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The Vapor Saturation Method for Preparing Aqueous Solutions of Solid Aromatic Hydrocarbons

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A new method to prepare aqueous solutions saturated with solid aromatic hydrocarbons by making use of solute vapor is presented. Air is bubbled through an organic solvent in which an excess quantity of a solid hydrocarbon to be studied has been added, and the resulting vapor is introduced into water and circulated in a closed system. An aqueous solution saturated with a solid solute can thus be prepared in a short time without any need to remove solute microcrystals. Of benzene, cyclohexane, and 1-octanol used as organic solvents, 1-octanol is most promising for this purpose. Solubilities in water at 25.0 °C of nine aromatic hydrocarbons have been measured: Naphthalene, biphenyl, anthracene, phenanthrene, fluoranthene, (*o*-, *m*-, *p*-)terphenyl, and triphenylene. This method can be used for these solutes except phenanthrene.

The aqueous solubility of aromatic hydrocarbons is a fundamental physicochemical property important in both applied and theoretical chemistry. In recent years, partition studies on hydrophobic substances between 1-octanol and water have become of interest, which require convenient techniques to provide accurate solubility data.

For the preparation of aqueous solutions saturated with liquid or solid solutes, the most widely used technique is the "shake-flask" method.1—14) This technique usually consists of two steps: (1) A mixture of water and an excess quantity of a solute is mechanically shaken for at least 24 h; (2) to ensure the removal of the excess solute phase, the mixture is allowed to stand for at least 24 h, centrifuged, or filtered. The second step is important in solubility measurements since hydrocarbons can exist in colloidal, micellar, or microparticulate form in appreciable quantities.

In order to speed up these time-consuming steps, the "generator column" method has recently been proposed.15—19) This method adopts continuous pumping of water through a column filled with an inert support material, such as glass or quartz beads, coated with the solute of interest. When this method is combined with a second column packed with a hydrophobic support, the dissolved solute can be easily concentrated, and, moreover, in conjunction with the chromatographic technique, impurities in the solute material, when present, can be separated.

The aqueous solubility of various volatile nonelectrolytes has been observed to obey Henry's law.20—24) This means that liquid or solid solute itself is not necessarily in contact with water to prepare aqueous solutions saturated with the solute, instead, the saturated vapor of solute at a constant temperature can be used. Based on this idea, we have proposed a method which involves a circulation of solute vapor in a closed system through water.25) This technique has proved useful for saturating water with benzene or alkylbenzenes.26—28) This technique, however, cannot be applied to such solutes as are present in solid state, probably due to the lack of effective vaporization of solid solute.

This study is concerned with the development of a new method to prepare aqueous solutions saturated with solid aromatic compounds. To a suitable organic solvent a solid solute to be studied is added in excess so that a part of the solute is always present in solid state in the solvent. Then, air is bubbled through the organic solvent, and the resulting vapor is introduced into water and circulated in a closed system. Our objects are (1) to compare solubility results with those reported in literatures, (2) to see the effect of organic solvents used to dissolve solid solutes on the solute aqueous solubility, and (3) to search such a possibility that the present method might offer some information about binary systems consisting of an aromatic hydrocarbon and an organic solvent.

Experimental

Materials. Distilled deionized water was used throughout this work. Naphthalene, biphenyl (98%), fluoranthene (98%), (*o*-, *m*-, *p*-)terphenyls, and triphenylene (97%), each of analytical reagent grade, and anthracene and phenanthrene, each of authentic (guaranteed) sample, were used as solutes without further purification; the minimum purities specified by the manufacturers (Wako Pure Chemical and Nakarai Chemicals Co.) are given in the parentheses. Benzene (99.5%), cyclohexane (99.5%), and 1-octanol (95%) were used as organic solvents to dissolve solid solutes. Amberlite XAD-2 resin (Rohm and Hass) of 80—100 mesh was used, when necessary, to concentrate solutes dissolved in water.

