2908 © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 2908—2912 (1989) [Vol. 62, No. 9

A Modified Vapor Saturation Method for Preparing Aqueous Solutions of Solid Aromatic Hydrocarbons

Isao SANEMASA,* Kazunari ISHIBASHI, Masaya KUMAMARU, and Toshio DEGUCHI
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860

(Received April 3, 1989)

An excess quantity of a solid hydrocarbon is dispersed in water, and then air is bubbled through the aqueous phase to produce the solute vapor. The vapor is introduced into a separate water phase and circulated in a closed system. Aqueous solutions saturated with some solid aromatic hydrocarbons can be prepared in a relatively short time without any need to remove solute microcrystals. It can be confirmed whether the solubility obeys Henry's law. The present method provides us with rough enthalpy of sublimation of a solute if its solubility follows Henry's law. Biphenyl, naphthalene, phenanthrene, and anthracene were examined as solutes.

We recently proposed a method to prepare aqueous solutions saturated with solid aromatic hydrocarbons.[1] The principle is as follows: a solid solute is added in excess to a suitable organic solvent so that a part of the solute is always present in solid state in the solvent, then, air is bubbled through the solvent, and the resulting vapor is introduced into water to circulate in a closed system. It was found that 1-octanol was the most suitable solvent for preparing aqueous solutions saturated with solid aromatic hydrocarbons.

The present work concerns a modification of the previous method. The organic solvent was not used here, but water was used to disperse solid solutes. This work aims to see whether or not the modification is successful and, if successful, to confirm whether Henry's law holds for some solid aromatic hydrocarbons.

Experimental

Materials. The solid aromatic hydrocarbons used as solutes are the same as those examined in the previous paper.[1] Distilled deionized water was used throughout this work.

Apparatus and Procedures. The apparatus used for preparing aqueous solutions saturated with solute vapor is essentially the same as that previously used,[2] except for some minor modification. The apparatus was composed of two main glass parts: a pear-shaped long-necked vessel of 50 cm^3 capacity in which ca. 0.5 g of solid hydrocarbon roughly powdered by agate mortar was placed together with ca. 20 cm^3 water (we call this vessel the "solute reservoir") and a separatory funnel of 200 cm^3 capacity in which 150 cm^3 water was placed (we call this funnel the "solubility flask"). These two vessels were connected with glass and Teflon tubes incorporated with a Viton diaphragm airpump (Iwaki Type AP-32 Z) and a round-bottom flask of 200 cm^3 capacity to trap fine solute powders.

The temperature of the solubility flask was held at 25±0.1 °C by circulating water from a thermostated water bath through a jacket surrounding the funnel. The solute reservoir and the trap-flask were immersed in a separate water bath kept constant at any desired temperature below 25 °C. The temperature of a chamber containing the assembled apparatus was always kept higher than that of the solute reservoir.

By means of the pump, air was bubbled at a flow rate of ca. 0.5 dm^3 min^{-1} through the solute reservoir via a glass capillary, and the resulting solute (and water) vapor was introduced through the trap-flask into water in the solubility flask to disperse via a glass capillary, and circulated in the closed system. After solubility equilibrium was attained, a suitable portion of the aqueous solution was transferred from the separatory funnel into a glass test tube, in which a 5 cm^3 portion of cyclohexane had previously been placed, and weighed; prior to the operation of stopcock attached to the funnel bottom, the funnel position was slightly lowered so as to allow air to enter the funnel through its top opening. Extractions were made after diluting the aqueous phase to 20 cm^3 with water.

The cyclohexane extract, after dehydrated with anhydrous sodium sulfate, was analyzed by UV absorption (biphenyl: 247.5, naphthalene: 285, phenanthrene: 250, anthracene: 251.5 nm) with a Hitachi 100-50 spectrophotometer and by fluorescence for anthracene (excitation 253.6, emission 378 nm) with a JASCO FP-770 spectrofluorometer.

For each solute, a calibration curve was prepared by extracting a 5 cm^3 portion of the standard cyclohexane solution containing a known amount of the solute with 20 cm^3 water.

Results and Discussion

The Time Required for Saturating Water with Solute Vapor. The circulation rate of solute vapor may affect the time for attaining the equilibrium solubility, and high circulation rates are desirable to reduce the time required. In the present work, however, the circulation rate was suppressed to be moderate, because at higher circulation rates extraordinarily high "solubility" values were sometimes observed probably due to accidental contamination with solute fine powders. The time necessary to saturate is as follows: 1 h for biphenyl and naphthalene, 6 h for phenanthrene, and 20 h for anthracene.

