

Mechanism of Adsorption of Phenols by Carbon Black from Aqueous Solution^{1,2)}

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(Received April 3, 1971)

The adsorption of phenols by carbon black from aqueous solution was investigated to discuss the mechanism of interaction on the adsorbent surface, referring to the partition coefficient in *n*-octanol/water system, P_X .

The shape of adsorption isotherm was discussed with respect to the position of substituents and also the degree of dissociation.

There was found a linear relationship between Langmuir constant a and $\log P_X$. This result was explained thermodynamically on the assumption of a surface layer on the carbon black, concluding that the surface layer is considered to play the similar role to *n*-octanol layer in the partition experiment.

Free energy of adsorption calculated from Langmuir constant b seemed to be an apparent one and to be influenced predominantly by the free energy of binding.

Regarding the relationship between the adsorbed amount at an identical equilibrium concentration, M_e , and the equilibrium concentration at an identical adsorbed amount, C_m , the following equation was derived:

$$\log M_e = (1/\lambda) \log (1/C_m) + k$$

where λ and k are constant.

Plotting $\log M_e$ against $\log P_X$ the derivatives were classified into groups I and II, suggesting the increase in adsorption of group I may be predominantly due to the tendency of the hydrophobic bonding, while that of group II may be influenced by the free energy of binding in addition to the tendency of the hydrophobic bonding.

In this series of works,⁴⁾ discussions have been made as to the adsorption of drugs by carbon black from aqueous solution on the basis of hydrophobic interaction and also as to the correlation between the adsorbability and the biopharmaceutical or pharmacological data. The term "hydrophobic" interaction mentioned above seems to have corresponded to the description by Jardetzky⁵⁾ that "hydrophobic" bonding includes van der Waals and pi-electron interactions. In other words, it means a general mutual bonding of the moieties more lipophilic than water.

Although the details of the adsorption mechanism has never been fully elucidated, it has been suggested that the adsorption of such aromatic compounds as phenols by active carbon is influenced by the oxygen-containing functional groups present on the surfaces of carbon⁶⁾ and that the orientation of these aromatic molecules on the interface is a factor in determining the shape of adsorption isotherms.⁷⁻⁹⁾ For example, a charge-transfer inter-

- 1) This paper forms Part XXII of "Physico-chemical Approach to Biopharmaceutical Phenomena." Preceding paper, Part XXI: N. Nambu, T. Nagai, and H. Nogami, *Chem. Pharm. Bull.* (Tokyo), **19**, 1058 (1971).
- 2) A part of this work was presented at the 90th Annual Meeting of the Pharmaceutical Society of Japan, Sapporo, July, 1970, No. OB10-1.
- 3) Location: *Hongo, Bunkyo-ku, Tokyo.*
- 4) a) H. Nogami, T. Nagai, and H. Uchida, *Chem. Pharm. Bull.* (Tokyo), **17**, 176 (1969); b) H. Nogami, T. Nagai, and S. Wada, *ibid.*, **18**, 348 (1970); c) H. Nogami, T. Nagai, and N. Nambu, *ibid.*, **18**, 1643 (1970); d) T. Oguma, T. Nagai, and H. Nogami, *ibid.*, **19**, 124(1971); e) H. Umeiyama, T. Nagai, H. Nogami, and T. Oguma, *ibid.*, **19**, 412 (1971).
- 5) O. Jardetzky, "Biopolymers," Symposia No. 1, 1964, pp. 501-514.
- 6) R.W. Coughlin, F.S. Ezra, and R.N. Tan, *J. Colloid & Interface Sci.*, **28**, 386 (1968).
- 7) C.H. Giles, T.H. MacEwan, S.N. Nakhwa, and D. Smith, *J. Chem. Soc.*, **1960**, 3973.
- 8) J.S. Mattson, H.B. Mark, Jr., M.D. Malbin, W.J. Weber, Jr., and J.C. Critenden, *J. Colloid & Interface Sci.*, **31**, 116 (1969).
- 9) A. Frumkin and B. Damaskin, "International Congress of Polarography," Butterworths Scientific Publications, London, 1966, p. 263.

action has been postulated by Mattson, *et al.*⁹⁾ In the present study, it was found that the free energy of adsorption calculated from Langmuir constant b was not correlated with logarithm of the partition coefficient in *n*-octanol/water system, as will be described later. Therefore, it makes confusing to express both the adsorption and the partition in the term "hydrophobic" interaction.

