

# 水銀は水に濡れるか？

熊本大学大学院自然科学研究科  
理学専攻化学講座  
實政 勲

最終講義 2009年2月20日

昭和 43年 3月 熊本大学理学部化学科卒業

卒業研究：永井英夫 先生

希土類元素のペーパークロマトグラフィーによる分離

昭和 48年 3月 東京工業大学 大学院博士課程 修了 (理学博士)

先生 地球科学

小澤竹二郎 先生 火山ガス

桂 敬 先生 溶融塩・熱力学

OZAWA,  
eous Solutions of Inorganic Acids.  
1746 (1972).

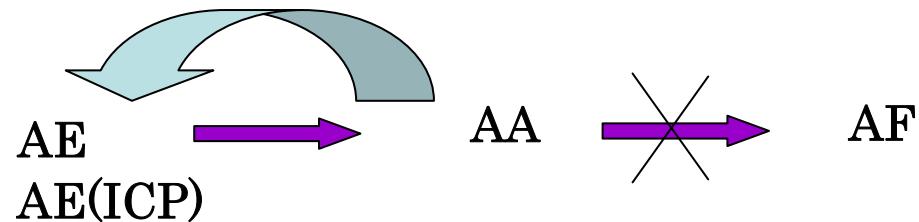
$\text{La}^{3+}$ )<sub>2</sub> in Acid Solutions.  
46, 3416 – 3422 (1973).

昭和 48年 (1973 年) 4月

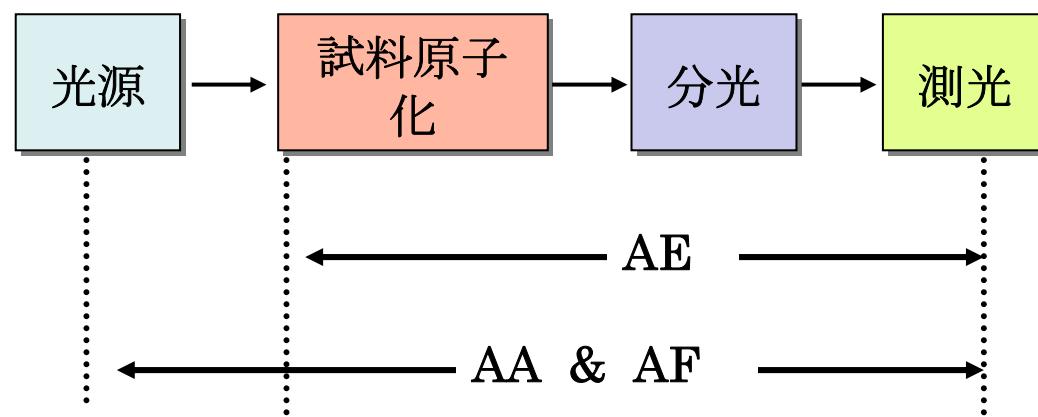
熊本大学助手 (理学部化学科)

# 原子吸光法

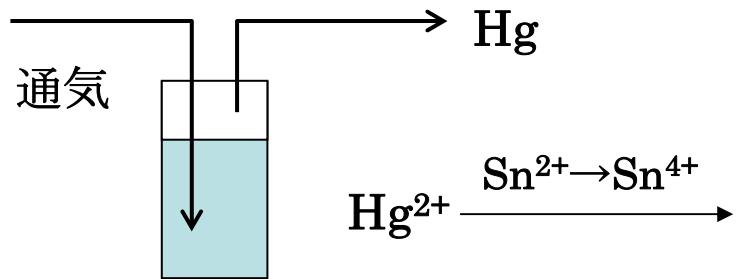
## 原子ペクトル分析法の歴史



## 装置の構成



水銀の原子吸光分析  $\longrightarrow$  還元気化法 (cold-vapor 法)



Hg の水相一気相間の分配



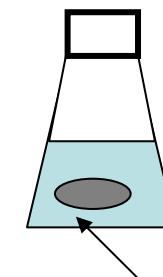
水溶液中での Hg の溶解度

溶解度測定

{ 飽和水溶液の調製  
溶質濃度の測定

従来の方法

Shake-flask 法



過剰量の溶質

水銀は水に濡れるか？

水溶液

界面

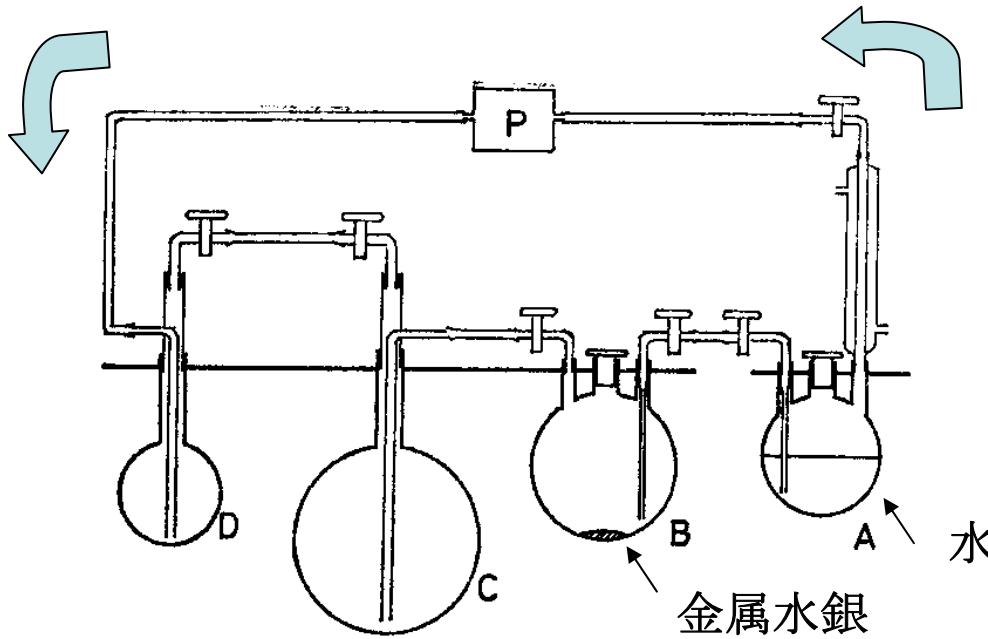
金属水銀

飽和水蒸気  
+  
水銀蒸気

金属水銀の溶解度



水銀蒸気の溶解度



June, 1975]

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1795—1798 (1975)

## The Solubility of Elemental Mercury Vapor in Water

Isao SANEMASA

*Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto 860*

(Received September 17, 1974)

The solubility of mercury vapor in water has been measured by means of atomic absorption spectrophotometry over the temperature range of 5—60 °C under atmospheric pressure. The aqueous solubility obeys Henry's law at each temperature. The solubilities and the Henry coefficients are reported. From the solubility data, the heat of the solution of mercury vapor in water is found to be —5.3 kcal/mol. The relationship between the Henry coefficient,  $k$ , and the solution temperature,  $T$ , is expressed by  $\log k = -1078 \times 1/T + 6.250$ . From this equation, the solubilities at 70—100 °C are estimated. The solubility of the mercury vapor in sea water has also been measured over the temperature range of 5—30 °C. A salting-out effect on the solubility is observed. The practical application of the aqueous solubility of the mercury vapor is discussed from the analytical point of view.

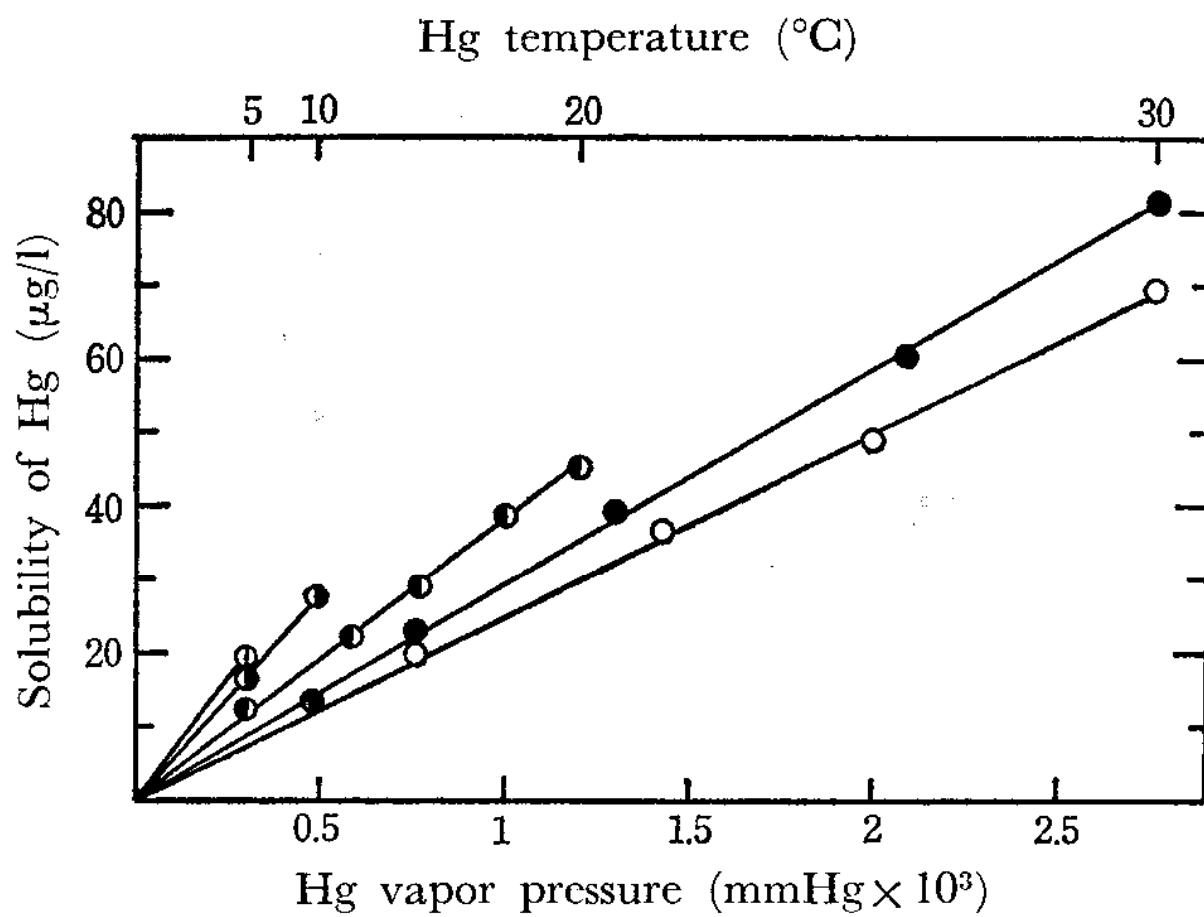


Fig. 2. The dependence of mercury solubility on mercury vapor pressure in pure water at 5 °C(○), 10 °C(●), 20 °C(◐), 30 °C(●) and in sea water at 30 °C(○).

TABLE 1. Hg SOLUBILITY AND HENRY COEFFICIENTS

Temp. (°C)	Solubility (μg/l) <sup>a)</sup>	Henry coefficient
Pure water		
5	19.2	233
10	27.4	262
20	45.0	391
30	81.3	500
40	137	650
50	218	852
60	368	1010
70	$5.6 \times 10^2$	$13 \times 10^2$
80	8.5	15
90	12	19
100	18	23
Sea water		
5	17.2	
10	23.6	
15	31.6	
20	40.6	
25	54.9	
30	69.7	

a) Solubility is expressed in μg/l for convenience which is transformed into mole fraction by multiplying  $8.98 \times 10^{-11}$ .

## 性 質

これらの元素のいくつかの性質を表19・1にあげた。亜鉛とカドミウムは、白色、光沢があるが曇りやすい金属である。等構造である Be および Mg と同じで、完全な六方最密パッキングからはずれて六回軸方向に伸びた構造をもっている。水銀は常温で輝きのある液体である<sup>3)</sup>。いずれも重金属としては著しく揮発性であり、水銀はもちろん特異的なほど揮発性である。水銀は单原子气体となり、20°Cでかなりの蒸気圧( $1.3 \times 10^{-3}$  mmHg)をもっている。極性および非極性のいずれの溶媒にも驚くほどよく溶け、たとえば空気を含まない水に 25°Cで  $6.39 \times 10^{-7}$  g l<sup>-1</sup> 溶ける<sup>4)</sup>。

水銀は、揮発性と毒性が高いため、常に密栓わなければならない。水銀は、希水溶液から、の不均化によってこれらの還元のために水銀(II)を生成する。

Zn と Cd はいずれも非酸化性の酸とたやすく

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培風館

3) M. C. Wilkinson, *Chem. Rev.*, 82, 575 (1972) (Hg の界面の性質).

4) I. Sanemasa, *Bull. Chem. Soc. Jpn.*, 1975, 1795.

Andersson, Maria E. et.al.,  
**Determination of Henry's law constant for elemental mercury.**  
Chemosphere (2008), 73(4), 587-592.

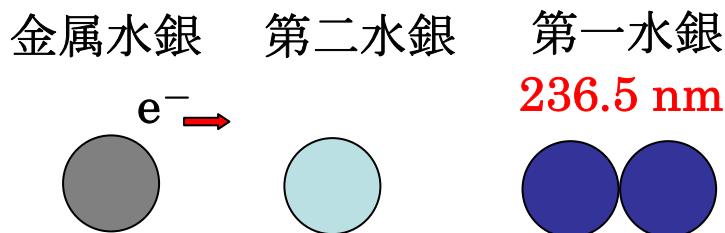
Lai, Soon-Onn et. al.,  
**Estimation of mercury loadings to Lake Ontario: Results from the Lake Ontario atmospheric deposition study (LOADS).**  
Atmospheric Environment (2007), 41(37), 8205-8218.

Cardona-Marek, Tamara et. al.,  
**Mercury Speciation, Reactivity, and Bioavailability in a Highly Contaminated Estuary, Berry's Creek, New Jersey Meadowlands.**  
Environmental Science & Technology (2007), 41(24), 8268-8274.