Apparatus and Procedures. The apparatus used for preparing aqueous solution saturated with solute vapor is essentially the same as that previously used,25) except some minor modifications. The apparatus was composed of two main glass parts: a pear-shaped vessel of 30 cm^3 capacity in which a solid solute was placed together with an organic solvent (we call this vessel the "solute reservoir") and a pear-shaped vessel of 80 cm^3 capacity with a narrow orifice in the bottom in which up to 50 cm^3 water was placed (we call this vessel the "solubility flask"). A Viton diaphragm airpump (Iwaki Type AP-32 Z) was incorporated into the assembly. The apparatus was fixed on a board and immersed, except the airpump part, in a water bath thermostated at 25.0±0.1 °C; the temperature of the airpump part was kept a few degrees higher than 25 °C.

An excess quantity of a solid aromatic hydrocarbon was added to an Erlenmeyer's flask and dispersed in an organic solvent by applying ultrasonic vibrations (Kaijo Denki "Sono Cleaner Mini") for ca. 1 h, and a 5—10 cm^3 portion with some solute crystals was pipetted out of the flask and transferred into the solute reservoir. By means of the pump, air was bubbled at a flow rate of ca. 0.5 or 1 dm^3 min^{-1} through the solute reservoir via a sintered glass ball, and the resulting vapor of the organic solvent and solid aromatic hydrocarbon was introduced through a trap into water in the solubility flask to disperse via a sintered glass ball, and circulated in a closed system.

After solubility equilibrium was attained, the apparatus was withdrawn out of the bath. A glass plug attached to the bottom of the solubility flask through a Teflon tube was removed, and a suitable portion of the aqueous phase was transferred to a 50 cm^3 cylindrical separatory funnel, in which 5 cm^3 of $CHCl_3$ had previously been placed; the funnel had been calibrated so that the volume of a water sample taken in can be read out to 0.1 cm^3. The extract, after dehydrated with anhydrous sodium sulfate, was analyzed with a Hitachi 100-50 spectrophotometer. In handling three solutes, anthracene, *p*-terphenyl, and triphenylene, 100 cm^3 of water sample (2X50 cm^3) was passed through an XAD-column and the solute adsorbed on the resin was eluted out with 5 cm^3 of $CHCl_3$.

Measurements were repeated on at least four water samples separately prepared, and the avarage was taken as the solubility.

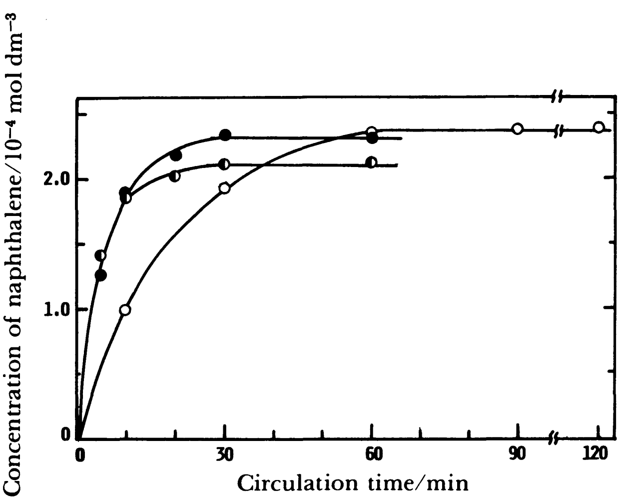

Fig. 1. Concentration of naphthalene in water at 25 °C vs. vapor circulation time. Vaporized from benzene(◐), cyclohexane(●), and 1-octanol(○) solutions.