The term "equilibrium solubility" is used in this paper to describe the solubility obtained under the condition that the temperature of the solute reservoir differs from that of the solubility flask.

The equilibrium solubility can be attained from both directions: approaches from either lower or

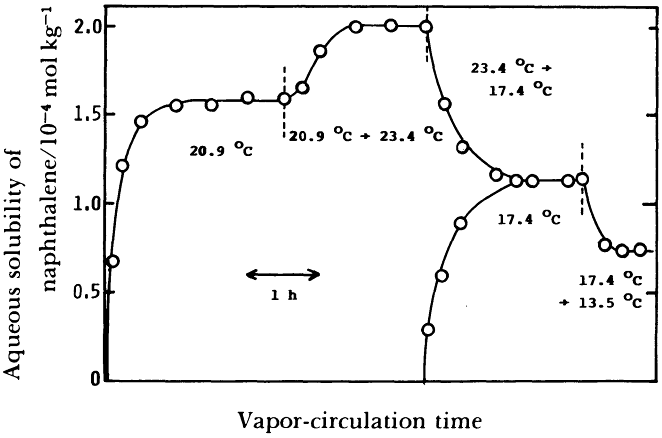

Fig. 1. Equilibrium solubility vs. vapor-circulation time. The temperature of solute reservoir in which solid naphthalene had been placed together with water was set as specified in Figure, while that of solubility flask was held constant at 25 °C.

Table 1. Equilibrium Solubility of Solid Aromatic Hydrocarbons in Water at 25 °C

Temperature of solute	Solute vapor pressure[a]	Equilibrium solubility[b]
°C	Pa	mol kg^{-1}
Biphenyl		
13.7	0.311	1.35×10^{-5}
20.1	0.621	2.60
23.1	0.852	3.48
24.9	1.03	4.25
Naphthalene		
16.6	4.60	1.05×10^{-4}
20.5	6.95	1.54
23.1	9.07	1.99
24.9	10.88	2.38
Anthracene		
10.9	1.08×10^{-4}	$0.329(0.389)\times10^{-7}$
15.2	2.06	0.646(2.22)
19.1	3.62	1.09(3.03)
20.7	4.55	1.21(3.30)
22.1	5.55	1.49(3.69)
23.1	6.38	1.64(3.80)
24.1	7.34	1.83(4.11)
24.8	8.08	2.08(4.10)
24.9	8.19	2.20(4.33)
Phenanthrene		
15.4	0.711×10^{-2}	2.34×10^{-6}
20.7	1.36	4.09
21.9	1.57	4.33
23.0	1.79	5.18
24.2	2.07	5.91
25.0	2.27	6.22

a) The vapor pressure data of biphenyl,[3] naphthalene,[4] anthracene,[5] and phenanthrene,[5] are taken from the literature. b) Values of anthracene in the parentheses were obtained by UV absorption measurements, and these values are unreliable for the solubility data owing to some unknown impurities present in this hydrocarbon (see Text).

higher vapor pressure. This is illustrated in Fig. 1, which shows how naphthalene concentration in water at 25 °C varies with the circulation time after the temperature of the solute reservoir was changed.

Equilibrium Solubility and Solute Vapor Pressure. In Table 1 are given the equilibrium solubility values obtained under the experimental condition that the temperature of the solute reservoir was varied while that of the solubility flask was held constant at 25 °C. The equilibrium solubility of each solute is found to be proportional to the solute vapor pressure (Fig. 2). That is, solubility obeys Henry's law

$$P = K_{\mathrm{H}}X_2, \tag{1}$$

where P is the partial pressure of the solute, X_2 is the mole fraction of the dissolved solute, and K_{H} is the Henry's law constant. Here, the solute in water being in equilibrium with the solid solute in the solute reservoir, we have taken the partial pressure of the solute to be equal to the vapor pressure of pure solid at the temperature of the solute reservoir. The vapor pressure at any desired temperature of each solid hydrocarbon, biphenyl,[3] naphthalene,[4] anthracene,[5] and phenanthrene,[5] has been estimated from the literature. The Henry's law constant at 25 °C and the aqueous solubility in mol kg^{-1} determined from K_{H} are summarized in Table 2. The solubility thus determined for the solute studied in this work is in reasonable agreement with that reported in our previous work and that cited therein.[1]

The Aqueous Solubility of Anthracene. In the beginning of this work, the anthracene solubility has been measured by the UV absorption method. Then, it appeared, as can be seen from Table 1, that the equilibrium solubility plotted against the anthracene vapor pressure, does not follow Henry's law, and that the solubility at 25 °C, 4.33×10^{-7} mol kg^{-1}, is two times larger than our previous value. We, then, adopted the fluorescence method to determine the concentration of anthracene, and found that Henry's law holds for this solute and that the solubility is in a reasonable agreement with our previous value.[1] We speculate that this is caused by some impurities present in anthracene and that the impurity is volatile and responds to UV absorption, but not to fluorescence measurements. The present method uses water as the disperse medium, and hence, some impurities are readily volatilized and dissolved into the separate water phase.