Kuss, Joachim et. al.,  
**Variability of the Gaseous Elemental Mercury Sea-Air Flux of the Baltic Sea.**  
Environmental Science & Technology (2007), 41(23), 8018-8023.

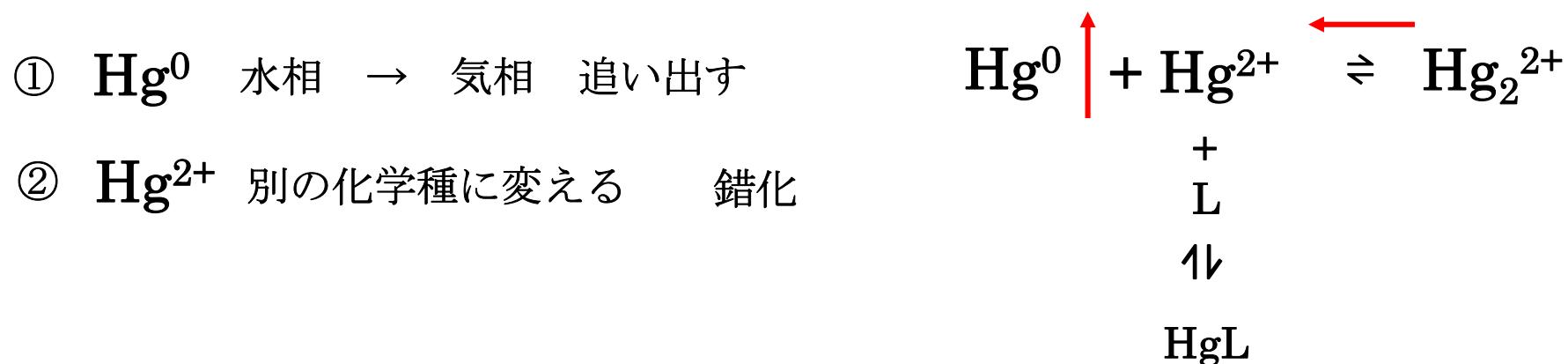
Hines, Neal A. et. al.,  
**Mercury inputs and outputs at a small lake in northern Minnesota.**  
Biogeochemistry (2007), 84(3), 265-284.

Peters, Stephen C. et. al.,  
**Mercury Emission to the Atmosphere from Experimental Manipulation of DOC and UVR in Mesoscale Field Chambers in a Freshwater Lake.**  
Environmental Science & Technology (2007), 41(21), 7356-7362.



第一水銀の生成速度の研究  $\longrightarrow$  第一水銀の不均化速度の研究

- 第一水銀の生成速度・・・測定できない
- ← 第一水銀の不均化速度・・・測定できるかもしれない



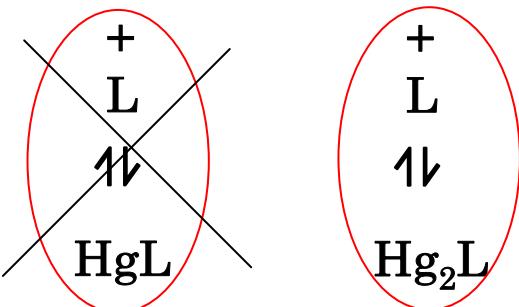
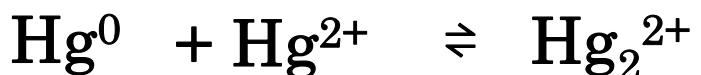
# Kinetics of the Disproportionation Reaction of Mercury(I) with Hydrogen Cyanide in Acidic Solutions

ISAO SANEMASA

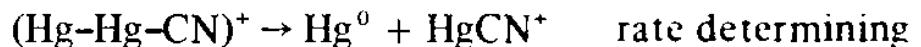
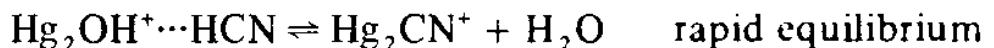
Received November 18, 1975

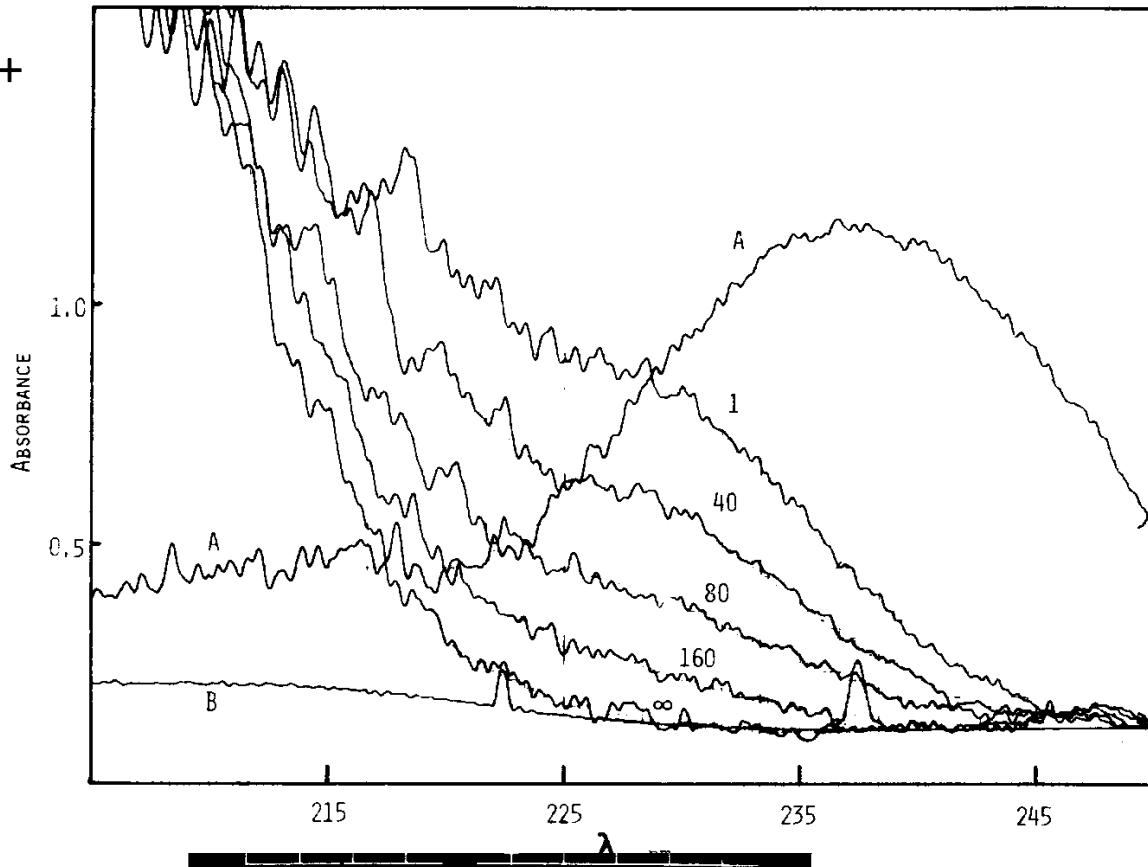
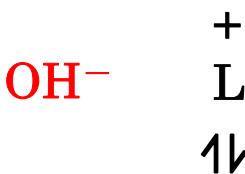
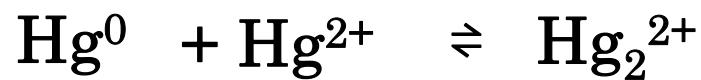
AIC50828O

The kinetics of the disproportionation reaction of mercury(I) with HCN in perchloric acid solutions have been measured by the stopped-flow method. The rate law is given by  $-d[Hg(I)]/dt = 2.2 \times 10^3 [Hg(I)][HCN][H^+]^{-1} \text{ M s}^{-1}$  at 25 °C. The activation parameters are  $\Delta H^* = 9.5 \pm 0.2 \text{ kcal mol}^{-1}$ ,  $\Delta S^* = -11.6 \pm 0.6 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . The rate constant,  $k_1$ , for the possible rate-determining reaction  $Hg_2OH^+ + HCN = Hg^0 + HgCN^+ + H_2O$  is calculated to be  $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The breaking of the Hg-Hg bond is considered to be the rate-determining step in the disproportionation reaction with HCN. Discussions on some possible mechanisms are made.

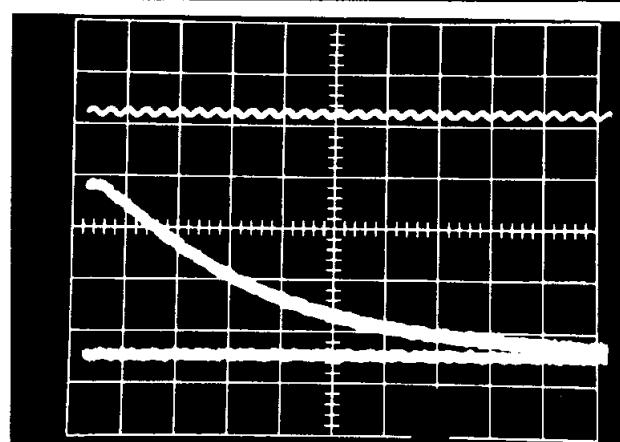


group which is favorable to HCN. The following mechanism is proposed:





**Figure**  
spectra  
(0.029  
curves  
essenti  
decay  
 $10^{-5}$  M  
(unfor



by a rapid-scan  
M) with NaOH  
fibers beside the  
lowest curve is  
baseline for these  
of  $\text{Hg}_2^{2+}$  ( $2.5 \times$   
the decay curves  
listed to B).

# Kinetics of the Disproportionation Reaction of Mercury(I) in Alkaline Solutions

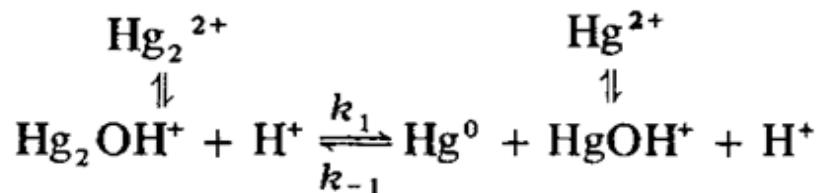
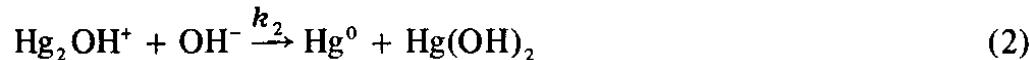
ISAO SANEMASA

Received February 10, 1977

AIC70113G

The kinetics of the disproportionation reaction of mercury(I) in alkaline solutions have been measured by the stopped-flow method. The rate law is given by  $-d[Hg_2OH^+]/dt = k_1[Hg_2OH^+] + k_2[Hg_2OH^+][OH^-]$  in alkaline concentrations of 0.00454–0.04915 M. The values for  $k_1$  and  $k_2$  at 25 °C and  $\mu = 0.1$  are estimated to be  $9.0 \pm 0.2 \text{ s}^{-1}$  and  $(2.8 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The activation parameters associated with  $k_1$  and  $k_2$  are  $\Delta H_1^* = \Delta H_2^* = 12 \pm 1 \text{ kcal mol}^{-1}$ ,  $\Delta S_1^* = -14 \pm 4 \text{ cal mol}^{-1} \text{ deg}^{-1}$ , and  $\Delta S_2^* = -7.2 \pm 1.8 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . The proposed mechanism is as follows:  $Hg_2^{2+} + OH^- \rightleftharpoons Hg_2OH^+$ , rapid equilibrium;  $Hg_2OH^+ \rightarrow Hg^0 + HgOH^+$ ,  $k_1$ ;  $Hg_2OH^+ + OH^- \rightarrow Hg^0 + Hg(OH)_2$ ,  $k_2$ . General discussions on the disproportionation mechanism of mercury(I) ions were made.

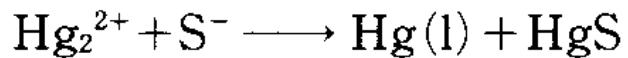
the reaction is suggested from the form of the observed rate law to be as follows



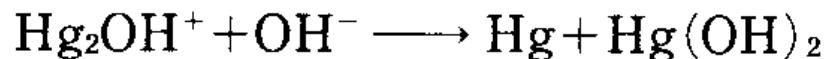
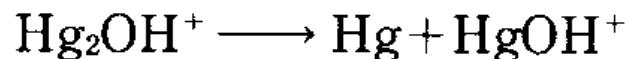
$$k_1 = 9.0 \text{ s}^{-1}$$

$$k_{-1} = 9.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

め存在しない。ここにあげた場合の反応は次のようである。



OH<sup>-</sup> および CN<sup>-</sup> との反応は速度論的に研究されている<sup>7)</sup>。その律速段階は Hg—Hg 結合の開裂であると思われる。すなわち



- 7) I. Sanemasa, *Inorg. Chem.*, 16, 2786 (1977); 15, 1973 (1976).