Originally, "hydrophobic" bonding of undissociated molecules such as phenols in the present cases should be due to the free energy change of escaping from water which is a func-

TABLE I. Langmuir Constants a and b , Adsorbed Amount at Equilibrium Concentration $2 \times 10^{-3}M$, M_c , at pH 7.45 for No. 1—22 and pH 5.62 for No. 23—39, Apparent Free Energy of Adsorption, $-RT \ln b$, Partition Coefficient to *n*-Octanol, P_x , Apparent Enthalpy, ΔH_{app} , Apparent Entropy, ΔS_{app} , All at 30° and Wave length where the Concentration was Determined According to UV Absorption Method, λ

No.	Samples	$a \times 10^3$ (mole/g)	$b \times 10^3$ (M ⁻¹)	$M_c \times 10^3$ (mole/g)	$-RT \ln b$ (kcal/ mole)	$\log P_x$	$\Delta H_{app}^{a)}$ (kcal/ mole)	$\Delta S_{app}^{b)}$ (e.u.)	λ (μ m)
1	phenol	2.25	3.11	0.91	3.45	1.51	7.5	36.1	270
2	<i>o</i> -nitrophenol	3.23	6.89	1.83	3.94				280
3	<i>m</i> -nitrophenol	2.37	22.24	1.91	5.01	2.00			273
4	<i>p</i> -nitrophenol	2.22	11.84	1.53	4.26				400
5	<i>m</i> -aminophenol	2.00	9.05	1.31	4.11	0.212	9.5	44.9	282
6	<i>o</i> -methylphenol	2.50	7.55	1.50	3.99				271
7	<i>m</i> -methylphenol	2.37	8.45	1.47	4.06	2.07 ^{c)}			271
8	<i>p</i> -methylphenol	2.41	8.83	1.51	4.09	1.99	0.15	14.0	277
9	<i>o</i> -chlorophenol	2.61	10.07	1.72	4.16	2.20 ^{c)}			274
10	<i>m</i> -chlorophenol	2.74	10.14	1.82	4.17	2.55 ^{c)}			274
11	<i>p</i> -chlorophenol	2.58	11.74	1.72	4.26	2.53	-2.15	6.96	280
12	<i>o</i> -bromophenol	2.67	15.00	1.95	4.41	2.40 ^{c)}			274.5
13	<i>p</i> -bromophenol	2.74	14.60	2.03	4.38	2.74	-2.4	6.53	280
14	<i>o</i> -methoxyphenol	2.21	11.04	1.51	4.22	1.33			274.5
15	<i>p</i> -methoxyphenol	2.40	11.28	1.64	4.23	1.37	4.85	30.5	287.5
16	2,4-dinitrophenol	1.04	22.44	0.83	4.65				257
17	2,4-dichlorophenol	3.57	11.20	2.45	4.23				291
18	2,4,6-trichlorophenol	3.15	8.36	1.94	4.05				312
19	<i>p</i> -ethylphenol	3.23	8.61	2.00	4.08	2.58	-2.25	4.55	276
20	3-methyl-4-chlorophenol	3.85	9.29	2.46	4.12				280
21	resorcinol	1.59	13.07	1.14	4.33		0.8	16.9	273
22	2,4,6-trinitrophenol	1.16	32.04	1.00	4.87				355
23	salicylaldehyde	2.78	15.00	2.05	4.41	1.65			256
24	<i>p</i> -hydroxybenzaldehyde	2.22	13.64	1.60	4.34	1.35	0.35	15.5	283
25	methyl <i>p</i> -hydroxybenzoate	2.53	17.95	1.94	4.51	1.99			245
26	<i>p</i> -phenolsulfonamide	1.40	14.25	1.02	4.37	0.055	-3.8	1.88	236
27	salicylamide	2.17	14.38	1.61	4.38	1.25	-2.9	4.88	298
28	<i>p</i> -hydroxybenzamide	1.54	15.12	1.13	4.41	0.253	-5.8	-4.59	252
29	ethyl <i>p</i> -hydroxybenzoate	3.17	19.69	2.58	4.56	2.35			255
30	<i>p</i> -hydroxyacetanilide	1.59	19.69	1.24	4.56	0.357	-2.3	7.46	243
31	<i>m</i> -ethoxyphenol	2.56	16.25	1.91	4.45	1.98			273
32	sulfanilamide	1.48	15.00	1.12	4.41				258
33	pyrocatechol	1.62	10.83	1.09	4.20	0.849	1.25	18.0	276
34	hydroquinone	1.80	17.34	1.36	4.49	0.495	0.85	17.6	288
35	<i>p</i> -anisaldehyde	2.94	12.59	2.12	4.30	1.76			283
36	aniline	1.93	5.02	0.98	3.74	0.89	3.55	24.1	280
37	benzaldehyde	2.63	8.44	1.60	4.06	1.45	-4.5	-1.45	248
38	<i>p</i> -nitrobenzamide	2.35	17.70	1.81	4.50	0.821			265
39	acetophenetidine	1.80	37.00	1.57	4.95	1.56			246