Table 1. Dependence of Aqueous "Solubilities" of Naphthalene, Biphenyl, and *p*-Terphenyl on Organic Solvents Used to Dissolve the Solutes

Solute	Organic solvent used to dissolve the solute	Aqueous solubility measured/mol dm^{-3}
Naphthalene	Benzene	2.10×10^{-4}
	Cyclohexane	2.30×10^{-4}
	1-Octanol	2.35×10^{-4}
Biphenyl	Cyclohexane	3.92×10^{-5}
	1-Octanol	4.57×10^{-5}
p-Terphenyl	Benzene	3.8×10^{-8}
	1-Octanol	7.8×10^{-8}

Results

Factors Affecting Aqueous Solubility. The time required for saturating water with solute vapor will depend highly on the vapor circulation rate. In order to speed up the process, high circulation rates are desired. In practice, however, the rate was set at ca. 0.5 dm^3 min^{-1} for 1-octanol and at ca. 1 dm^3 min^{-1} for benzene and cyclohexane. With higher rates, the dead volume of the solute reservoir was so small that the organic solvent was caused to splash to a considerable degree into the adjacent trap. When 1-octanol, more viscous than the other two, was used, the circulation rate needed to be suppressed, otherwise part of the solvent was carried away into the trap.

At the prescribed circulation rate, the aqueous phase was found to become saturated with a solute in 30 min when benzene or cyclohexane was used as organic solvent and in 90 min in the case of 1-octanol. The results observed for naphthalene are shown in Fig. 1. The concentration of solute in the "saturated" aqueous solution was found to depend upon the organic solvent used to dissolve solid aromatic hydrocarbons. For three different solutes the effect of organic solvents on their aqueous solubilities were studied (Table 1). The highest "solubility" was observed when the solid solute was dissolved in 1-octanol, while the lowest was observed with benzene.

Solubility of Solid Aromatic Hydrocarbons in Water. With 1-octanol as organic solvent, aqueous solutions saturated with solid aromatic hydrocarbons with two or three benzene rings were prepared, and each solubility at 25.0 °C was determined. The results are given in Table 2 together with literature values. There have been published a large number of data for naphthalene, biphenyl, anthracene, and phenanthrene and a less number for fluoranthene and triphenylene, but no data, to our knowledge, on terphenyls.

The present vapor saturation method was found inapplicable to phenanthrene; no reproducible results were obtained for this solute, and, moreover, the estimated "solubility" was far lower than the lowest literature value. Cyclohexane was used instead of 1-

Table 2. Solubilities of Solid Aromatic Hydrocarbons in Water at 25 °C

Solute	Solubility/mol dm^{-3}	
	This work	Literature value
Naphthalene	$(2.35\pm0.06)\times10^{-4}$	{2.34,[7] 2.36,[8] 2.39,[17] 2.43,[5,6,14] 2.45,[10] 2.46,[1] 2.47,[9,19] 2.472,[15] 2.53,[13] 2.54,[11] 2.62,[4] 2.68,[3]}$\times10^{-4}$
Biphenyl	$(4.57\pm0.05)\times10^{-5}$	{3.85,[1] 3.91,[12] 4.35,[18] 4.5,[9] 4.57,[10] 4.59,[5] 4.80,[6] 4.85,[3] 4.86,[13] 4.9[19]}$\times10^{-5}$
Anthracene	$(2.5\pm0.1)\times10^{-7}$	{2.30,[8] 2.50,[15,17] 2.6,[19] 4.1,[9] 4.17,[10] 4.2,[5,19] 4.47[2]}$\times10^{-7}$
Phenanthrene		{5.58,[1] 5.61,[17] 5.62,[15] 6.0,[6] 6.46,[8] 6.62,[5,19] 7.08,[10] 7.24,[9] 9.0[2]}$\times10^{-6}$
Fluoranthene	$(1.4\pm0.1)\times10^{-6}$	{1.02,[15] 1.26,[10] 1.3,[9,19] 1.32[2]}$\times10^{-6}$
o-Terphenyl	$(5.38\pm0.02)\times10^{-6}$	
m-Terphenyl	$(6.56\pm0.02)\times10^{-6}$	
p-Terphenyl	$(7.8\pm0.6)\times10^{-8}$	
Triphenylene	$(1.8\pm0.2)\times10^{-7}$	{0.29,[16] 1.86,[10] 1.88,[2] 1.9[9]}$\times10^{-7}$