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水銀をテーマにした研究

有機非電解質の水溶解度の研究

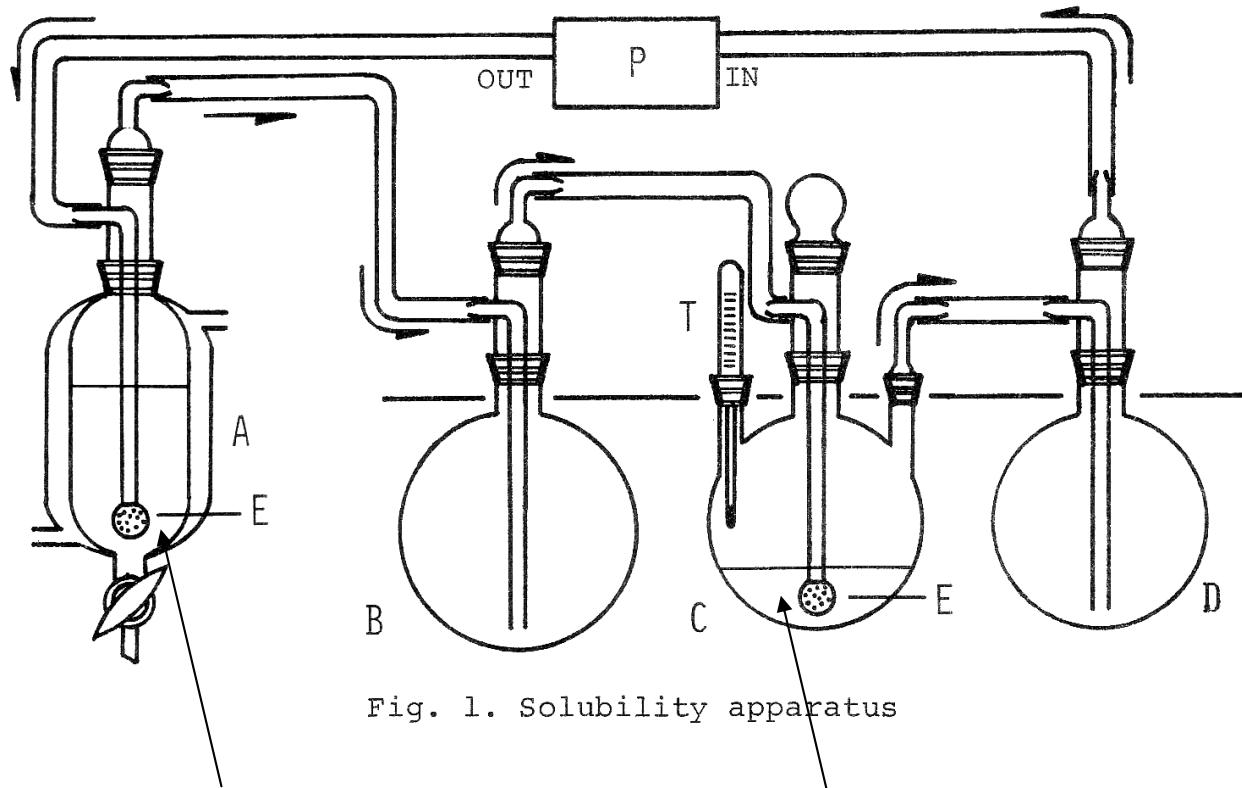


Fig. 1. Solubility apparatus

水溶液

過剰量の溶質

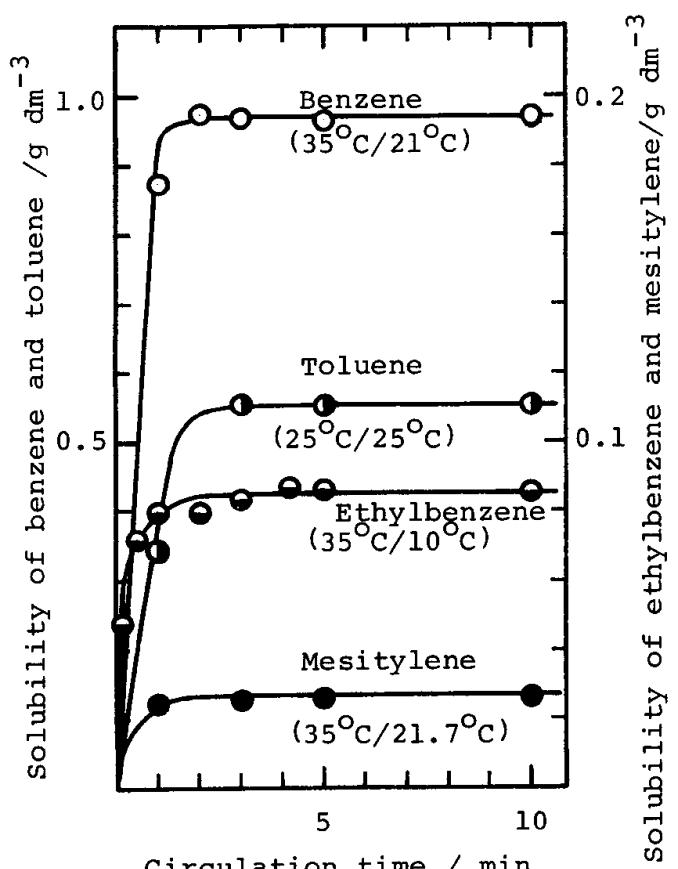


Fig. 3. Concentration vs. circulation time  
(Temp. of water / Temp. of solute)

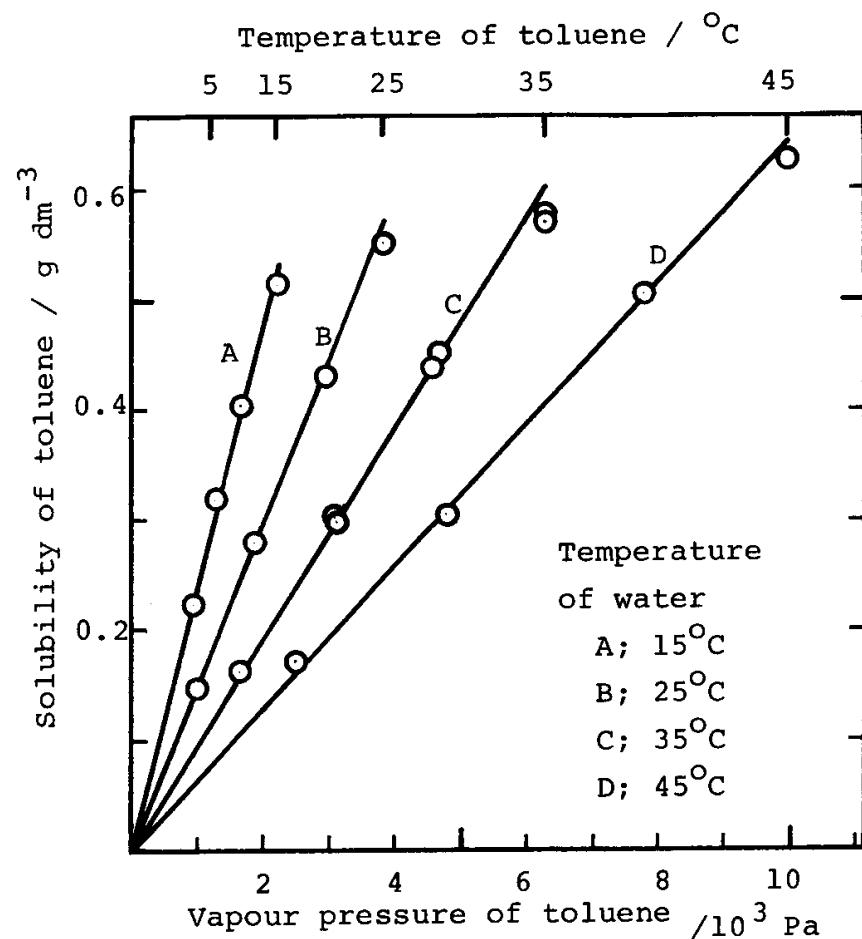


Fig. 4. Solubility vs. vapour pressure  
of toluene

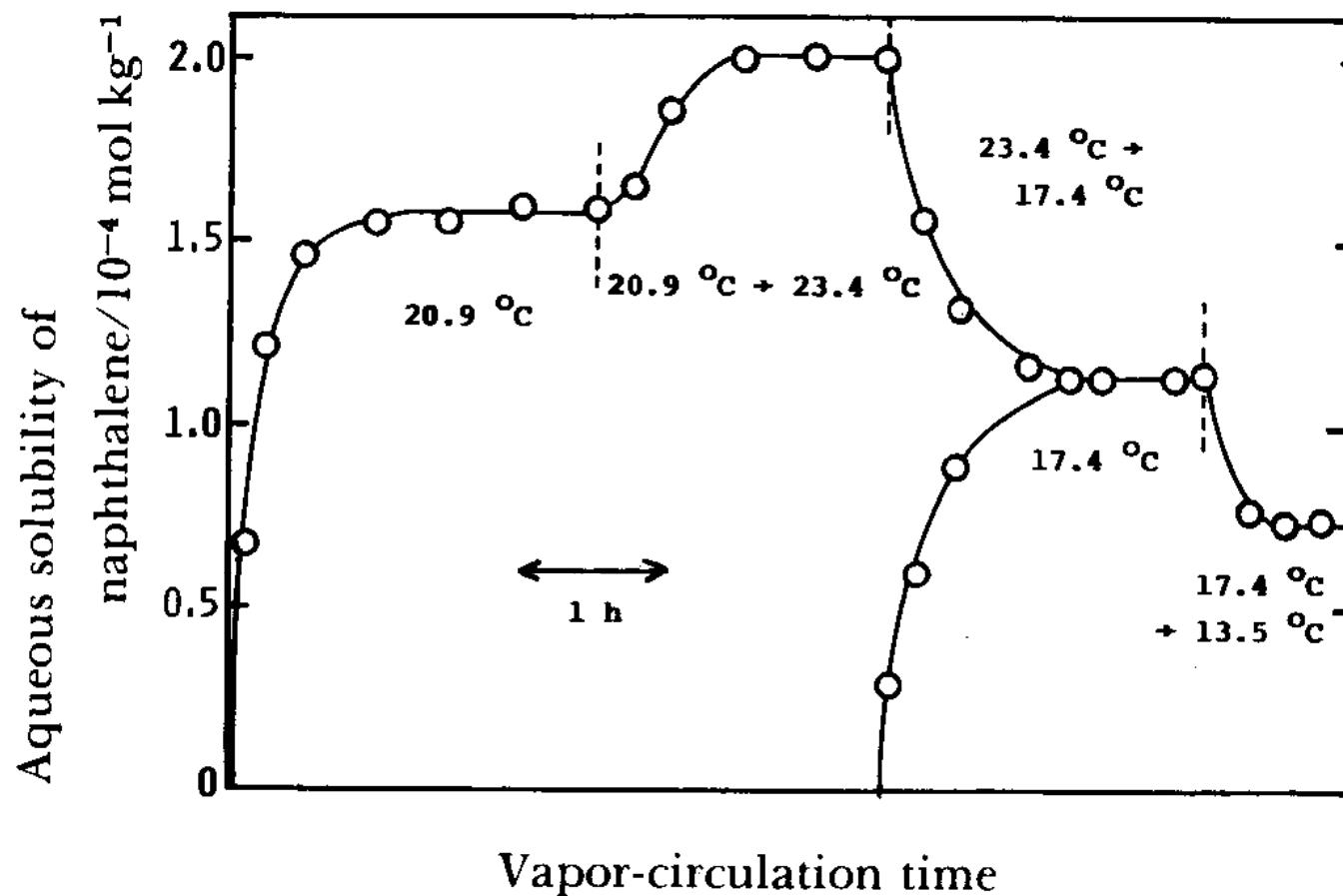


Fig. 1. Equilibrium solubility vs. vapor-circulation time. The temperature of solute reservoir in which solid naphthalene had been placed together with water was set as specified in Figure, while that of solubility flask was held constant at  $25^\circ\text{C}$ .

