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The Solubility of Benzene–Hydrocarbon Binary Mixtures in Water

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The solubility in water at 25.0 °C of benzene-hydrocarbon binary mixtures has been studied for different ratios between benzene and toluene, ethylbenzene, (*o*-, *m*-, *p*-)xylene, propylbenzene, chlorobenzene, and cyclohexane. Aqueous solutions saturated with mixed solutes were prepared by making use of the solute vapor. The solubility of individual constituent in the binary mixture was found to change linearly with mole fraction over a whole range of the composition. This is not the case for the benzene-cyclohexane system: the solubility of each component deviates positively from the linear change of solubility with composition. The solubility of each component of benzene-1-octanol mixture in water was also measured by adding the mixture of various compositions directly to water. The positive deviation for the solubility of each component was observed. The relationship between the 1-octanol/water partition coefficient of a solute and the aqueous solubility of pure liquid solute which forms a nonideal solution in 1-octanol was discussed.

We have previously reported a method of preparing aqueous solutions saturated with a solute such as benzene and alkylbenzenes.[1] The solute vapor in equilibrium with liquid solute is introduced into water and circulated in a closed system. The experimental characteristic of this method is that the equilibrium of the solute at different desired concentrations can be attained rapidly by adjusting the temperature of solute phase separated from aqueous phase, while the temperature of the aqueous phase is kept constant. We have demonstrated by this technique that the equilibrium solubility of sparingly soluble solutes in water changes linerly with the solute vapor pressure, in other words, the solubility obeys Henry's law.[1–3]

We will report further application of the method. Instead of changing the temperature of single liquid solute, mixed binary solutes of various compositions are used. The vapor pressure of the constituent solute varies with mole fraction in the mixed solute phase. The equilibrium solubility of each constituent is measured as a function of the mole fraction. We assume that Henry's law is applied to individual solute, because the concentration of solute in aqueous phase is usually very low. When Raoult's ideal solution law is held to mixed solute, the equilibrium solubility of the constituent solute in water is expected to be proportional to the mole fraction of solute mixture.

The solubility of a large variety of hydrocarbons has been extensively studied to accumulate data. There are, however, only a few reports concerning the aqueous solubility of mixed solutes in different composition. It is important to know what is the critical factor in determining the aqueous solubility of the constituent solute, because mixture of organic compounds rather than a solute is what we encounter in the natural aqueous environment, 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 in aqueous and organic phases. Partition coefficients of a number of chemicals in organic solvent and water, especially in 1-octanol/water system, have been extensively studied. The partition coefficient of the molecule is a measure of its relative solubility in two solvents; the coefficient has been determined under the condition that the solute concentration is extreamely low. When the solute forms a nonideal solution with organic solvent, we need to know how aqueous solubility of the solute changes with its concentration in the organic layer and what is the dominant factor in the aqueous solubility. Is there any solubilization effect of 1-octanol dissolved in water? The effect is probable only when there is an appreciable octanol-solute interaction in aqueous solution.[4] The benzene-1-octanol binary mixture was studied from interest in these problems.

Experimental

Materials. Deionized re-distilled water was used throughout this work. Benzene (99.5%), toluene (99%), ethylbenzene (98%), (*o*-, *m*-, and *p*-)xylene (each 98%), propylbenzene (97%), chlorobenzene (99%), cyclohexane (98%), and 1-octanol (95%) of analytical reagent grade with the minimum purity in the parentheses were used as solutes without further purification. When 1-octanol was used to prepare calibration curves for determining its concentrations in aqueous and benzene-1-octanol phases after equilibrium, 1-octanol was purified by distillation under reduced pressure.