a) $\Delta H_{app} = d(-RT \ln b)/d(1/T)$

b) $\Delta S_{app} = d(-RT \ln b - \Delta H_{app})$

c) calculated from the data by T. Fujita, J. Iwasa and C. Hansh, *J. Am. Chem. Soc.*, **86**, 5175 (1964)

tion of partition coefficient and should be discriminated from van der Waals, π -electron interactions and others. On the basis of this view, the adsorption of phenols was investigated in this study in order to discuss the mode of interaction on the carbon black, referring to the partition coefficient in *n*-octanol/water system. Phenols were chosen because of their simplicity in structure compared with other homologues in medical use.

Experimental

Materials—Carbon black marketed as "Seisei Shirasagi" by Takeda Chemical Ind. was used after the same treatment as described in a previous paper.¹⁰ The rest of the materials were of the purest reagent grade.

Procedure for Determination of the Adsorbed Amount by Batch Method—Twenty mg of carbon black was added in 10 ml of the respective compounds in 1/15 M phosphate buffer solution (pH 5.62 or 7.45) at 30° or 50°, and then procedure was carried out in the same way as described in the previous paper.¹⁰

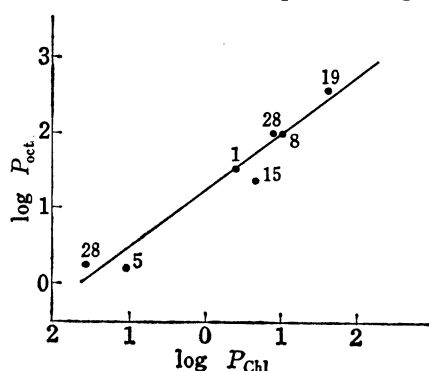


Fig. 1. Relationship of Phenols between Partition Coefficient to *n*-Octanol, P_{Oct} , and that to Chloroform, P_{ChI} , at pH 5.62

Quantitative Determination of Phenols—After diluting the sample with the same buffer solution as used for the adsorption experiment mentioned above, the concentration of the compound was determined according to ultraviolet (UV) absorption method using a Hitachi 124 spectrophotometer at the respective wavelengths shown in Table I.

Determination of Partition Coefficient—Twenty ml of 1/15 M phosphate buffer solution (pH 5.62) containing 10^{-3} M of the compound was mixed with 10 ml *n*-octanol or chloroform, shaken for 2.5 hr at 25° (unless otherwise stated) and then the concentration in aqueous layer was determined in the same way as described above to obtain the partition coefficient. Partition coefficients of phenols to *n*-octanol and to chloroform were well correlated with each other, as shown in Fig. 1. Thus, *n*-octanol seemed to behave as a normal organic solvent to phenols.

Result and Discussion

Adsorption Isotherms of Phenols by Carbon Black from Aqueous Solution

The adsorption isotherms obtained for all the samples of phenols were well described with Langmuir equation (1).

$$1/M = 1/a + 1/abC \quad (1)$$

where M is the adsorbed amount at the concentration C in solution at equilibrium, a the amount adsorbed when the entire surface is covered by a monolayer, and b the equilibrium constant of adsorption process. The values of a and b obtained were listed in Table I, in which the values of the adsorbed amount at 2×10^{-3} M of equilibrium concentration are also listed.