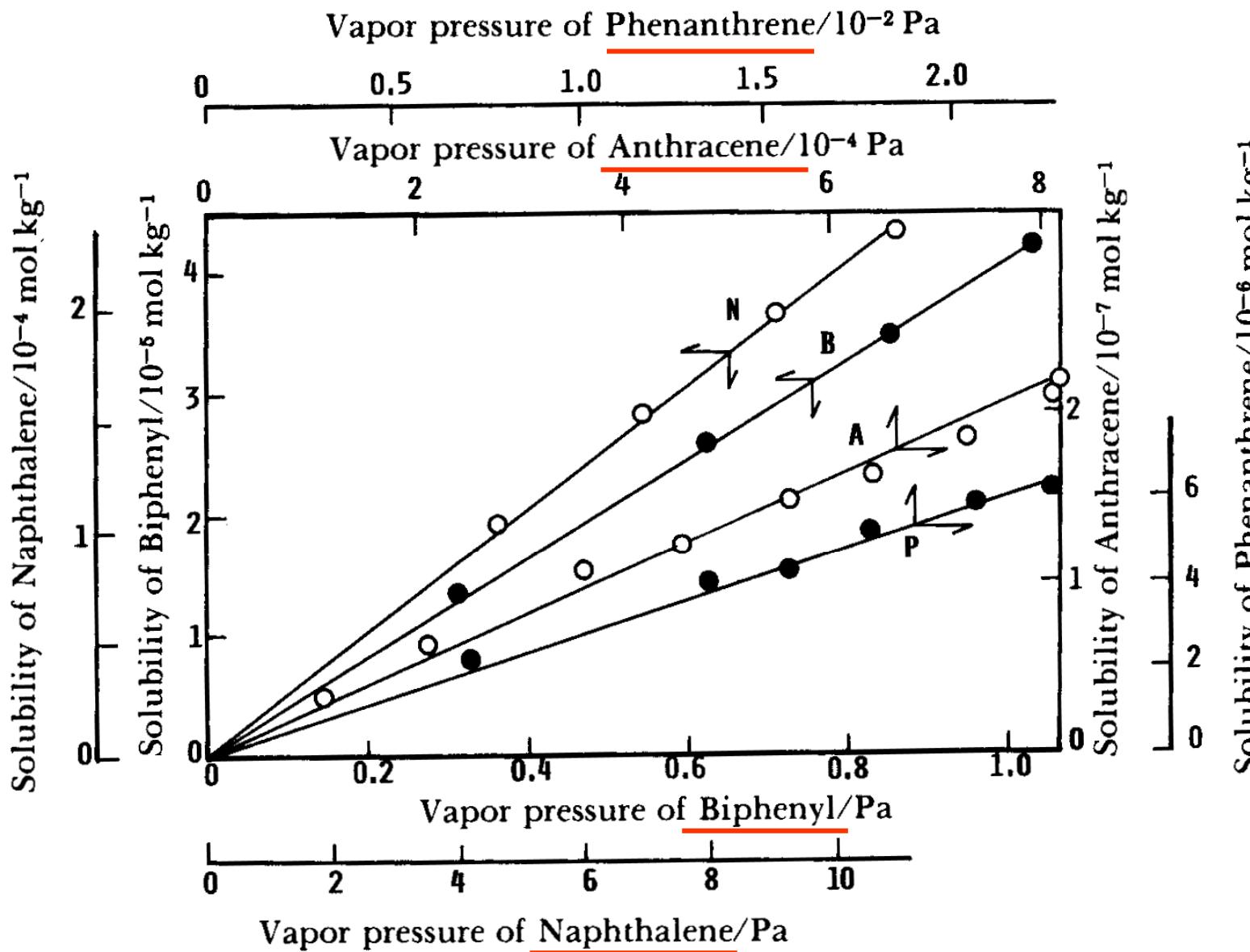
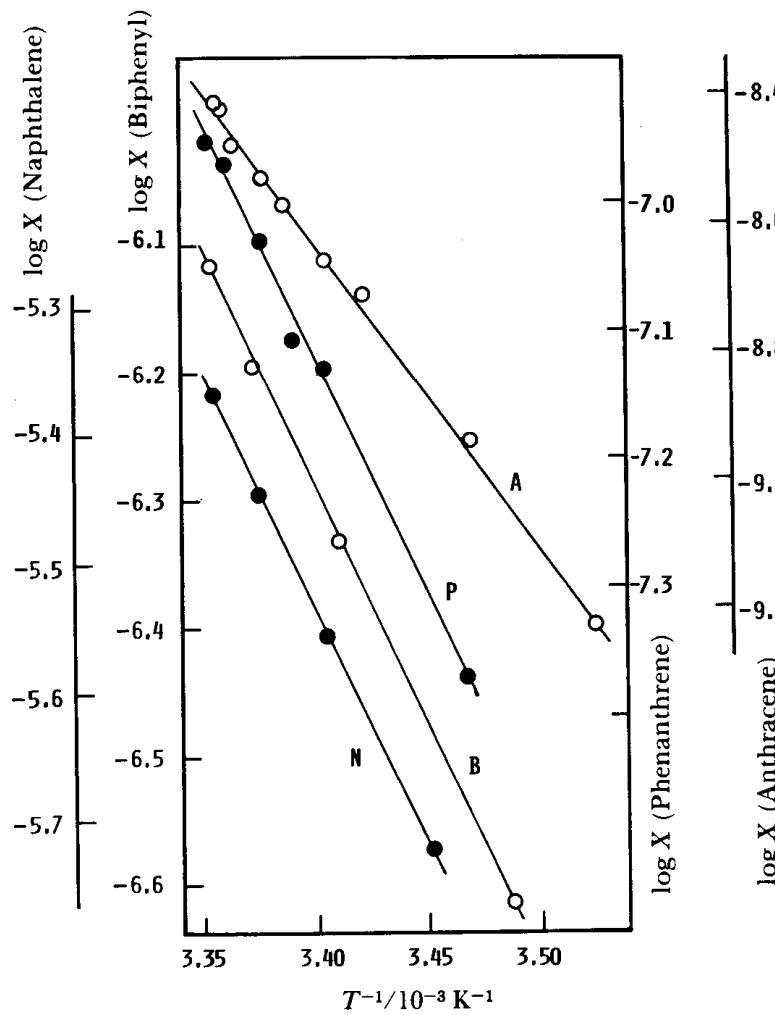


Fig. 2. Equilibrium solubility vs. solute vapor pressure. Biphenyl (B), naphthalene (N), anthracene (A), and phenanthrene (P).



$$P = K_H X_2$$

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2}$$

$$\log X_2 = \frac{-\Delta H_{\text{sub}}}{2.303R} \frac{1}{T} + \text{const.}$$

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

Solute	$\Delta H_{\text{sub}}/\text{kJ mol}^{-1}$		
	This work	Literature data	
Biphenyl	72.4	72.8, <sup>11)</sup>	75.8 <sup>3)</sup>
Naphthalene	71.0	72.4, <sup>5)</sup>	72.6, <sup>12)</sup> 75.8 <sup>13)</sup>
Anthracene	90.9	91.8, <sup>13)</sup>	103.8, <sup>3)</sup> 104.5 <sup>12)</sup>
Phenanthrene	73.3	86.6, <sup>3)</sup>	92.5, <sup>12)</sup> 95.0 <sup>13)</sup>

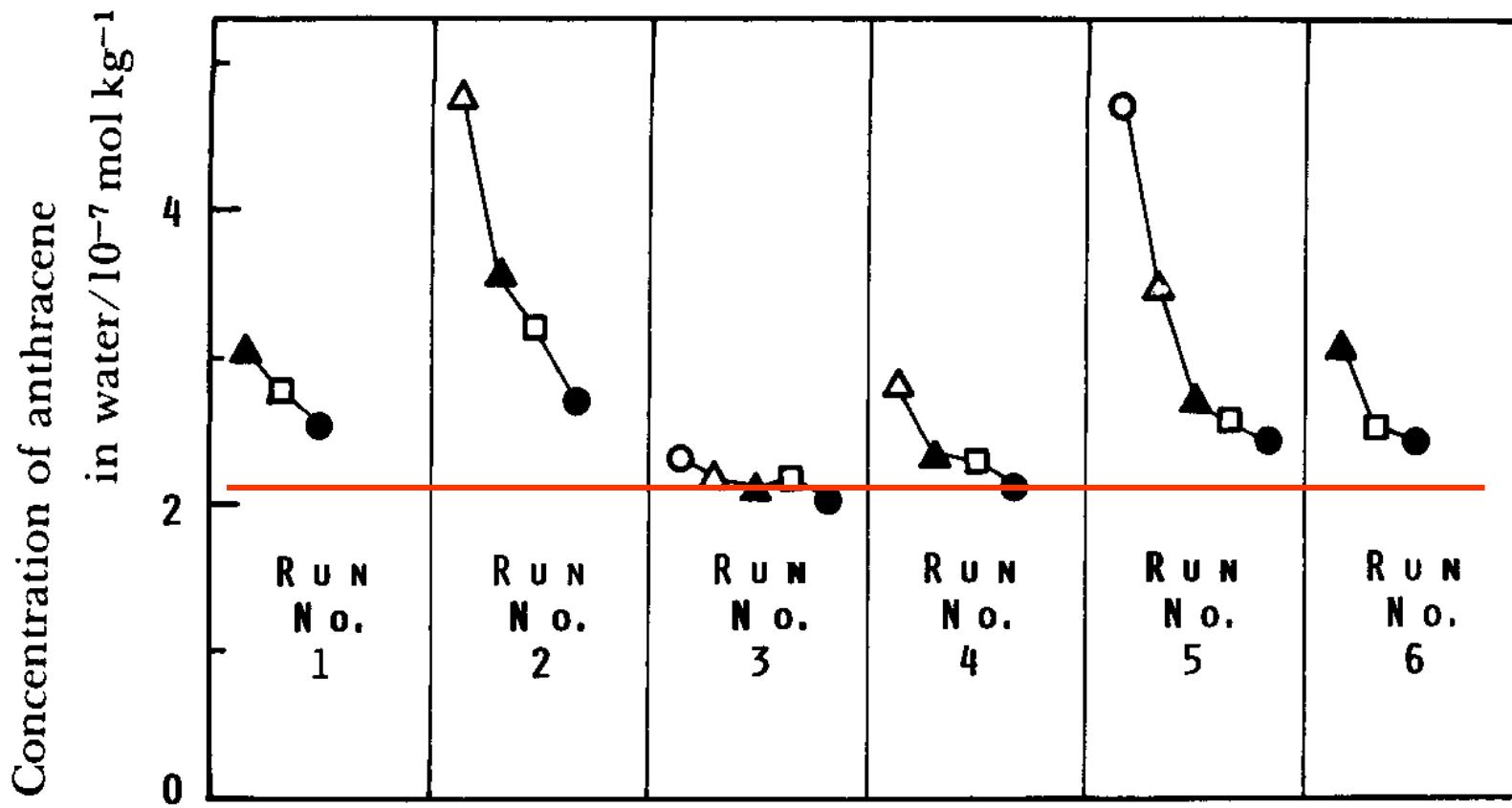


Fig. 4. Concentration of anthracene in water prepared by "shake-flask" technique, six replicated runs. The solid anthracene was stirred in water, and then, allowed to stand for 5( $\circ$ ), 7( $\Delta$ ), 9( $\blacktriangle$ ), 11( $\square$ ), and 14 days( $\bullet$ ).

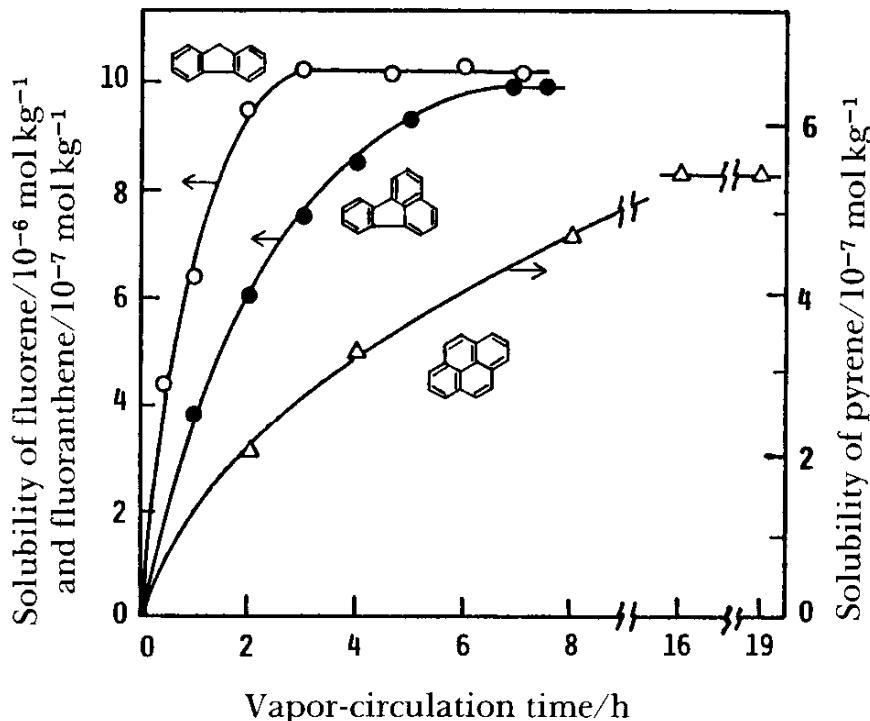


Fig. 1. Solute concentrations in water at 25 °C vs. solute-vapor-circulation time. Fluorene (○), fluoranthene (●), and pyrene (△).

Table 1. Henry's Law Constant, Aqueous Solubility, and Enthalpy of Sublimation (Data at 25 °C)

Solute $K_H^a$ /10 <sup>4</sup> Pa	$S^b$ /10 <sup>-6</sup> mol kg <sup>-1</sup>		$\Delta H_{\text{sub}}^c$ /kJ mol <sup>-1</sup>
	This work	Literature data <sup>d</sup>	
Fluorene	43.0	10.2 (10.15, 11.9, 11.4)	86.8 (83.0, 88.8)
Fluoranthene	6.75	1.02 (1.02, 1.3, 1.32)	78.5 (103, 84.5)
Pyrene	5.89	0.569 (0.64, 0.653, 0.668, 0.733, 0.77)	97.5 (91.3, 93.8, 100)

a) Henry's law constant determined in this work. b) The solubility in water estimated from  $K_H$ . c) The enthalpy of sublimation estimated from equilibrium solubility. d) Taken from Ref. 13. e) Taken from Ref. 14.

## 溶質蒸気を利用する飽和水溶液の調製の特徴

1. ヘンリー則に従うかどうか実験的に確認できる。
2. 過剰の溶質が存在しない。
3.  $\left\{ \begin{array}{l} \text{Henry's Law Constant} \\ \text{Sublimation Enthalpy} \end{array} \right\}$  を容易に求めることができる。

Dohanyosova P, Fenclova D, Vrbka P, et al.