As was noted in the previous paper,[1] the literature data of anthracene solubility can be grouped into two well-defined values: 2.5 and 4.2×10^{-7} mol dm^{-3}. The lower value has been reported by researchers who adopted either the fluorescence technique[6] or the combination of HPLC-separation and absorption measurement.[7] This clearly indicates that some impurities are responsible for the higher solubility

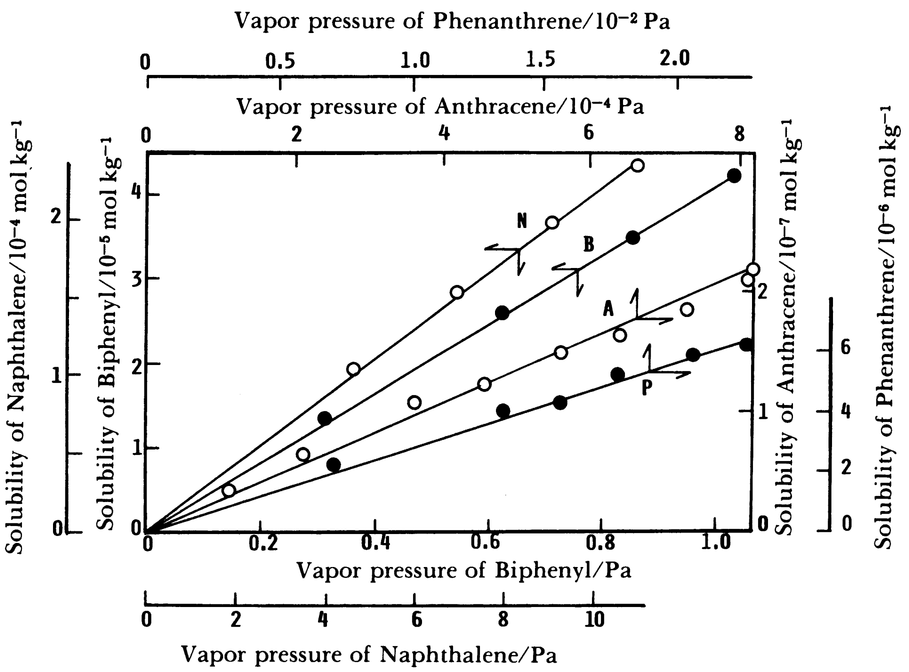

Fig. 2. Equilibrium solubility vs. solute vapor pressure. Biphenyl (B), naphthalene (N), anthracene (A), and phenanthrene (P).

Table 2. Henry's Law Constant and Aqueous Solubility at 25 °C

Solute	$P^{a)}$	$K_H^{b)}$	$S^{c)}$
	Pa	Pa	mol kg^{-1}
Biphenyl	1.04	1.34×10^6	4.30×10^{-5}
Naphthalene	10.98	2.52×10^6	2.42×10^{-4}
Anthracene	8.31×10^{-4}	2.11×10^5	2.18×10^{-7}
Phenanthrene	2.27×10^{-2}	1.96×10^5	6.45×10^{-6}

a) The vapor pressure of solid hydrocarbon at 25 °C taken from the literature. b) Henry's law constant determined in this work. c) The solubility of hydrocarbon in water estimated from K_H.

value of anthracene. May et al., who used the latter technique, assumed the impurity to be phenanthrene. If it is true, so long as the fluorescence technique is used, the presence of phenanthrene would increase considerably the apparent solubility of anthracene owing to the relatively high solubility of phenanthrene which also has fluorescence. We have analyzed both the cyclohexane extract of aqueous solution saturated with the vapor of anthracene and the cyclohexane solution of this solid hydrocarbon by gas chromatography (Shimadzu GC-14A, detector: FID, column packing: BBBT, temperature: 195 °C). As the result, phenanthrene was detected in neither of the cases.

In our previous study, where the UV absorption technique was employed, the value close to the present fluorescence result was obtained. This is probably due to that the impurities in the solid anthracene are soluble in such an organic solvent as 1-octanol. That is, they remain soluble in 1-octanol, while volatile in water.