Apparatus and Procedures. The apparatus used for preparing aqueous solutions saturated with solute vapor was essentially the same as that previously reported.[1]

The apparatus is composed of two main parts: A separatory funnel (300 cm^3) with a surrounding jacket and a pear-shaped flask (50 cm^3) which is immersed in a thermostated bath. We will call the former "solubility flask," and the latter "solute reservoir." These were connected to each other with Teflon or glass tubes. Water of 100 cm^3 and a binary liquid hydrocarbon mixture of 10 cm^3 were placed in the solubility flask and in the solute reservoir, respectively. The temperature of thermostated bath was kept at 25.0±0.1 °C, and that of solubility flask was also held at the same temperature by circulating water from the bath through surrounding jacket. The assembled apparatus was placed in a chamber, whose temperature was kept a little higher than 25 °C to avoid condensation of the solute vapor inside the apparatus. The solute vapor generated by bubbling air through the solute reservoir via a sintered glass ball was introduced into the solubility flask by a Viton diaphragm airpump and was circulated at 1.5 dm^3 min^{-1}.

After the solubility equilibrium was attained (it takes 10 min), each 30 cm^3 portion of the aqueous solution was transferred successively by a stopcock attached to the bottom of solubility flask into three cylindrical separatory funnels of 50 cm^3 capacity, to which each 5 cm^3 volume of an extractant had been placed in advance. The organic extracts were analyzed by a Hitachi 164 gas chromatograph (column packing, PEG-1000; detector, hydrogen flame ionization). Cyclohexane or benzene was used as extractant; the latter was used only in the case of analyzing cyclohexane in benzene–cyclohexane system. A suitable volume of internal standard had been previously added to the extractant; *p*-xylene was used in benzene–toluene and benzene–cyclohexane systems, toluene in other systems.

The composition of mixed solute in the solute reservoir was analyzed in the following way. After the solubility equilibrium had been attained, a 5 cm^3 portion was pipetted off from the solute reservoir, diluted to 25 cm^3 with the same solvent used in extracting the solute from aqueous phase, and analyzed by gas chromatography. In this case, the solvent itself serves as an internal standard.

In the case of benzene–1-octanol system, an aqueous solution saturated with 1-octanol was not obtaied by the solute vapor circulation technique mentioned above. Then, each 60 cm^3 of mixed solute of various compositions was added to water (200 cm^3) in a 360 cm^3 glass bottle with a stopper and equilibrated by stirring overnight with a Teflon-enclosed magnet in a thermostated bath at 25.0±0.1 °C. The bottle was designed to make it easy to take out the aqueous solution through a stopcock attached to bottle side near the bottom. The solutes in 20 cm^3 portions of the aqueous solution were extracted with cyclohexane containing an internal standard and analyzed by gas chromatography. As the internal standard, toluene was used to analyze benzene and 1-hexanol to analyze 1-octanol. The solute phase after equilibrium was also analyzed by gas chromatography to determine the composition. A 5 cm^3 portion of the solute phase was taken out of the bottle and diluted to 25 cm^3 with cyclohexane which serves as internal standard.

Results

The Time Required for Attaining the Solubility Equilibrium. Aqueous solution to be saturated with solute vapor reached equilibrium with each solute of the binary mixture after 10 min at a circulation rate of vapor of 1.5 dm^3 min^{-1} (Fig. 1). In the case of benzene–1-octanol system, it was also confirmed that overnight stirring of the aqueous phase with the mixed solute solution is sufficient to attain equilibrium with each solute.

The Composition of Binary Solute Mixture and Solubility of Component Solutes in Water. The solubility of component solutes of binary mixture in water at 25.0 °C is given in Tables 1 to 3 and shown in Figs. 2 to 5 as a function of mole fraction of the component.

A single component solubility in water at 25.0 °C determined by circulating the solute vapor was 2.07×10^{-2} (benzene), 5.65×10^{-3} (toluene), 1.37×10^{-3} (ethylbenzene), 1.68×10^{-3} (*o*-xylene), 1.33×10^{-3} (*m*-xylene), 1.51×10^{-3} (*p*-xylene), 4.15×10^{-4} (propylbenzene), 3.78×10^{-3} (chlorobenzene), and 6.27×10^{-4} mol dm^{-3} (cyclohexane) and that determined by adding liquid solute directly to water was 2.22×10^{-2} (benzene) and 4.11×10^{-3} mol dm^{-3} (1-octanol). These values are in reasonable agreement with our previous estimations and with literature values.[1,5,6)]