Measurement of aqueous solubility of hydrophobic volatile organic compounds by solute vapor absorption technique: Toluene, ethylbenzene, propylbenzene, and butylbenzene at temperatures from 273 K to 328 K

JOURNAL OF CHEMICAL AND ENGINEERING DATA 46 (6): 1533-1539 NOV-DEC 2001

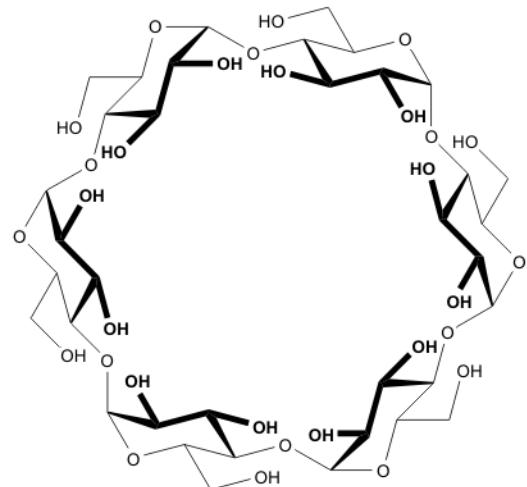
In this paper we describe our new implementation of a solute vapor absorption (SVA) method inspired by the ideas of Sanemasa et al. and those of the exponential saturator and apply it for the determination of the aqueous solubility of lower *n*-alkylbenzenes (toluene, ethylbenzene, propylbenzene, and butylbenzene) over a broad temperature range. The interest in the aqueous solubility of alkylbenzenes stems again from both practical and theoretical

水銀をテーマにした研究

有機非電解質の水溶解度の研究

シクロデキストリンによる有機非電解質の包接に関する研究

## シクロデキストリン (CyD)

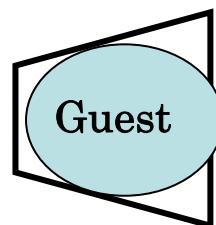


グルコピラノースを構成単位とする  
環状のオリゴ糖

構成単位 6 個 · ·  $\alpha$ -CyD

7 個 · ·  $\beta$ -CyD

8 個 · ·  $\gamma$ -CyD



底の抜けたバケツ状構造

分子の外側 · · 親水性  
空洞内部 · · 疎水性

包接体生成の会合定数の測定 { Guest の溶解度の測定  
Guest の揮発速度の測定

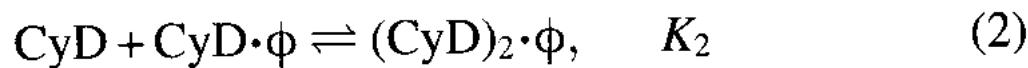
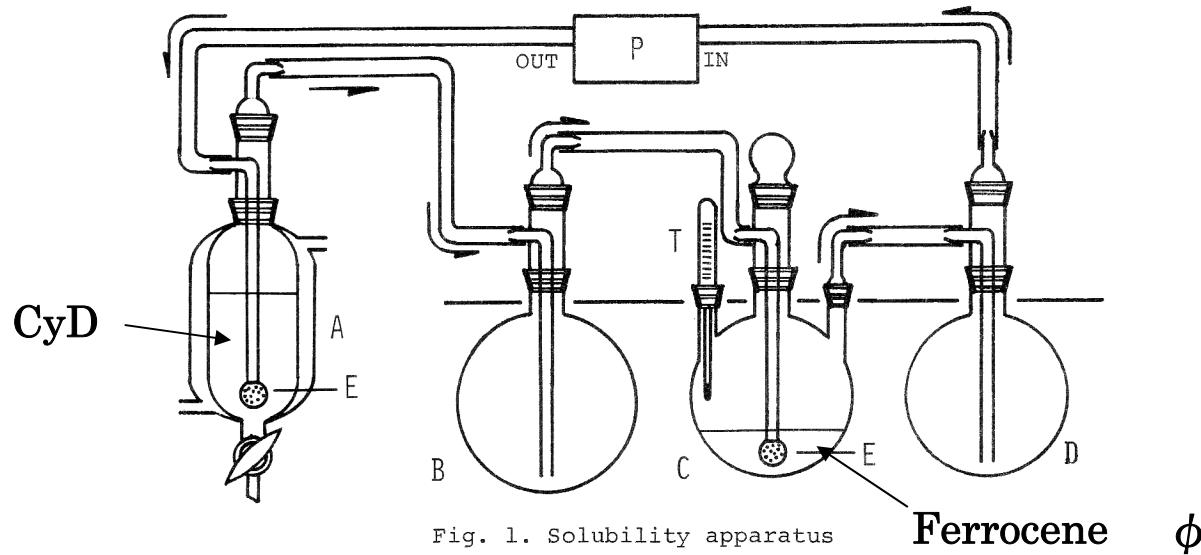
# Association Constants of Ferrocene with Cyclodextrins in Aqueous Medium Determined by Solubility Measurements of Ferrocene

Ji-Shi Wu, Kei Toda, Akira Tanaka, and Isao Sanemasa\*

Department of Environmental Science, Faculty of Science, Kumamoto University,  
Kurokami 2-39-1, Kumamoto 860-8555

(Received February 19, 1998)

The association constants of ferrocene with cyclodextrins (CyD's) in an aqueous medium at 25 °C have been determined by solubility measurements of ferrocene in both the absence and presence of CyD. The solubility of ferrocene in pure water was found to be  $(4.25 \pm 0.02) \times 10^{-5}$  mol dm<sup>-3</sup> at 25.0 ± 0.1 °C. The  $\beta$ - and  $\gamma$ -CyD's form only 1 : 1 complexes with ferrocene. The 1 : 1 association constants were determined to be  $(1.39 \pm 0.21) \times 10^2$  ( $\alpha$ ),  $(1.65 \pm 0.04) \times 10^4$  ( $\beta$ ), and  $(9.04 \pm 0.11) \times 10^2$  dm<sup>3</sup> mol<sup>-1</sup> ( $\gamma$ ). The 2 : 1 (CyD : ferrocene) association constant was  $(2.36 \pm 0.06) \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> ( $\alpha$ ). Ferrocene-included CyD precipitates were also prepared in water, and their stability upon drying in air was studied. The sublimation enthalpy of ferrocene in the temperature range of 290.65 to 298.15 K was estimated to be 74.2 ± 1.5 kJ mol<sup>-1</sup>.



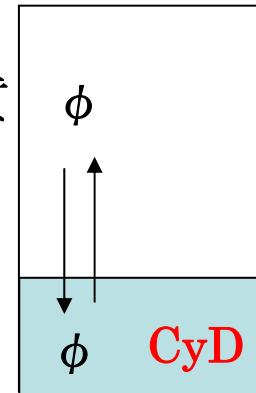
揮発性溶質

$$C_\phi = [\phi]_0 + [CyD \cdot \phi] + [(CyD)_2 \cdot \phi] \quad \text{Henry's law}$$

$$= [\phi]_0(1 + K_1 [CyD] + K_1 K_2 [CyD]) \quad (3)$$

$$C_{CyD} = [CyD] + [CyD \cdot \phi] + 2[(CyD)_2 \cdot \phi] \quad (4)$$

$$= [CyD](1 + K_1 [\phi]_0 + 2K_1 K_2 [\phi]_0 [CyD]).$$



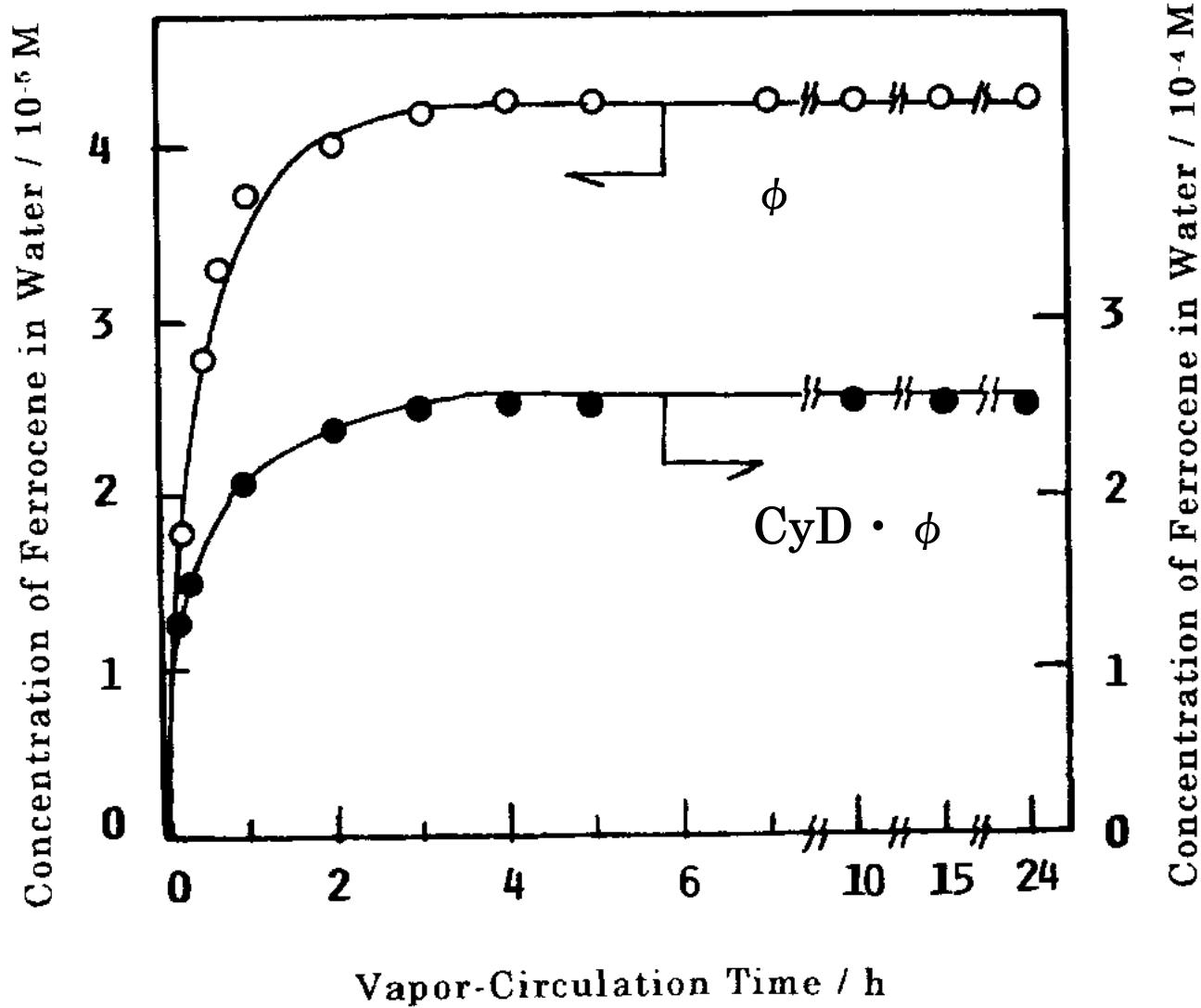


Fig. 1. Concentration of ferrocene in water (○) and in  $\beta$ -CyD ( $C_{\text{CyD}} = 5.00 \times 10^{-4}$  M) solution (●) at  $25.0 \pm 0.1$  °C as a function of ferrocene vapor-circulation time.

$$C_\phi = [\phi]_0 + [\text{CyD} \cdot \phi] + [(\text{CyD})_2 \cdot \phi]$$

$$= [\phi]_0(1 + K_1[\text{CyD}] + K_1K_2[\text{CyD}]^2)$$

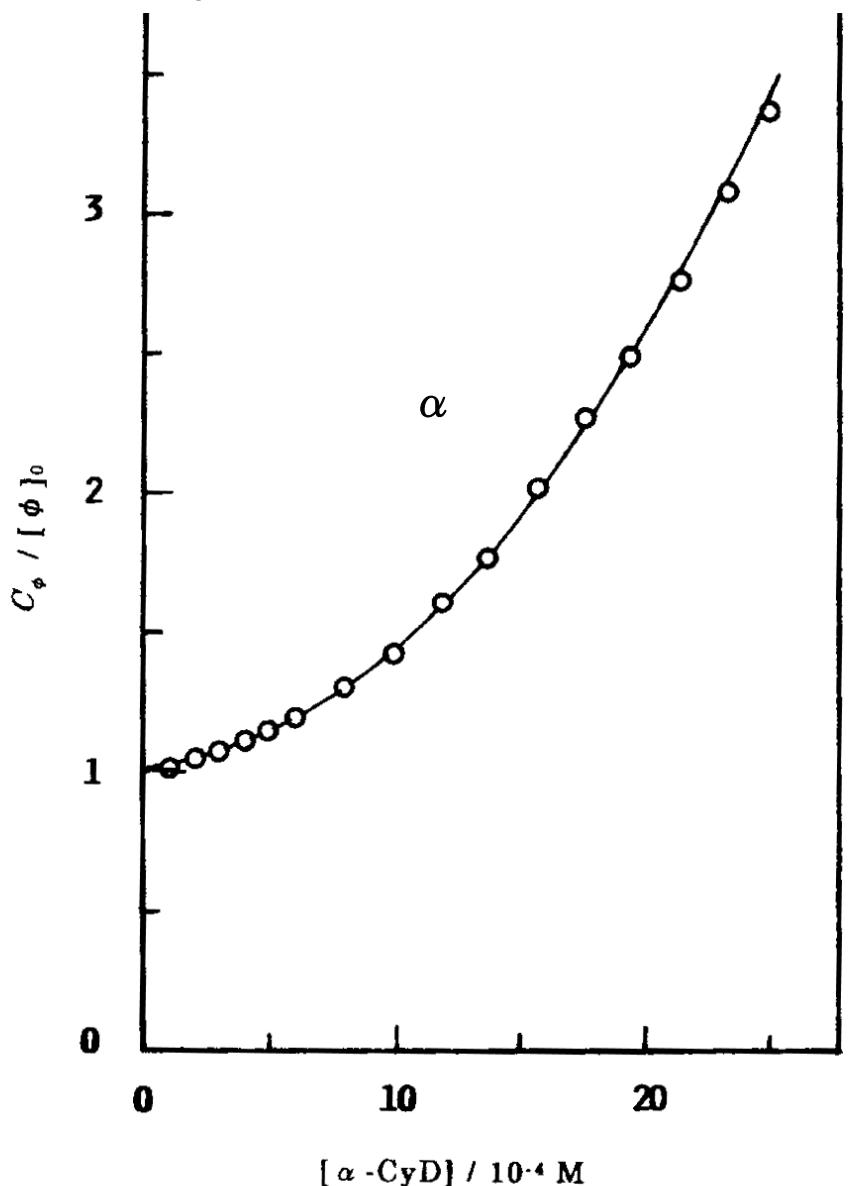


Fig. 2. Plots of  $C_\phi / [\phi]_0$  vs. concentration of free  $\alpha$ -CyD.