The Utility of the Vapor Saturation Method. The use of a disperse medium is favorable for generating the vapor of the solute which exists as solid at ordinary temperatures. For this purpose, benzene and cyclohexane cannot be used,[1)] but either 1-octanol or water is suitable. When water is used as the disperser, care should be taken, as was just mentioned above, of volatile impurities which might be present in the solid solute. The use of water as the disperser, however, makes the solubility system much simple, because the influence of 1-octanol, which is also dissolved in water, need not be considered.

We have studied aqueous solubility of volatile nonelectrolytes such as metallic mercury,[8)] benzene and alkylbenzenes,[2)] and iodine,[9)] and demonstrated that the solute vapor circulation method is useful to determine experimentally whether the solute follows Henry's law. This is also the case for the solid aromatic hydrocarbons studied here. The present method has a potential application to such studies that association of some hydrophobic solutes with aromatic hydrocarbons is to be determined in water by measuring the change of the solubility of aromatics.

The influence of temperature on the vapor pressure of a solid is given by the well-known equation

$$d \ln P/dT = \Delta H_{sub}/(RT^2), \qquad (2)$$

where P is the sublimation vapor pressure, ΔH_{sub} is the enthalpy of sublimation, and T and R have usual meaning. As the concentration of a solid solute in the aqueous phase increases, the solute crystallizes out when the partial pressure of the solid solute equals its sublimation vapor pressure. This is the case for what happens in the solute reservoir in our present approach. We, therefore, take the vapor pressure, P, which appears in Eqs. 1 and 2, equal to each other in its physical quantity. Then, by combining Eqs. 1 and 2, ΔH_{sub} can be estimated for a solid hydrocarbon. Here, it is assumed that ΔH_{sub} is independent of temperature over the range studied. For each solute studied in this work, $\log X$ was plotted against T^{-1} (Fig. 3), and we get a straight line with a slope which corresponds to $-\Delta H_{sub}/(2.303\times 8.314)$. The ΔH_{sub} value thus estimated over the temperature range of 15 to 25 °C is given in Table 3 together with some literature data. Reasonable agreements are found between data of this and the preceding works except for phenanthrene.

Two techniques have been used to prepare aqueous

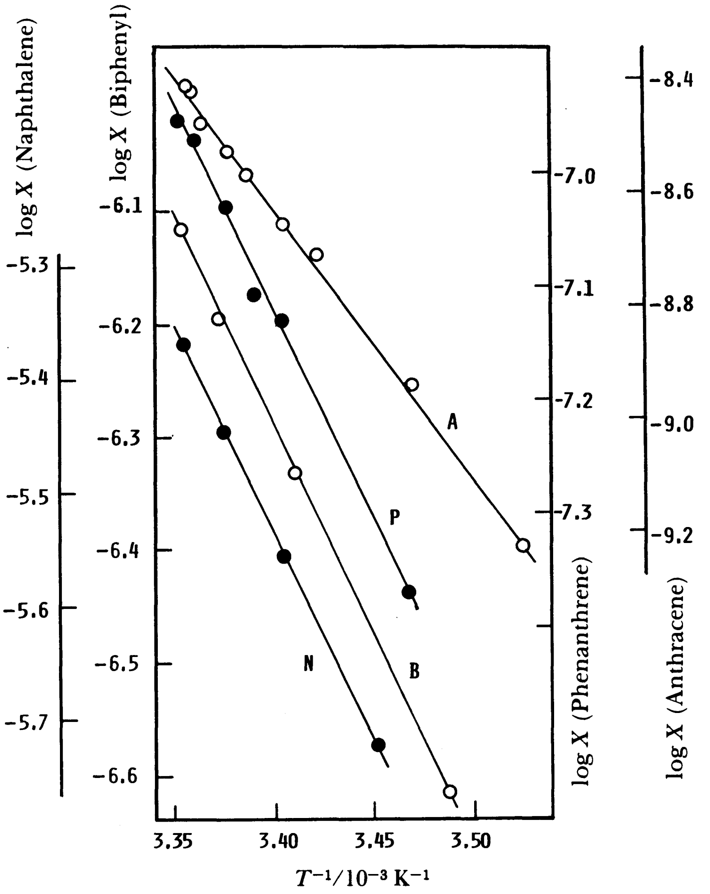

Fig. 3. $\log X$ vs. T^{-1}. X: equilibrium solubility at 25 °C in mole fraction; T: absolute temperature of solute; biphenyl (B), naphthalene (N), anthracene (A), and phenanthrene (P).