Discussion

The Technique to Prepare Aqueous Solutions Saturated with Solutes. Two techniques were used to prepare aqueous solutions saturated with solute: the circulation of solute vapor and the direct addition of liquid solute into water. The solubility of benzene determined by the latter technique was about 10% higher than that obtained by the former one. It is difficult at present to explain this discrepancy, but we suppose that the direct contact of liquid solute with water is liable to overestimated solubility due to formation of solute micro-emulsion dispersed in aqueous solution. The former technique being applied to the benzene–1-octanol system, the aqueous phase was saturated with benzene after circulation for 15 min, while the 1-octanol-saturated solution was not obtained even after 5 h at the same circulation rate. We first thought that the vapor circulation technique is inadequate for this system, because water dissolved in 1-octanol during circulation may prevent vaporization of 1-octanol (the solubility of water in 1-octanol is considerably high). Then, we tried to saturate water with 1-octanol vapor as follows; nitrogen gas was made to flow through the reservoir containing 1-octanol purified by distillation via a sintered glass ball or a glass capillary and introduced into the solubility flask. This technique, which we call the open method, gave aqueous solutions saturated with various solutes in the previous work.[1)] In the case of 1-octanol, however, the

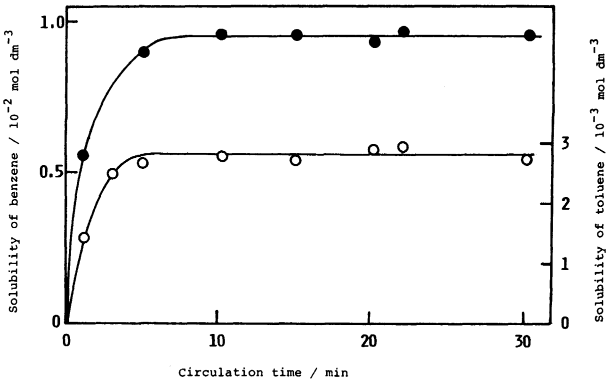

Fig. 1. The effect of the mixed solute vapor circulation time on the constituent solute solubility in water. The aqueous solubilities of benzene (●) and toluene (○) at 25°C. Mole fraction of benzene in the binary mixture is set at 0.48.

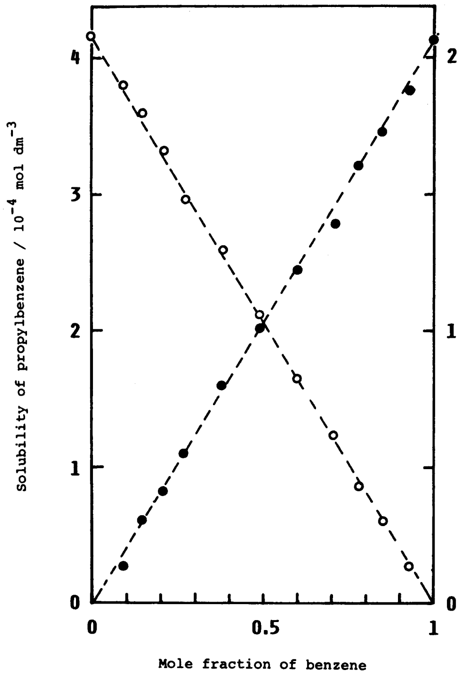

Fig. 2. Benzene-propylbenzene binary system. Aqueous solubilities of benzene (●) and propylbenzene (○) at 25°C as a function of the solute composition in the binary mixture.