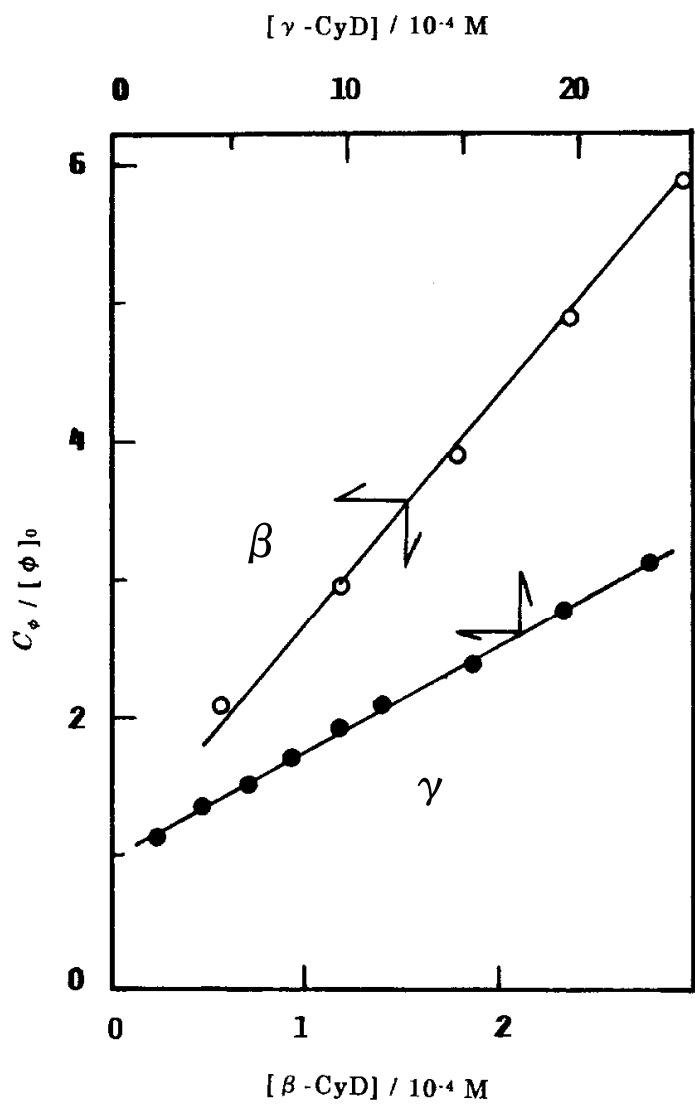


Fig. 3. Plots of  $C_\phi / [\phi]_0$  vs. concentration of free  $\beta$ -CyD (○) and  $\gamma$ -CyD (●).

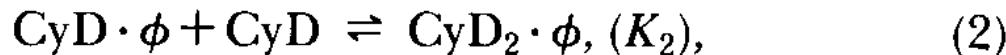
**Table 1.** Association Constants Obtained in This Work (Ferrocene–CyD in Aqueous Medium at 25 °C) and Those Reported in the Literature (Ferrocene–CyD in Nonaqueous Medium, Ferrocene-derivatives–CyD in Aqueous Medium)

Type of CyD	This work <sup>a)</sup>		Literature <sup>c)</sup>				
	Aqueous medium (Guest; ferrocene)	Nonaqueous medium (Guest; ferrocene) <sup>d)</sup>				Aqueous medium	
		Solvent		DMSO	DMSO : water (8 : 2)	Guest <sup>e)</sup>	FC <sub>1</sub> <sup>+</sup>
	$K_1/\text{dm}^3 \text{ mol}^{-1}$	$K_2^{\text{b})}/\text{dm}^3 \text{ mol}^{-1}$			$K_1/\text{dm}^3 \text{ mol}^{-1}$		
$\alpha$	$(1.39 \pm 0.21) \times 10^2$	$(2.36 \pm 0.06) \times 10^3$				240	420
$\beta$	$(1.65 \pm 0.04) \times 10^4$	—	83, 77	40	48, 60, 40	320, 350	1900
$\gamma$	$(9.04 \pm 0.11) \times 10^2$	—					1400
						400	170

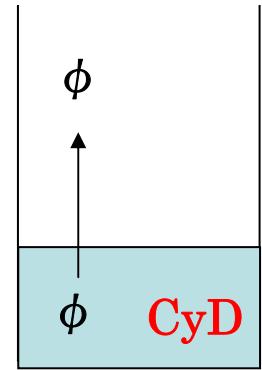
a) Total concentration of CyD;  $(1.00\text{--}26.0) \times 10^{-4} \text{ M}$  ( $\alpha$ ),  $(1.00\text{--}5.00) \times 10^{-4} \text{ M}$  ( $\beta$ ), and  $(1.00\text{--}24.0) \times 10^{-4} \text{ M}$  ( $\gamma$ ). b) The dash sign indicates that  $K_2$  was not evaluated. c) The temperature at which the data were obtained was not specified in the original papers. d) Taken from Refs. 1 and 2. e) Taken from Ref. 3; guests are alkyldimethyl(ferrocenylmethyl)ammonium salts, where the alkyl group is methyl (FC<sub>1</sub><sup>+</sup>) or heptyl (FC<sub>7</sub><sup>+</sup>).



# Guest の揮発速度の測定



$$dQ_\phi V^{-1}/dt = k[\phi], \quad (4)$$



$$C_{\text{CyD}} = [\text{CyD}] + [\text{CyD} \cdot \phi] + 2[\text{CyD}_2 \cdot \phi], \quad (5)$$

$$\begin{aligned} C_\phi &= [\phi] + [\text{CyD} \cdot \phi] + [\text{CyD}_2 \cdot \phi] + Q_\phi V^{-1} \\ &= [\phi] + K_1[\text{CyD}][\phi] + K_1 K_2 [\text{CyD}]^2 + Q_\phi V^{-1}, \end{aligned} \quad (6)$$

$$dQ_\phi V^{-1}/dt = k(C_\phi - Q_\phi V^{-1})/(1 + K_1[\text{CyD}] + K_1 K_2 [\text{CyD}]^2), \quad (7)$$

$$\ln(C_\phi - Q_\phi V^{-1}) = -kt/(1 + K_1[\text{CyD}] + K_1 K_2 [\text{CyD}]^2) + \ln C_\phi = -k't + \ln C_{\phi_0}, \quad (8)$$

$$k' = k/(1 + K_1[\text{CyD}] + K_1 K_2 [\text{CyD}]^2). \quad (9)$$

$$1/k' = K_1 K_2 C_{\text{CyD}}^2/k + K_1 C_{\text{CyD}}/k + 1/k, \quad (10)$$

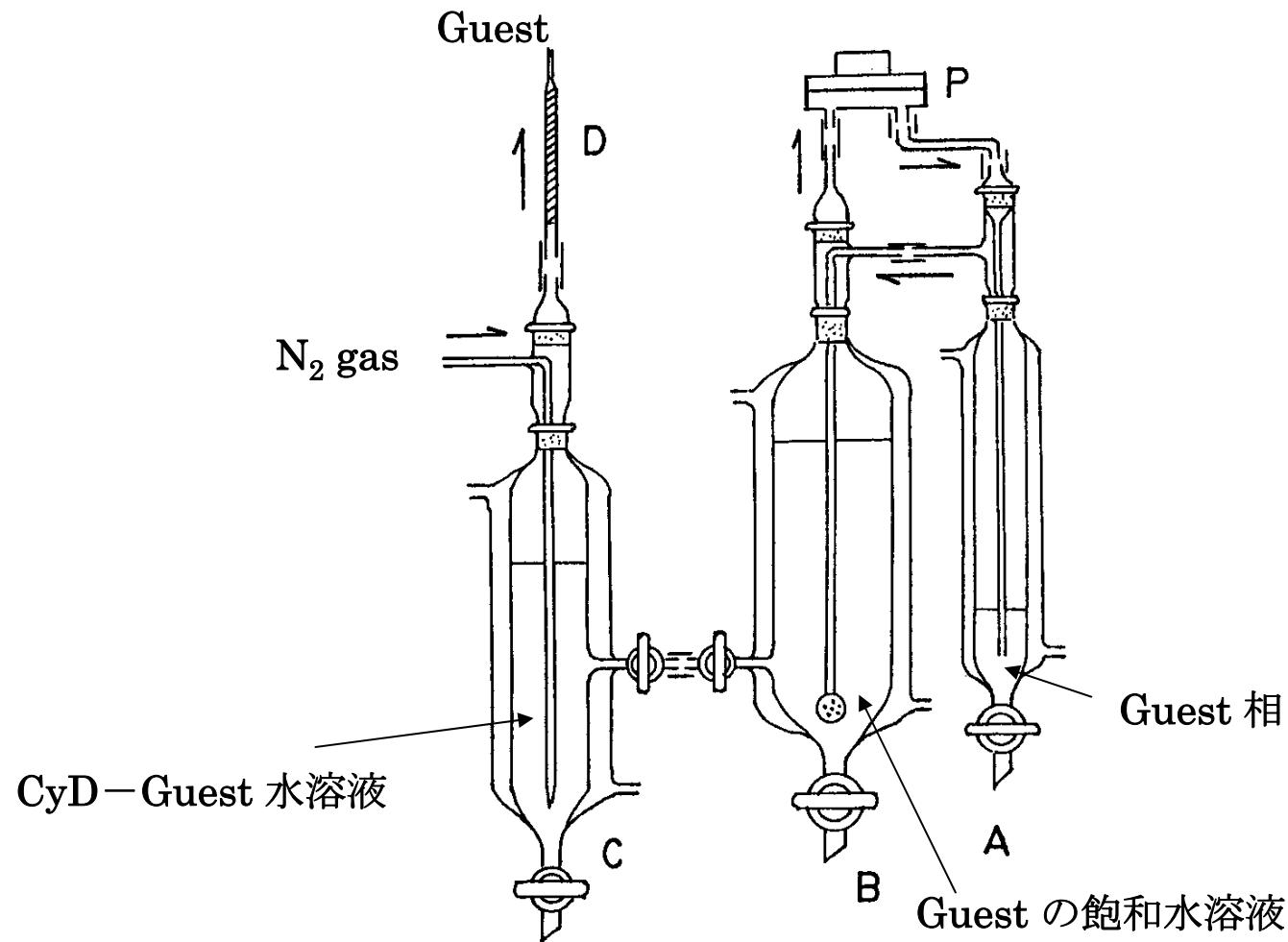


Fig. 1. The device used to prepare aqueous solutions saturated with guest and to volatilize the dissolved guest from aqueous to gaseous phase by nitrogen gas stream.

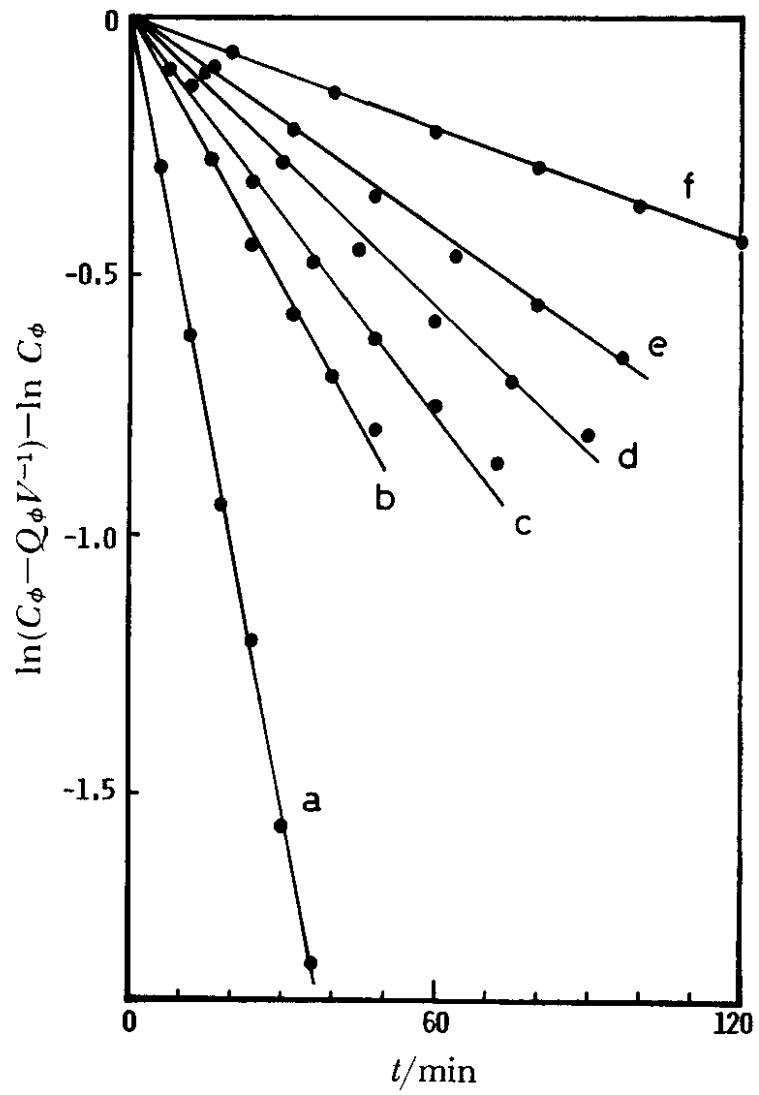
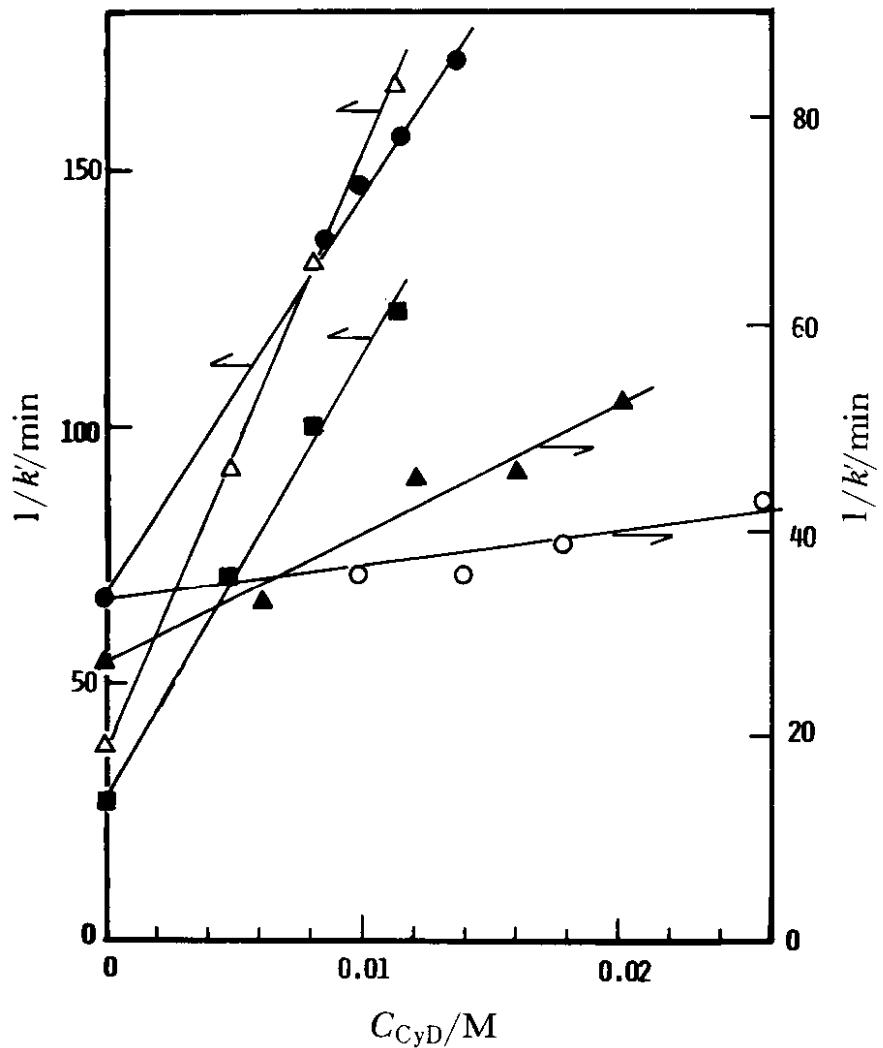


Fig. 1. Propylbenzene- $\alpha$ -CyD system. The plots of  $\ln(C_\phi - Q_\phi V^{-1}) - \ln C_\phi$  vs.  $t$  in the absence and presence of cyclodextrin.  $N_2$  gas flow rate  $19.9 \text{ cm}^3 \text{ min}^{-1}$ ;  $C_{\text{CyD}}/10^{-3} \text{ M}$ ; (a) 0, (b) 2.52, (c) 5.04, (d) 7.56, (e) 10.1, (f) 20.2;  $C_\phi/10^{-4} \text{ M}$ ; (a) 4.46, (b) 2.42, (c) 2.61, (d) 3.91, (e) 3.91, (f) 3.63.