Table 3. The Enthalpy of Sublimation Estimated from Equilibrium Solubility Over 15—25 °C

Solute	ΔH_{sub}/kJ mol^{-1}			
	This work	Literature data		
Biphenyl	72.4	72.8,[11]	75.8[3]	
Naphthalene	71.0	72.4,[5]	72.6,[12]	75.8[13]
Anthracene	90.9	91.8,[13]	103.8,[3]	104.5[12]
Phenanthrene	73.3	86.6,[3]	92.5,[12]	95.0[13]

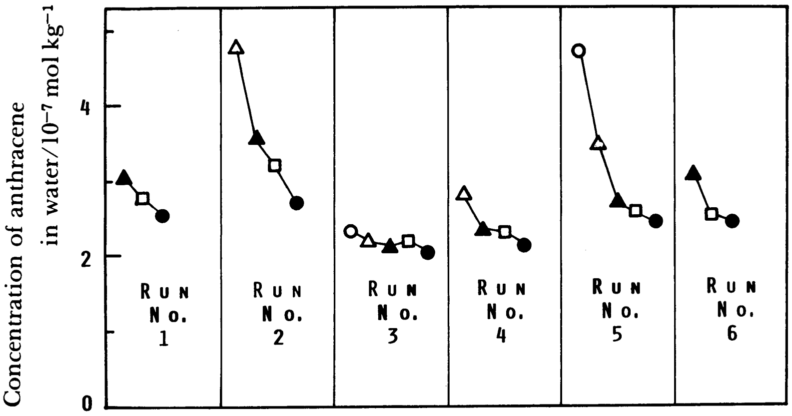

Fig. 4. Concentration of anthracene in water prepared by "shake-flask" technique, six replicated runs. The solid anthracene was stirred in water, and then, allowed to stand for 5(○), 7(△), 9(▲), 11(□), and 14 days(●).

solutions saturated with liquid or solid solutes: one is called "generator column,"[7] and the other "shake-flask." These techniques make the solute phase directly contact with water. The latter technique, most widely used for solubility studies, requires a long time to attain the solubility equilibrium and, subsequently, to settle the excess solute phase. In this work, we have also prepared aqueous solutions of anthracene by the conventional shake-flask method using the device described elsewhere,[10] to check the value obtained by the present solute vapor circulation method. The results of fluorescence measurements in six replicated runs are shown in Fig. 4. After an excess quantity of the solid hydrocarbon had been stirred in water for 24 h at 25 °C, the mixture was allowed to stand in the thermostated bath for two weeks, during which a portion of the aqueous phase was withdrawn periodically via a side-arm attached to the device. It was found that the solubility value approaches on standing for quite a long time the value obtained by the vapor circulation method. A "clear" aqueous phase appeared after the mixture was allowed to stand overnight. Nevertheless, considerably high "solubility" was observed. This is probably due to dispersion rather than true dissolution.

Advantages of the present method are (1) saturated solutions can be prepared in a relatively short time and (2) the removal of the excess solute phase is not required.

References

1) M. Akiyoshi, T. Deguchi, and I. Sanemasa, *Bull. Chem. Soc. Jpn.*, **60**, 3935 (1987).

2) I. Sanemasa, M. Araki, T. Deguchi, and H. Nagai, *Bull. Chem. Soc. Jpn.*, **55**, 1054 (1982).

3) A. Aihara, *Nippon Kagaku Zasshi*, **76**, 492 (1955).

4) L. Fowler, W. N. Trump, and C. E. Vogler, *J. Chem. Eng. Data*, **13**, 209 (1968).

5) R. S. Bradley and T. G. Cleasby, *J. Chem. Soc.*, **1953**, 1690.

6) F. P. Schwarz, *J. Chem. Eng. Data*, **22**, 273 (1977).

7) W. E. May, S. P. Wasik, and D. H. Freeman, *Anal. Chem.*, **50**, 175 (1978).

8) I. Sanemasa, *Bull. Chem. Soc. Jpn.*, **48**, 1795 (1975).

9) I. Sanemasa, T. Kobayashi, C. Y. Piao, and T. Deguchi, *Bull. Chem. Soc. Jpn.*, **57**, 1352 (1984).

10) I. Sanemasa, M. Kumamaru, K. Ishibashi, and T. Deguchi, *Bull. Chem. Soc. Jpn.*, **62**, 1061 (1989).

11) N. F. H. Bright, *J. Chem. Soc.*, **1951**, 624.

12) C. G. de Kruif, *J. Chem. Thermodyn.*, **12**, 243 (1980).

13) W. J. Sonnefeld, W. H. Zoller, and W. E. May, *Anal. Chem.*, **55**, 275 (1983).