \qquad (3)$$

where f_s and f_l are the fugacity of pure solid naphthalene and its supercooled liquid, ΔH_f is the heat of fusion of naphthalene, T_m is the melting temperature, T is the temperature of the system, and R is the gas constant. The data are available in the literature,[13] ΔH_f=18.979 kJ mol^{-1} and T_m=353.43 K, then, the activity coefficient of naphthalene in water is evaluated to be 6.68X10^4 at 25 °C using 4.52X10^{-6} as X_w. Using this value, activity coefficients of naphthalene in benzene, cyclohexane, and 1-octanol are determined from Eq. 1. The results are given in Tables 1 and 2.

The activity coefficient of a solute in binary mixtures has been usually determined by measuring vapor pressure of the constituent solute. In the system, however, where a solid solute is concerned, as in the pres-

Table 1. (Biphenyl, Naphthalene)-Benzene Binary Mixed Solute Solutions, the Aqueous Solubility at 25 °C and the Activity Coefficient in the Binary Mixtures

X_o[a)]	Aqueous solubility		Activity coefficient[c)]	
	Biphenyl	Benzene[b)]	Naphthalene	Benzene
	10^{-5} mol kg^{-1} or Naphthalene 10^{-4} mol kg^{-1}	10^{-2} mol kg^{-1}		
Biphenyl-benzene system				
0		2.14		
0.01	0.113	2.12		
0.05	0.625	2.03		
0.1	1.27	1.92		
0.15	1.91	1.82		
0.2	2.55	1.71		
0.25	3.19	1.60		
0.3	3.83	1.50		
0.35	4.47	1.39		
	4.75[d)]	1.40[d)]		
Naphthalene-benzene system				
0		2.14		1.00
0.01	0.0983	2.12	1.18	1.00
0.025	0.245	2.09	1.18	1.00
0.05	0.485	2.03	1.16	0.999
0.075	0.720	1.97	1.15	0.995
0.1	0.950	1.93	1.14	1.00
0.125	1.18	1.90	1.13	1.01
0.15	1.40	1.86	1.12	1.02
0.175	1.61	1.82	1.10	1.03
0.2	1.82	1.79	1.09	1.05
0.225	2.03	1.75	1.08	1.06
0.25	2.23	1.68	1.07	1.05
0.275	2.43	1.59	1.06	1.02
	2.52[d)]	1.60[d)]		

a) Mole fraction of biphenyl or naphthalene in benzene. b) Aqueous solubility of benzene in the naphthalene-benzene system at a given X_o was estimated from the solubility curve shown in Fig. 2. c) The biphenyl-benzene system is assumed to be ideal. d) These values were obtained in the excess of the solid solute, that is, the biphenyl or naphthalene phase appears separated from the organic liquid phase.

Table 2. (Biphenyl, Naphthalene)-(Cyclohexane, 1-Octanol) Binary Mixed Solute Solutions, the Aqueous Solubility at 25 °C and the Activity Coefficient of Biphenyl or Naphthalene in the Binary Mixtures