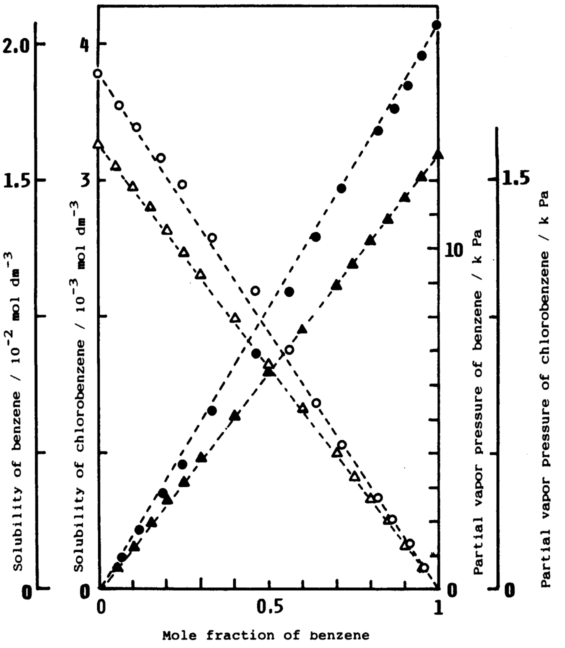

Fig. 3. Benzene-chlorobenzene binary system. Aqueous solubilities of benzene (●) and chlorobenzene (○) at 25°C and partial vapor pressures of benzene (▲) and chlorobenzene(△) at 25°C as a function of the solute composition in the binary mixture (the vapor pressure data taken from Ref. 10).

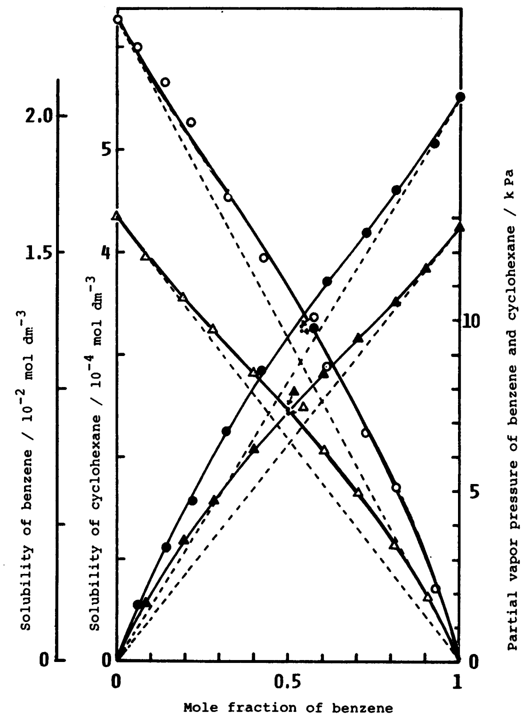

Fig. 4. Benzene-cyclohexane binary system. Aqueous solubilities of benzene (●) and cyclohexane (○) at 25°C and partial vapor pressures of benzene (▲) and cyclohexane (△) at 25°C as a function of the solute composition in the binary mixture (the vapor pressure data taken from Ref. 12).

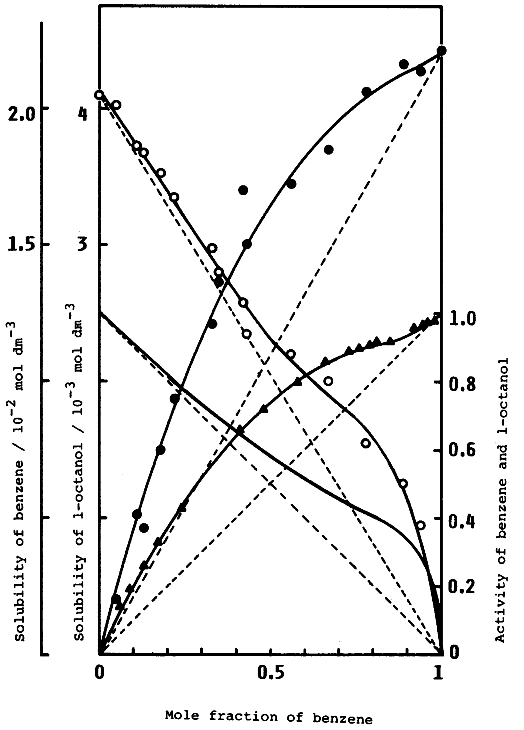

Fig. 5. Benzene-1-octanol binary system. Aqueous solubilities of benzene (●) and 1-octanol (○) at 25°C and activities of benzene(▲) and 1-octanol (△) at 20°C as a function of the solute composition in the binary mixture (the activity data taken from Ref. 14).