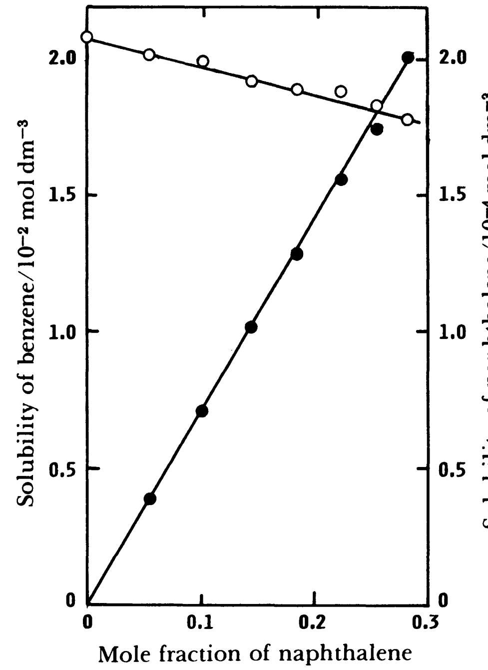

Fig. 2. Naphthalene-benzene binary system. Aqueous solubility of naphthalene(●) and benzene(○) at 25 °C.

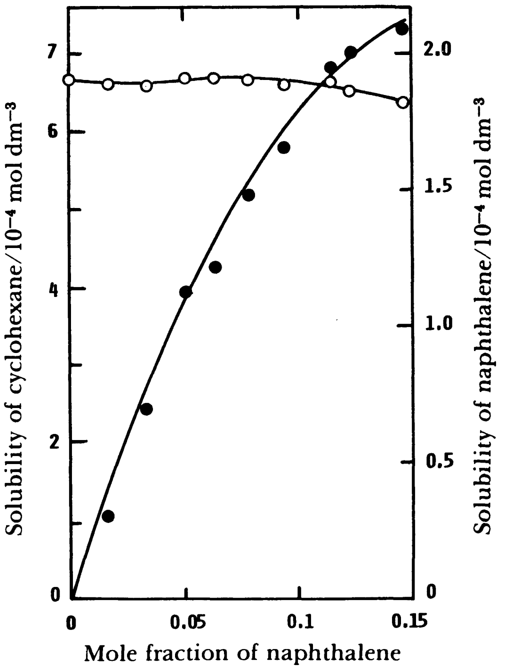

Fig. 3. Naphthalene-cyclohexane binary system. Aqueous solubility of naphthalene(●) and cyclohexane(○) at 25 °C.

octanol only to produce almost the same unsatisfactory results.

Naphthalene-Benzene and Naphthalene-Cyclohexane Binary Systems. A known quantity of naphthalene was added to a known amount of benzene or cyclohexane up to near saturation, and the vapor phase was circulated to saturate water. The concentration of each component in the water was measured after solubility equilibrium was attained.[29] The results are shown in Figs. 2 and 3 as a function of the mole fraction of naphthalene.

Discussion

Evaluation of the Present Method and Interpretation of Solubility Results. Although there are no available data on terphenyls, their solubility values estimated in this work seem to be reliable judging from their good reproducibility; the extremely low solubility observed for *p*-isomer may be ascribed to its relatively high melting point compared to the other two isomers. The generator column method gives an extremely low solubility for triphenylene,[16] but our value is in good agreement with the results obtained by the shake-flask method.