X_o[a)]	Aqueous solubility[b)]		Activity coefficient[b)]
	Biphenyl	Naphthalene	
	10^{-5} mol kg^{-1}	10^{-4} mol kg^{-1}	
Biphenyl-cyclohexane system			
0.01	0.479		3.73
0.025	1.05		3.27
0.05	1.92		2.99
0.075	2.67		2.77
0.1	3.31		2.58
0.125	3.84		2.39
0.15	4.26		2.21
0.175	4.56		2.03
0.25	4.75		1.48
	4.77[c)]		
Biphenyl-1-octanol system			
0.01	0.587(0.776)		4.57(4.54)
0.02	1.15(1.50)		4.48(4.41)
0.03	1.69(2.17)		4.37(4.27)
0.04	2.19(2.78)		4.26(4.12)
0.05	2.67(3.34)		4.15(3.97)
0.06	3.10(3.85)		4.03(3.82)
0.07	3.52(4.30)		3.92(3.67)
0.08	3.91(4.70)		3.80(3.52)
0.09	4.26		3.68
0.1	4.59		3.57
	4.72[c)]		
Naphthalene-cyclohexane system			
0.01		0.245	2.94
0.025		0.589	2.83
0.05		1.10	2.64
0.075		1.55	2.48
0.1		1.92	2.30
0.125		2.22	2.13
		2.50[c)]	
Naphthalene-1-octanol system			
0.01		0.246(0.325)	2.95(2.94)
0.02		0.485(0.636)	2.91(2.88)
0.03		0.717(0.934)	2.87(2.83)
0.04		0.943(1.22)	2.83(2.78)
0.05		1.16(1.49)	2.78(2.73)
0.06		1.37(1.75)	2.75(2.67)
0.07		1.58(1.99)	2.71(2.62)
0.08		1.78(2.23)	2.67(2.57)
0.09		1.97(2.45)	2.63(2.52)
0.1		2.16	2.59
		2.51[c)]	

a) Mole fraction of biphenyl or naphthalene in cyclohexane or 1-octanol. b) The aqueous solubility and the activity coefficient of biphenyl or naphthalene shown in the parentheses are those correspond to X_o^*, mole fraction of biphenyl or naphthalene in 1-octanol saturated with water. c) See footnote. d) In Table 1.

ent cases, the vapor pressure of the solid solute is too low to be accurately measured, and hence, only that of the solvent is measured. Then, the activity coefficient of the other less volatile component is estimated indirectly by means of the Gibbs-Duhem transformation. In contrast to this, the present approach gives direct information concerning the solid solute. There is, however, inevitable disadvantage in the present method that the system is not binary in a strict sense but ternary, because water itself participates more or less in the system. This seems not to be a serious problem when benzene or cyclohexane is used as a constituent component of binary systems.[14,15] This is, however, not the case for 1-octanol because the solubility of water in 1-octanol is very high.

The solubility of water in 1-octanol is reported to be 0.25 mole fraction at 25 °C.[16] This water content being considered, the mole fraction of a solute in water-free 1-octanol, X_o, should be corrected: $X_o = X_o^*/(0.75+0.25X_o^*)$,[17] where X_o^* refers to the mole fraction in water-saturated 1-octanol. Activity coeficients, corrected for water in 1-octanol, are given in Table 2.

The 1-octanol/water partition coefficient, $K_{o/w}$, is commonly defined as follows:

$$K_{o/w} = C_o/C_w = \gamma_w^* \bar{V}_w^* / (\gamma_o^* \bar{V}_o^*), \tag{4}$$

where C_o and C_w denote the molar concentration of a solute in 1-octanol saturated with water and that in water saturated with 1-octanol, respectively. The activity coefficient of a solute in water saturated with 1-octanol, γ_w^*, can be made equal to γ_w, and the partial molar volume of water saturated with 1-octanol, $\bar{V}_w^*$, can also be made equal to the molar volume of water,[18] because the solubility of 1-octanol in water is low. Using 0.018 $dm^3 mol^{-1}$ as $\bar{V}_w$ and 0.12 $dm^3 mol^{-1}$ as $\bar{V}_o^*$,[18] log $K_{o/w}$ values are found to be 4.1 for biphenyl and 3.5 for naphthalene. Here we used γ_o^* of 4.74 for biphenyl and 2.96 for naphthalene, which are estimated at infinite dilution of X_o^*, that is, $(\gamma_o^*)_{X_o^* \to 0}$. These log $K_{o/w}$ values obtained are comparable with those in the literature, 4.09 (biphenyl) and 3.36 (naphthalene).[18]

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17) This relation is drawn by combining three equations: $X_o = n_2/(n_1+n_2)$, $X_o^* = n_2/(n_1+n_2+n_3)$, and $X_3 = n_3/(n_1+n_3) = 0.25$, where subscripts 1, 2, and 3 refer to 1-octanol, solute, and water, respectively.

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