Table 1. Benzene–Toluene, –Ethylbenzene, –*o*-Xylene, –*m*-Xylene, –*p*-Xylene, –Propylbenzene, and –Chlorobenzene Binary Mixed Solute Solutions, the Aqueous Solubilities of Benzene and the Hydrocarbons at 25 °C as a Function of the Solute Composition in the Binary Mixtures

Mole fraction		Solubility/ 10^{-3} mol dm^{-3}	
C_6H_6	The other component	C_6H_6	The other component
	Benzene–Toluene		
0	1.000	0	5.65
0.040	0.960	0.750	5.20
0.170	0.830	3.50	4.60
0.290	0.710	6.50	3.66
0.440	0.560	8.40	3.29
0.497	0.503	9.50	2.74
0.618	0.382	13.1	2.16
0.673	0.327	13.4	1.83
0.702	0.298	14.2	1.67
0.833	0.167	17.4	0.959
0.916	0.084	18.1	0.459
1.000	0.000	20.7	0
	Benzene–*o*-xylene		
0	1.000	0	1.68
0.076	0.924	1.52	1.57
0.135	0.865	3.03	1.42
0.243	0.757	5.56	1.24
0.392	0.608	8.12	1.03
0.473	0.527	10.3	0.869
0.576	0.424	12.2	0.721
0.695	0.305	14.4	0.537
0.768	0.232	16.4	0.391
0.831	0.169	17.9	0.264
0.923	0.077	19.8	0.129
1.000	0	20.7	0
	Benzene–*p*-xylene		
0	1.000	0	1.51
0.079	0.921	1.45	1.38
0.151	0.849	2.87	1.28
0.265	0735	5.44	1.11
0.400	0.600	7.92	0.914
0.495	0.505	9.97	0.775
0.580	0.420	12.1	0.629
0.690	0.310	14.1	0.498
0.773	0.227	15.6	0.344
0.853	0.147	17.5	0.236
0.914	0.086	19.0	0.113
0.958	0.042	20.3	0.0630
1.000	0	20.7	0
	Benzene–chlorobenzene		
0	1.000	0	3.78
0.068	0.932	1.16	3.55
0.114	0.886	2.20	3.39
0.185	0.815	3.51	3.16
0.247	0.753	4.57	2.97
0.334	0.666	6.57	2.58
0.463	0.537	8.71	2.19
0.565	0.435	10.9	1.76
0.640	0.360	12.9	1.40
0.717	0.283	14.7	1.07
0.826	0.174	16.8	0.679
0.867	0.133	17.4	0.507
0.915	0.085	18.5	0.344
0.957	0.043	19.6	0.170
1.000	0	20.7	0
	Benzene–ethylbenzene		
0	1.000	0	1.37
0.147	0.853	2.86	1.18
0.268	0.732	5.02	1.03
0.384	0.616	7.42	0.857
0.486	0.514	9.26	0.715
0.570	0.430	11.4	0.571
0.660	0.340	13.2	0.458
0.742	0.258	15.4	0.329
0.800	0.200	16.7	0.244
0.888	0.112	18.4	0.122
1.000	0	20.7	0
	Benzene–*m*-xylene		
0	1.000	0	1.33
0.072	0.928	1.56	1.21
0.139	0.861	3.05	1.18
0.208	0.792	4.15	1.03
0.268	0.732	5.23	0.974
0.322	0.678	6.60	0.878
0.385	0.615	7.84	0.839
0.494	0.506	10.1	0.681
0.594	0.406	12.1	0.548
0.687	0.313	13.7	0.423
0.773	0.227	16.4	0.337
0.854	0.146	17.9	0.201
0.929	0.071	19.4	0.104
1.000	0	20.7	0
	Benzene–propylbenzene		
0	1.000	0	0.415
0.086	0.914	1.37	0.379
0.146	0.854	3.00	0.360
0.204	0.796	4.08	0.332
0.266	0.734	5.47	0.297
0.375	0.625	7.97	0.259
0.489	0.511	10.1	0.211
0.598	0.402	12.2	0.164
0.706	0.294	13.9	0.123
0.776	0.224	16.1	0.0866
0.842	0.158	17.3	0.0600
0.925	0.075	18.8	0.0270
1.000	0	20.7	0

aqueous solution obtained in this manner was far from saturation even after 6 h at the aeration rate ranging from 0.02 to 1.5 dm^3 min^{-1}. Thus, the possibility that water in 1-octanol may prevent 1-octanol from vaporizing can be excluded. Different cause should be sought.