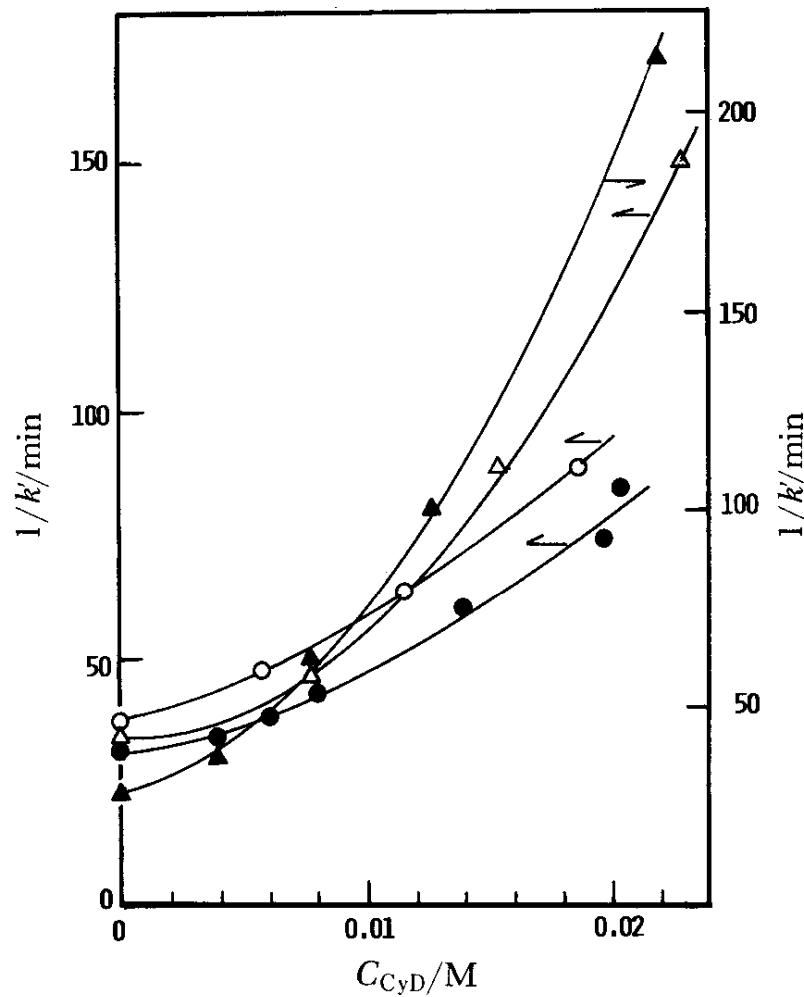
$$\ln(C_\phi - Q_\phi V^{-1}) = -k't + \ln C_\phi,$$

$$k' = k/(1 + K_1[\text{CyD}] + K_1 K_2 [\text{CyD}]^2).$$

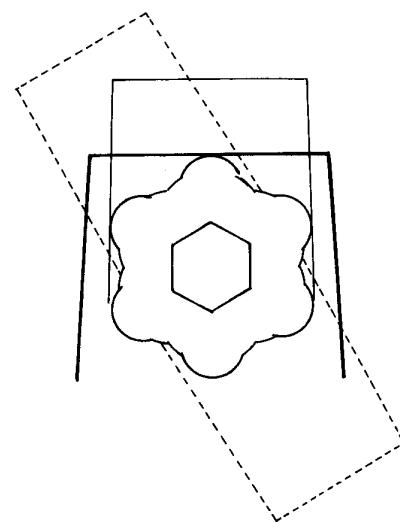
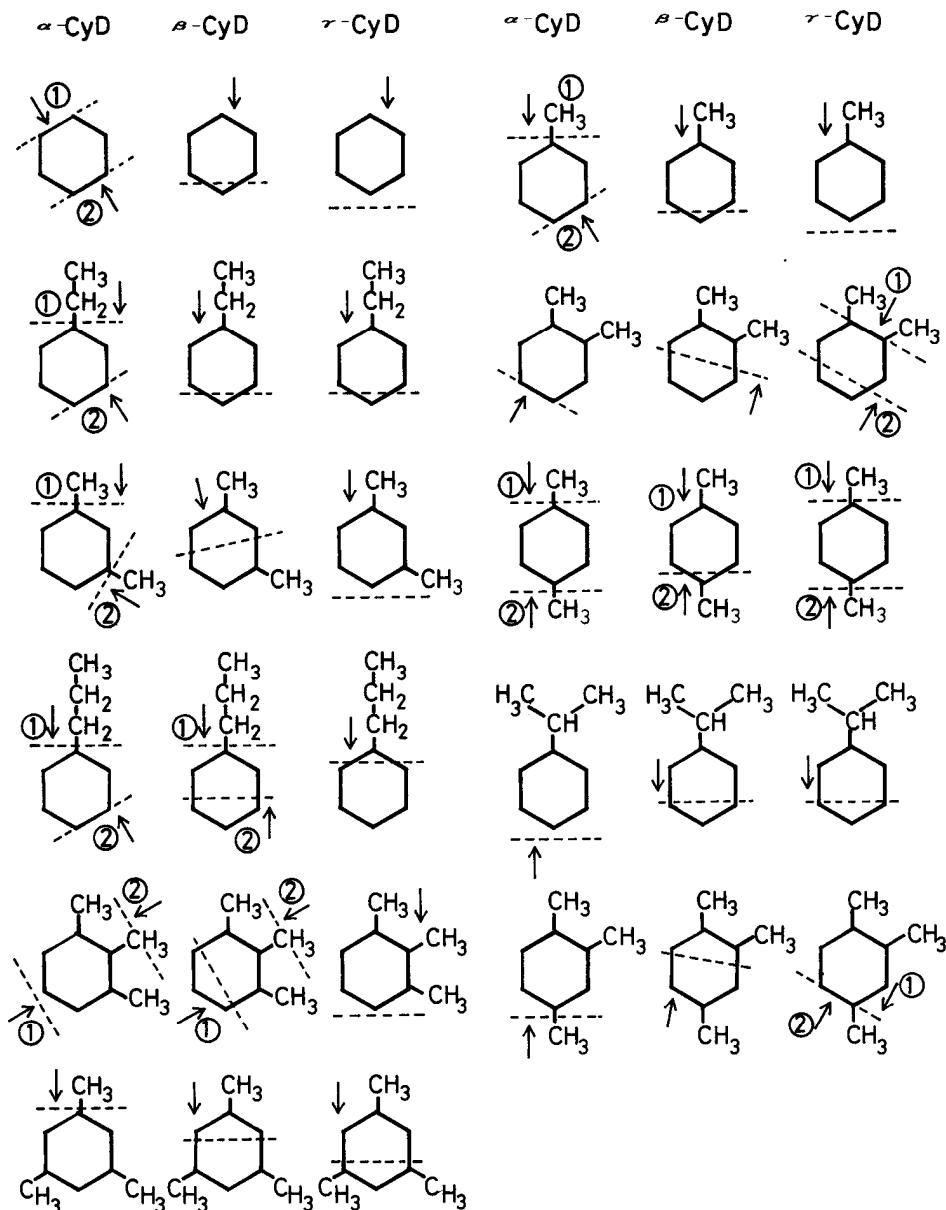
$$1/k' = K_1 K_2 C_{\text{CyD}}^2/k + K_1 C_{\text{CyD}}/k + 1/k,$$



**Fig. 2.** The plots of  $1/k'$  vs.  $C_{\text{CyD}}$ . Examples of straight line. Benzene- $\beta$ -CyD( $\bullet$ ), benzene- $\gamma$ -CyD( $\circ$ ), 1,2,4-trimethylbenzene- $\alpha$ -CyD( $\blacktriangle$ ), o-xylene- $\beta$ -CyD( $\triangle$ ), ethylbenzene- $\beta$ -CyD( $\blacksquare$ ).



**Fig. 3.** The plots of  $1/k'$  vs.  $C_{\text{CyD}}$ . Examples of parabolic curve. Benzene- $\alpha$ -CyD( $\bullet$ ), o-xylene- $\gamma$ -CyD( $\circ$ ), *p*-xylene- $\alpha$ -CyD( $\blacktriangle$ ), 1,2,3-trimethylbenzene- $\alpha$ -CyD( $\triangle$ ).



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Fig. 10. Host-guest inclusion model. The direction from which the host includes the guest and the extent to which the guest penetrates the host are indicated by an arrow and a dotted line, respectively. The numbers, 1 and 2, in the circle refer to the binding sites corresponding to  $K_1$  and  $K_2$ , respectively.

Table 2. Association Constants of 1:1 (Host:Guest)  
Complexation at 25°C, Comparison  
with Those in Literatures

Guest-Host	Association constant/dm <sup>3</sup> mol <sup>-1</sup>	
	Our studies	Literature
Benzene- $\alpha$ -CyD	17 <sup>6)</sup>	31.6 <sup>8)</sup>
- $\beta$ -CyD	1.2×10 <sup>2</sup> <sup>6)</sup>	169, <sup>8)</sup> 196 <sup>9)</sup>
- $\gamma$ -CyD	12 <sup>6)</sup>	9.1 <sup>8)</sup>
Naphthalene- $\alpha$ -CyD	83 <sup>7)</sup>	
- $\beta$ -CyD	6.3×10 <sup>2</sup> <sup>7)</sup>	685, <sup>10)</sup> 730, <sup>11)</sup> 850, <sup>12)</sup> 186 <sup>14)</sup>
- $\gamma$ -CyD	1.3×10 <sup>2</sup> <sup>7)</sup>	
Anthracene- $\beta$ -CyD	2.3×10 <sup>3</sup>	420, <sup>14)</sup> 32.39 <sup>15)</sup>
- $\gamma$ -CyD	1.5×10 <sup>3</sup>	9.41 <sup>15)</sup>
Phenanthrene- $\beta$ -CyD	1.5×10 <sup>3</sup>	170 <sup>13)</sup>
Naphthacene- $\beta$ -CyD	3.4×10 <sup>3</sup>	221 <sup>14)</sup>