For anthracene, the solubility values reported to data are grouped into two well-defined values: 2.5 and 4.2×10^{-7} mol dm^{-3}. May et al.,[15] whose value belongs to the lower, attributed the higher value to the structural isomer, phenanthrene, present as an impurity. It is, however, still difficult to explain why one group is almost constantly 1.7 times as high as the other. When we consider that, as they insist, anthracene is contaminated with phenanthrene in at least 2% in most commercial products (the quantity sufficiently large for saturating water), that phenanthrene is ca. 20 times as water-soluble as anthracene, and that the molar absorptivity of phenanthrene is ca. 0.4 times that of anthracene at the same measuring wavelength in the same extractant, the "apparent" solubility of anthracene in water amounts to ca. 9 times the "true" solubility. Is there such a possibility that phenanthrene molecules once dissolved in water would come out to be held on the solid anthracene surface and that adsorption equilibrium would be realized between phenanthrene molecules in water and those in the solid surface to yield constantly the 1.7 times overestimated solubility of anthracene? Is there not such a possibility that anthracene molecules would dimerize in water in contact with solid anthracene? In any event, the present vapor saturation approach supports the lower value for this solute solubility.

The present method failed to saturate water with phenanthrene. At present we cannot provide satisfactory explanations to this failure. It is probable that the solid phenanthrene phase is to include 1-octanol molecules to form a complexed phase, presumably, with a changeable composition depending upon certain variables such as the ratio of solvent to solute and the size and surface state of solid particles. Since literature values themselves are scattered over a relatively wide range compared to the other solutes, we further speculate that water molecules also are more or less liable to be incorporated in the solid phenanthrene phase. There is, however, no evidence to support this.

Applicability of the Present Method. There are two potential applications of the method proposed here. One is to study the solubilizing effect of coexisting solutes such as surfactant on the aqueous solubility of solid aromatic hydrocarbons. Such studied should be conducted in the absence of solute phase of interest in excess, otherwise coexisting solute molecules will be adsorbed on the solid solute surface to change solution properties. The present method meets this requirement.

The other application of this method is to study the aqueous solubility of solid hydrocarbon as a function of its composition in an organic solvent used to dissolve the solid solute. Here, we have studied systems naphthalene–benzene and naphthalene–cyclohexane as examples. As can be seen from Figs. 2 and 3, the solubility of naphthalene increases almost linearly with its mole fraction in benzene, but this is not the case with cyclohexane. This seems to reflect the situation that the former system is nearly an ideal solution, whereas the latter system is far from being ideal.[30,31]

A question should naturally arise that the organic solvent phase is to get saturated with water vapor so as never to be made up by any "pure" binary system. We nevertheless approximate it a "binary" system, because the solubility of water in organic solvents such as benzene and cyclohexane is sufficiently low (in the case of 1-octanol this approximation is not valid because of high water solubility in this solvent).

The aqueous phase is to be saturated not only with the solid solute of interest but also with the organic solvent used to dissolve the solid solute, so that another question should arise as to whether any interaction between both the solutes takes place in the aqueous phase. Chiou et al.[32] have suggested a solubilization effect of 1-octanol; the solubility of a solute in water which has been saturated with 1-octanol is larger than that in 1-octanol-free water. This effect probably present itself only when there is an appreciable 1-octanol–solute interaction in the aqueous phase. Miller et al.,[19] on the other hand, have demonstrated, by using polynuclear aromatic hydrocarbons, biphenyl, and polychlorinated biphenyls as solutes, that 1-octanol saturated in water has little effect on the solubility of the substances in water. If any interaction does occur between solutes in water, benzene would have a stronger effect than 1-octanol and cyclohexane, because the concentration of benzene saturated in water is larger than those of 1-octanol and cyclohexane by one and two orders of magnitude, respectively.

It seems reasonable to interpret the dependence of the aqueous solubility of the solid hydrocarbon solutes on the organic solvents used to dissolve them (Table 1) in terms of the solute vapor pressure. We cannot discuss this point since no solute vapor pressures in the solute–organic solvent systems were measured in this study.

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