Concerning with the vapor circulation technique, it should be mentioned that, as was pointed out in the previous paper,[2] the liquid solute in the reservoir will gradually be in equilibrium with water during the

Table 2. Benzene-Cyclohexane Binary Mixed Solute Solution, the Aqueous Solubility and Henry's law Coefficient at 25 °C

Mole fraction		Solubility/ 10^{-3} mol dm^{-3}		Vapor pressure[a]/ kPa		K_H[b]/ 10^4 kPa	
C_6H_6	C_6H_{12}	C_6H_6	C_6H_{12}	C_6H_6	C_6H_{12}	C_6H_6	C_6H_{12}
0	1.000	0	0.627	0	13.01	—	115
0.067	0.933	2.10	0.601	1.348	12.18	3.57	113
0.149	0.851	4.26	0.567	2.768	11.21	3.61	110
0.222	0.778	5.92	0.528	3.873	10.33	3.62	109
0.325	0.675	8.40	0.455	5.253	9.27	3.48	113
0.424	0.576	10.7	0.393	6.438	8.136	3.33	115
0.541	0.459	12.0	0.323	7.727	6.946	3.58	119
0.612	0.388	14.0	0.288	8.468	6.129	3.36	118
0.725	0.275	15.8	0.222	9.636	4.809	3.38	120
0.814	0.186	17.3	0.171	10.57	3.451	3.39	112
0.924	0.076	19.0	0.073	11.79	1.475	3.45	112
1.000	0	20.7	0	12.71	0	3.41	—

a) The vapor pressure at desired mole fraction was estimated based on the data presented in Ref. 12. b) Henry's law coefficient: K_H=(vapor pressure in Pa)/(solubility in mole fraction).

Table 3. Benzene-1-Octanol Binary Mixed Solute Solution, the Aqueous Solubility at 25 °C, the Activity at 20 °C, and the Ratio

Mole fraction		Solubility/ 10^{-3} mol dm^{-3}		Activity[a]		Ratio[b]	
						10^3	10^4
C_6H_6	1-Octanol	C_6H_6	1-Octanol	C_6H_6	1-Octanol	C_6H_6	1-Octanol
0	1.000	0	4.11	—	1.00	—	1.35
0.048	0.952	2.06	4.02	0.112	0.954	3.02	1.32
0.106	0.894	5.07	3.73	0.207	0.905	2.27	1.35
0.178	0.822	7.53	3.52	0.332	0.838	2.44	1.32
0.219	0.781	9.33	3.36	0.394	0.799	2.35	1.32
0.329	0.671	12.1	2.98	0.548	0.706	2.51	1.32
0.352	0.648	13.6	2.79	0.580	0.686	2.37	1.37
0.435	0.565	15.0	2.35	0.676	0.624	2.50	1.48
0.559	0.441	17.2	2.19	0.780	0.540	2.52	1.37
0.666	0.334	18.6	2.01	0.853	0.477	2.55	1.32
0.780	0.220	20.7	1.55	0.913	0.413	2.45	1.48
0.894	0.106	21.6	1.26	0.954	0.329	2.45	1.45
0.942	0.058	21.3	0.953	0.965	0.278	2.52	1.62
1.000	0	22.2	0	1.00	—	2.50	—

a) The activity at 20 °C was evaluated at desired mole fraction from the activity vs. mole fraction curve illustrated in Ref. 14. b) The ratio of the activity at 20 °C to the aqueous solubility at 25 °C in mole fraction.

vapor circulation, and hence, the solute phase is no longer "pure" binary system. Yet we can neglect the contribution of water to the partial vapor pressure of constituent solute in the binary mixture, because the solubility of water in liquid hydrocarbons used in this study is as low as 3×10^{-3} in mole fraction.[7]