水銀をテーマにした研究

有機非電解質の水溶解度の研究

シクロデキストリンによる有機非電解質の包接に関する研究

イオン交換樹脂による有機非電解質の捕捉に関する研究

## **Uptake of Alkanes and Alcohols by Ion-Exchange Resins in Aqueous Solution**

**Isao SANEMASA,<sup>†</sup> Misuzu NAKAHARA, and Jin-Zi ZHENG**

## **Uptake of Cycloalkanes and Bicyclic Aromatic Compounds by Ion-Exchange Resins from Aqueous Solutions**

**Isao SANEMASA,<sup>†</sup> Megumi IZUNO, and Yuka FUJII**

## **Uptake of Benzene and Alkylbenzenes by Cation- and Anion-Exchange Resins from Aqueous Solutions**

**Isao SANEMASA**

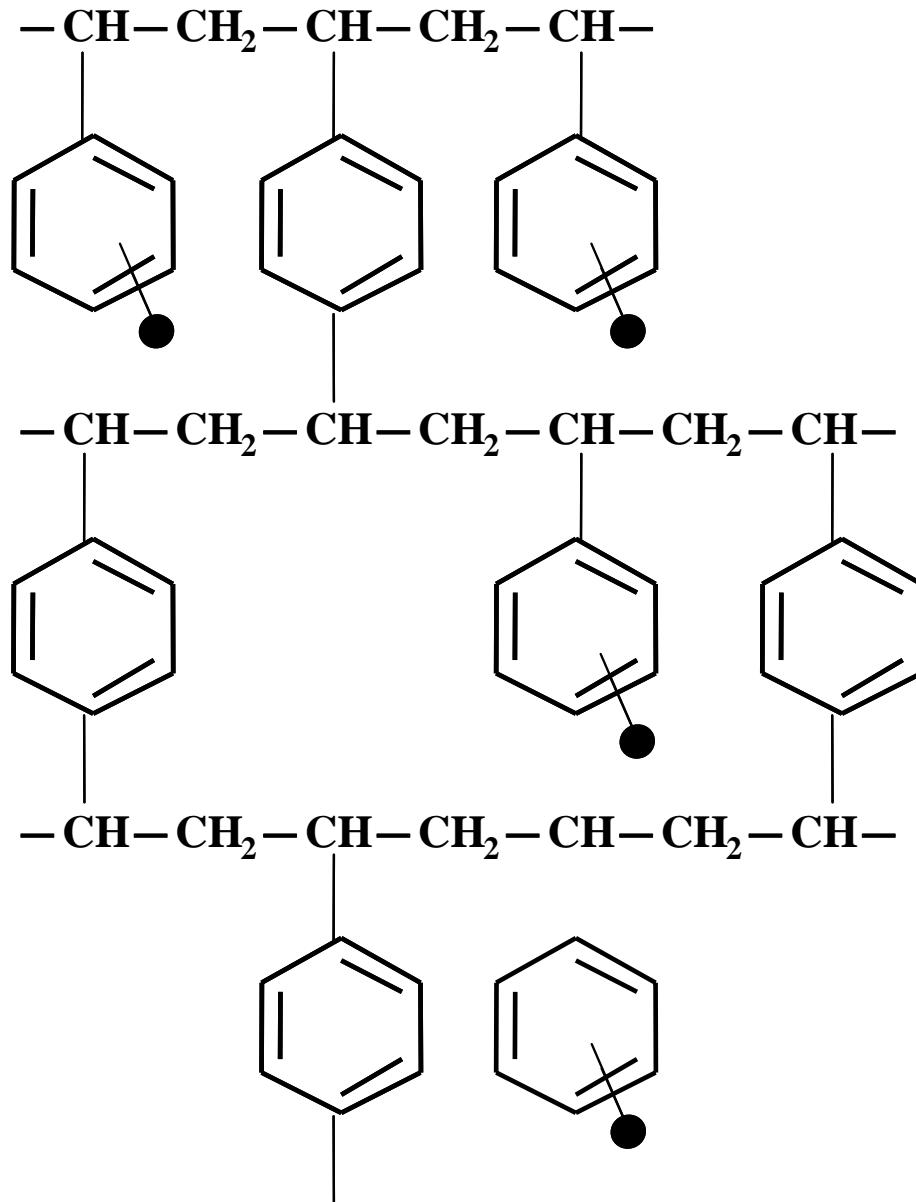
## **Uptake of Iodine and Bromine by Ion-Exchange Resins in Aqueous Solution**

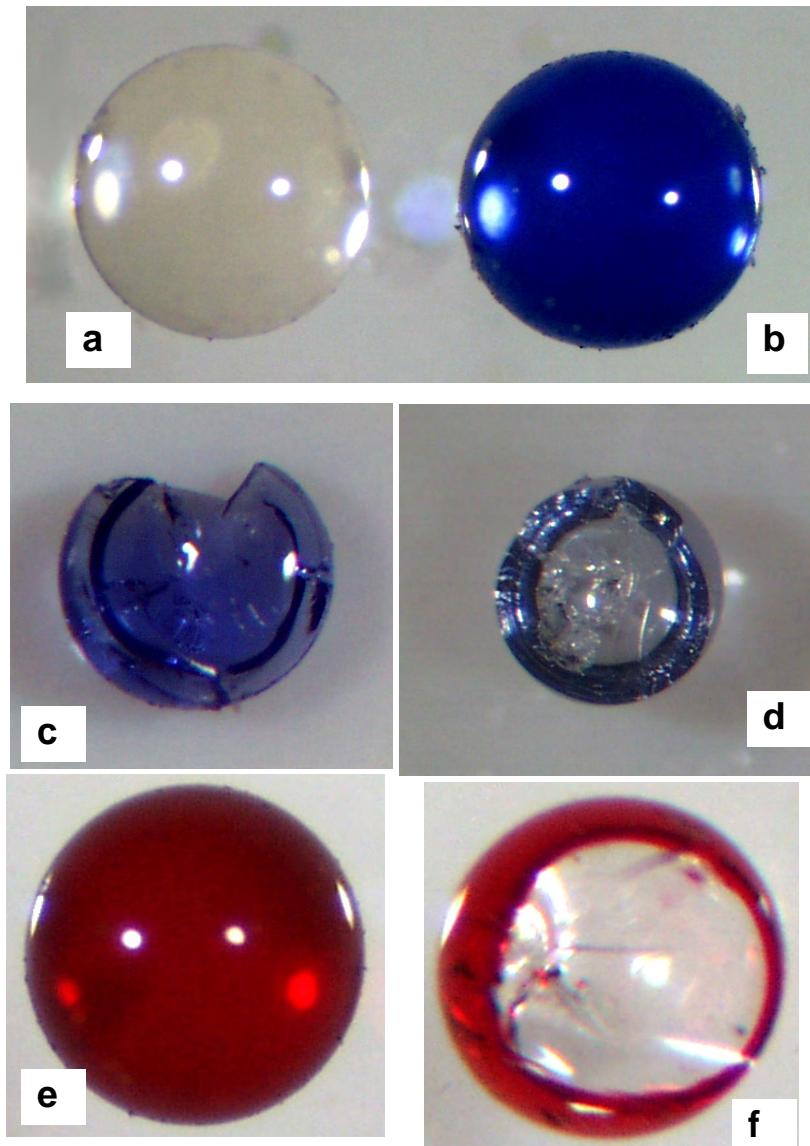
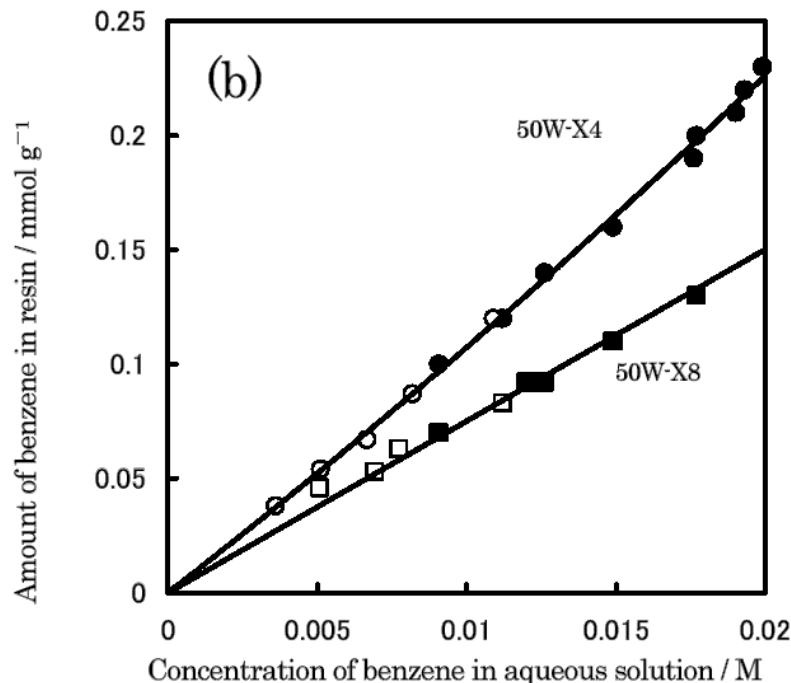
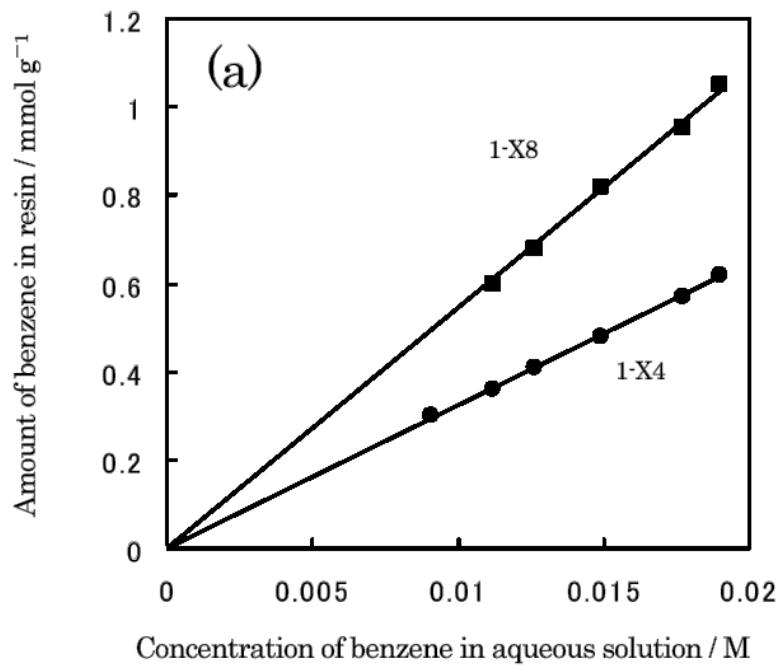
**Isao SANEMASA,<sup>†</sup> Michiko YOSHIDA, and Asami ABE**

● イオン交換基

陽イオン交換樹脂  
 $-\text{SO}_3^-$

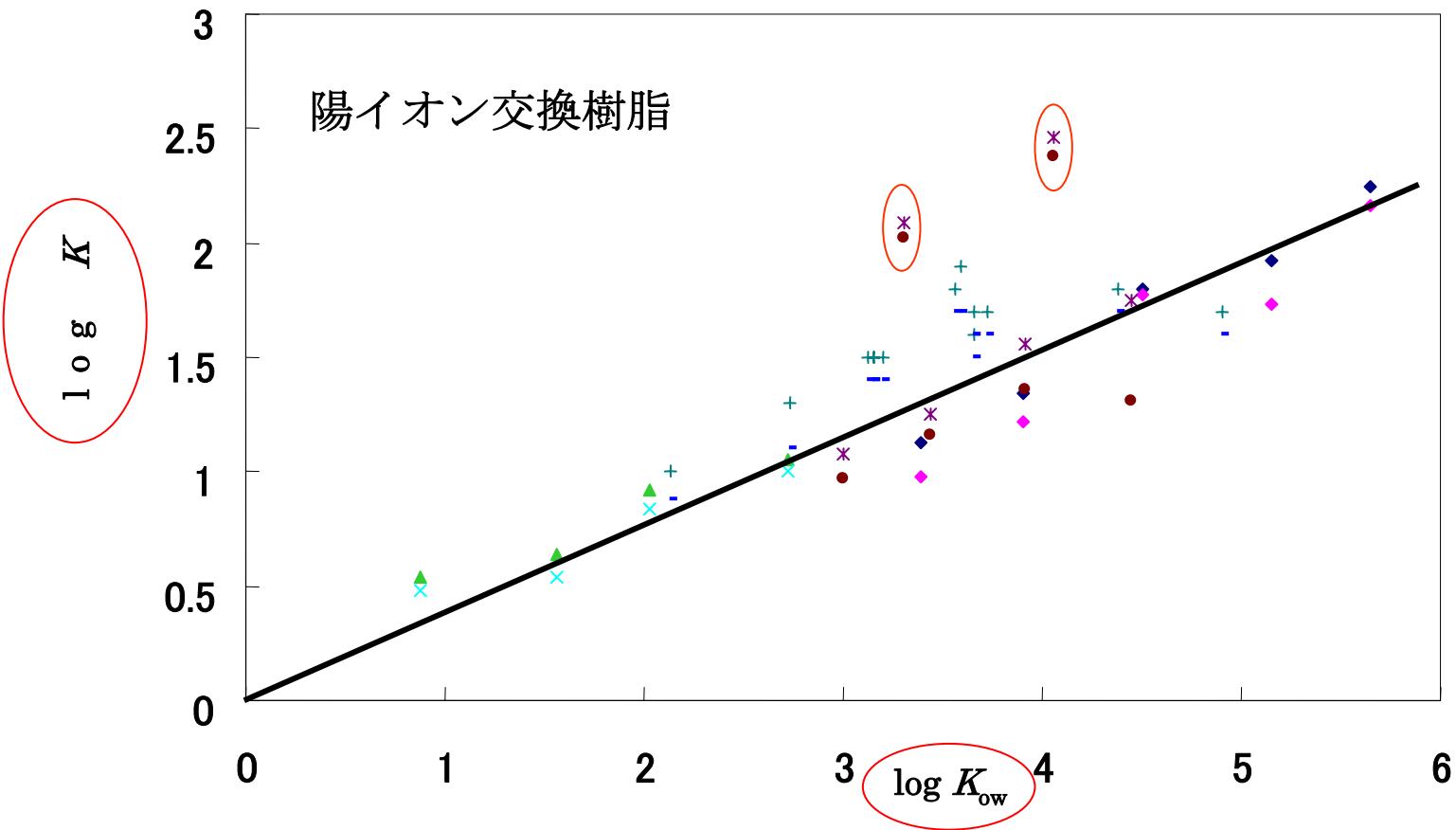
陰イオン交換樹脂  
 $-\text{CH}_2\text{N}^+(\text{CH}_2)_2\text{CH}_2$





Dowex 1-X4  
20–40 mesh

Acid Red 1  
(anionic dye)



Pentane  
Hexane  
Heptane  
Octane  
Nonane

1-Butanol  
1-Pentanol  
1-Hexanol  
1-Heptanol

Cyclopentane  
Cyclohexane  
Cycloheptane  
Cyclooctane

Naphthalene  
Biphenyl

Benzene  
Toluene  
(*o,m,p*)-Xylene  
*n*-Propylbenzene  
Trimethylbenzene  
Isopropylbenzene  
*n*-Butylbenzene  
*n*-Pentylbenzene

1. 樹脂への捕捉機構は、吸着ではなく、分配である。
2. 分配係数の対数値 ( $\log K$ ) と  $\log K_{ow}$  との間にほぼ直線の相関がある。
3. ベンゼン環を有する溶質は樹脂に強く捕捉される。  
樹脂マトリックスの  $\pi$  電子と芳香環との  $\pi - \pi$  相互作用が働いている。

従来、イオン交換樹脂は電解質のみを捕捉すると考えられていた



**有機溶媒による溶媒抽出**

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イオン交換樹脂による有機非電解質の捕捉に関する研究

揮発性の溶質

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