The Aqueous Solubility of Two Solutes Which Form Ideal or Near-Ideal Binary Mixtures. The solubility of the constituent solutes in the seven binary mixtures, benzene-toluene, -ethylbenzene, -(*o*-, *m*-, *p*-) xylene, -propylbenzene, and -chlorobenzene, changed almost linearly with its mole fraction over a whole range of the composition. Assuming that Henry's law holds for the dissolution of each component in water, the linear relationship between the aqueous solubility and the solute mole fraction indicates that the solute forms an ideal or nearly ideal solution with benzene.[8] In such a system, the solubility of the solute at any composition can be easily estimated by multiplying unit solubility by mole fraction of the component. It should be emphasized, however, that the mixed solute solution cannot be taken at once as being ideal, because an experimental error of 5% or so is inevitable in the solubility determinations. For instance, chlorobenzene does not form ideal solution with benzene.[9,10] Data in the literature[10] on the relationship between vapor pressure and mole fraction at 25 °C are plotted for each component in Fig. 3. The maximum deviations of vapor pressure from Raoult's law, 1.65% for chlorobenzene and 0.65% for benzene, both positive, occur at 0.5 mole fraction. The same positive deviations cannot be expected from the present study unless the accuracy of solubility measurements is improved.

The Aqueous Solubility of Two Solutes Which Form Non-Ideal Binary Mixtures. In the cases of benzene-cyclohexane and -1-octanol, the plots of the aqueous solubility of a component vs. the composition of binary solute mixture exhibit noticeable deviations from linear relationship. This arises from nonideality of these mixed solute solutions. It is well-known that benzene forms nonideal solution with cyclohexane.[11,12] We can evaluate the activity coefficients for cyclohexane, γ_a, and for benzene, γ_b, at respective mole fraction, X_a and X_b, by the equation,[13] $RT \ln \gamma_{a(b)} = X_{b(a)}^2[A_0 - A_1(1-4X_{a(b)}) + A_2(1-8X_{a(b)}+12X_{a(b)}^2)]$; the constants, A_0, A_1, and A_2 for each component are determined from the data presented in Ref. 12 to be 1318.8, −42.95, and 38.31 (cyclohexane) and 1312.9, −44.19, and 54.77 (benzene), respectively. The partial vapor pressure of the component, P_i, is expressed as $P_i = X_i \gamma_i P_i^\circ$, where X_i, γ_i, and P_i° is the mole fraction of component in the liquid solute mixture, the activity coefficient, and the pure solute vapor pressure, respectively. Figure 4 shows the partial vapor pressure as a function of the mole fraction. The solubility curve appears to be similar in shape to the corresponding vapor pressure curve. For a quantitative consideration, the ratio of the partial pressure to the equilibrium solubility in water for each component at the same mole fraction in binary mixture was determined (the ratio refers to Henry's law coefficient). We can see from Table 2 that the ratio is almost constant over a whole range of the mixed solute composition. This indicates that Henry's law is valid to the aqueous solubility of the constituent.

With respect to the benzene-1-octanol binary system, the activity of each component at 20 °C is available,[14] and literature data are plotted in Fig. 5. The activity and solubility curves for the corresponding component appear to resemble each other: both the activity and the solubility of 1-octanol change almost linearly in higher mole fraction region of 1-octanol and decrease steeply in its lower mole fraction region, while those of benzene exhibit large positive deviations from the postulated ideal linear lines in higher mole fraction region of benzene. However, as can be seen from Table 3 where ratios of the activity at 20 °C to the solubility at 25 °C are given, large discrepancies are noticeable for benzene and 1-octanol in each lower mole fraction region. These discrepancies may be attributable partly to inaccuracy of solubility measurements. It is doubtful, however, whether the activity determined in the absence of water is applicable to the present case. The water content in 1-octanol amounts to 0.25 mole fraction.[6] Yet the activity of each solute seems to dominate the aqueous solubility of benzene-1-octanol binary mixture.

The 1-Octanol/Water Partition and Aqueous Solubility of the Solute Which Forms Non-Ideal Solution with 1-Octanol. Chiou et al. have suggested a "solubilization" effect of 1-octanol;[15] the solubility of a solute in water which has been saturated with 1-octanol is larger than that in 1-octanol-free water. Miller et al., on the other hand, have demonstrated using polynuclear aromatic hydrocarbons and polychlorinated biphenyls that the presence of dissolved 1-octanol in water has little effect on the solubility of the substances in water.[4] Considerably low solubility in 1-octanol-saturated water is apparent in their data, though the authors did not mention it. This is presumably caused by the state of organic substances. The 1-octanol present saturated in water is transferred in part to the organic substances in the solid state. Then, the organic substance is no longer pure one-component system, that is, the mole fraction becomes lower than unity. This may be responsible for low solubility of the organic substances in 1-octanol-saturated water.

Our present results support Miller et al. The positive deviation of solubility of benzene in water from the ideal solubility line observed for the benzene-1-octanol system is not due to the solubilization effect by 1-octanol, but is caused by the formation of a nonideal solution from benzene and 1-octanol.

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

$$k_{o/w} = C_o/C_w, \qquad (1)$$

where C_o and C_w denote the molar concentration of solute in 1-octanol saturated with water and that in water saturated with 1-octanol, respectively. Considering mutual solubility of 1-octanol and water, an equation which correlates the partition coefficient with the solubility of pure liquid solute in water, S, was proposed by Chiou et al.[15] as follows:

$$\log K_{o/w} = -\log S - \log \bar{V}^{o*} - \log \gamma_o^* + \log(\gamma_w^*/\gamma_w), \qquad (2)$$

where $\bar{V}^{o*}$ is the partial molar volume of 1-octanol saturated with water, γ_o^* is the activity coefficient of the solute in 1-octanol saturated with water, and γ_w^* and γ_w refer to the activity coefficient of the solute in water saturated with 1-octanol and that in pure water, respectively. This equation is derived based on the assumption that the solute concentrations both in aqueous and 1-octanol phases are sufficiently low.

For various liquid solutes, especially for homologous series, the log $K_{o/w}$ vs. −log S plots have been found to be linear with inclinatios close to unity.[16] There have been published, however, some experimental data which clearly display the slopes significantly lower than unity.[4,15,16] Chiou et al. assumed that the solubilization effect of 1-octanol in water is one of the reasons of significantly lower inclination than the ideal value of −1.[15] We will propose the viewpoint that the liquid solute forms a nonideal mixed solution with 1-octanol. Let us consider the case of benzene-1-octanol. The $K_{o/w}$ of benzene, which is the reverse of tangent of aqueous solubility vs. solute concentration in 1-octanol curve at infinitely diluted with 1-octanol, is not constant, but depends on the composition of octanol phase. In practice, $K_{o/w}$ is to be measured at a definite solute composition, and $K_{o/w}$ value thus determined is always larger than that expected under infinitely diluted condition. This causes the inclination of log $K_{o/w}$ vs. $-\log S$ plot to be smaller than unity. The circumstances are reversed when the solubility of the solute in water deviates negatively from the ideal solubility. The solute composition in 1-octanol should, therefore, be as low as possible, especially in such a case that the solute-1-octanol mixed solution is far from being ideal.

The Solvent Extraction and Aqueous Solubility of the Solute to be Extracted. When the solvent extraction is considered in general under the conditions that mutual solubility of extractant and water is low and further that the solute concentration in extractant and in water is sufficiently low, Eq. 2 can be written in the form;

$$\log K_{\mathrm{org/w}} = -\log S - \log V^{\mathrm{org}} - \log \gamma_{\mathrm{org}}, \qquad (3)$$

where $K_{\mathrm{org/w}}$ is the partition coefficient of the solute between organic extractant and aqueous phase, V^{org} is the molar volume of pure extractant, and γ_{org} refers to the activity coefficient of the solute in pure extractant. Combining Eq. 1 with Eq. 3, we can derive %E, the extraction percentage of the solute from an aqueous phase of v_{w} dm^3 to an organic phase of v_{org} dm^3,

$$\%E = 100/(1 + S\, V^{\mathrm{org}}\gamma_{\mathrm{org}} v_{\mathrm{w}} v_{\mathrm{org}}^{-1}). \qquad (4)$$

This equation is useful in predicting the degree of extraction of the solute at a definite volume ratio of aqueous phase to organic phase with known values of solubility in water of pure solute to be extracted, the molar volume of pure extractant, and the solute activity coefficient in extractant. It should be emphasized that the %E depends on whether the extractant-solute system deviates positively or negatively from Raoult's law.

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