There was no remarkable difference in adsorption isotherm among the respective *ortho*, *meta* and *para* derivatives of methylphenol, chlorophenol, bromophenol (no datum for *m*-bromophenol) and methoxyphenol (no datum for *m*-methoxyphenol). This result suggested that these phenols may take a flat configuration on the carbon black surface in the similar way to the adsorption of nitrophenols in undissociated state (pH 2.0) on the active carbon

10) H. Nogami, T. Nagai, E. Fukuoka, and H. Uchida, *Chem. Pharm. Bull.* (Tokyo), **16**, 2248 (1968).

reported by Mattson, *et al.*,⁸⁾ while the *ortho* derivatives of benzoic acids of the same substituents as above were less adsorbed than the *meta* and *para* ones under the dissociated condition as reported in a previous paper.^{4e)}

The differences in the shape of adsorption isotherm suggested those in the adsorption mechanism. For example, the adsorption isotherms of phenol, *p*-methylphenol and *p*-ethylphenol are of lower curvature, as shown in Fig. 2, and those of 2,4-dinitrophenol and 2,4,6-trinitrophenol in dissociated state under the present experimental condition (pH 7.45) get bended with the increase in equilibrium concentration, as shown in Fig. 3.

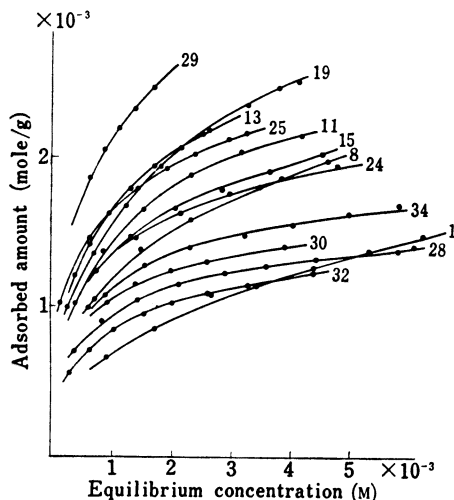


Fig. 2. Adsorption Isotherms of Phenols by Carbon Black at 30°, represented by the Same No. as in Table I

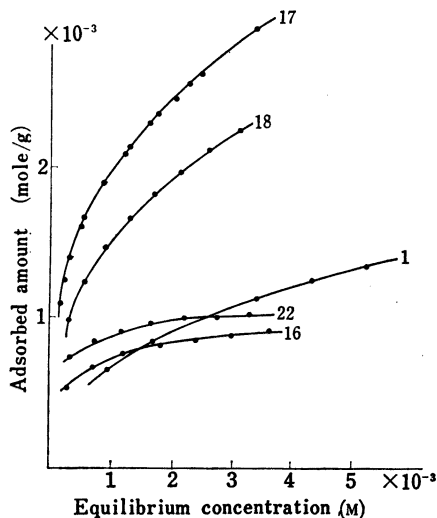


Fig. 3. Adsorption Isotherms of Phenols by Carbon Black at 30°, represented by the Same No. as in Table I

The intramolecular hydrogen bonding seemed to give effect on the adsorption and the *ortho* effect in the case of hydroxybenzamide was greater than that in the case of hydroxybenzaldehyde as follows:

$$\log M_c (o\text{-hydroxybenzaldehyde}) - \log M_c (p\text{-hydroxybenzaldehyde}) = 0.107$$

$$\log M_c (\text{salicylamide}) - \log M_c (p\text{-hydroxybenzamide}) = 0.157$$

where M_c is the adsorbed amount at 2×10^{-3} M of equilibrium concentration.

This result was similar to that of partition coefficient, P_x , as follows:

$$\log P_x (o\text{-hydroxybenzaldehyde}) - \log P_x (p\text{-hydroxybenzaldehyde}) = 0.302$$

$$\log P_x (\text{salicylamide}) - \log P_x (p\text{-hydroxybenzamide}) = 0.992$$

Relationship of Phenols between Langmuir Constant α in the Adsorption by Carbon Black and the Partition Coefficient in *n*-Octanol/Water System

Obtaining the values of α according to equation (1) and then plotting them against logarithm of partition coefficient, $\pi = \log P_x / P_H$, there was found a linear relationship, as shown in Fig. 4, where P_x and P_H are the partition coefficients of each phenol derivative and phenol itself, respectively.

With respect to the adsorption by carbon black, it seemed possible to assume a surface layer, as shown in Fig. 5, and then the chemical potential of the adsorbate component in the surface layer, μ^s , and that in the bulk phase, μ^b , are considered to be expressed as follows:

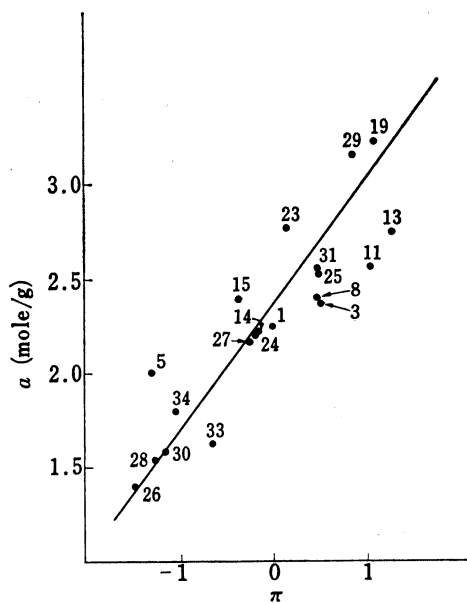


Fig. 4. Relationship of Phenols between Langmuir Constant a at 30° and Logarithm of Partition Coefficient, $\pi = \log P_x/P_H$, where P_x and P_H are the Partition Coefficients to n -Octanol of Each Phenol Derivatives and Phenol itself, respectively, represented by the Same No. as in Table I

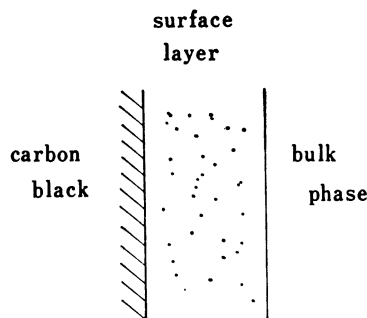


Fig. 5. Schematic Diagram of the Vicinity of Carbon Black Surface

$$\begin{aligned}\mu^s &= G_B + G_M^s + G_I^s + G_H^s + r^s \\ \mu^b &= G_M + G_I + G_H\end{aligned}\quad (2)$$

where G_B , G_M , G_I , G_H and r are the free energies of binding, mixing, iceberg formation, hydration, and expelling of water from the surface, respectively, the affix s meaning the surface layer.

At equilibrium, $\mu^s = \mu^b$. Then, equation (2) is modified as follows, placing $-T(\Delta S_M - \Delta S_M^s)$ on the right hand, which corresponds to the free energy of the transfer accom-

panying adsorption of the component from the bulk phase to the surface layer.

$$\begin{aligned}(\Delta H_B - T\Delta S_B) + (\Delta H_M^s - \Delta H_M) + \Delta H_I^s - \Delta H_I - T(\Delta S_I^s - \Delta S_I) + \Delta H_H^s - \Delta H_H \\ - T(\Delta S_H^s - \Delta S_H) + r^s = -T(\Delta S_M - \Delta S_M^s)\end{aligned}\quad (3)$$

where ΔH and ΔS are the enthalpy and the entropy, respectively, of the processes shown by the same suffixes as in equation (2), and T the absolute temperature.

When the adsorption takes place, $\Delta G_B (= \Delta H_B - T\Delta S_B)$ is negative. Since the more hydrophobic the molecule, the more it is adsorbed on carbon black, $(\Delta H_M^s - \Delta H_M)$ is considered to be negative. $(\Delta H_I^s - \Delta H_I)$ becomes positive because $\Delta H_I^s > 0$ and $\Delta H_I < 0$. According to Shinoda and Fujihira's analysis,¹¹⁾ the free energy due to the iceberg formation is regarded to be an enthalpy predominant effect at room temperature, and thus $\Delta H_I^s - \Delta H_I - T(\Delta S_I^s - \Delta S_I)$ becomes positive. Mattson, *et al.*⁹⁾ described on the basis of the disappearance of O-H stretch in infrared (IR) spectrum that there is some hydrogen bonding of phenols with surface groups involved, but this interaction is small and is not the primary cause for adsorption of phenols. Therefore, $\Delta H_H^s - \Delta H_H - T(\Delta S_H^s - \Delta S_H)$ is considered to be positive. r^s also is considered to be positive. Finally, the factors to make the left hand of equation (3) negative, *i.e.*, to make the adsorption increase, are $(\Delta H_B - T\Delta S_B)$ and $(\Delta H_M^s - \Delta H_M)$.

Next, with respect to the partition in n -octanol/water system, phenols were regarded to mixed well with both water and n -octanol because the values of partition coefficient, P_x , were almost the same between 27° and 47° . Therefore, the free energy of partition, ΔG_p , may be expressed as follows:

11) K. Shinoda and M. Fujihira, *Bull. Chem. Soc. Japan*, **41**, 2612 (1968).

$$\Delta G_P = -RT \ln (X_I/X_{II}) \propto \Delta H_M \quad (4)$$

where X_I and X_{II} are the mole fractions in water and in *n*-octanol, respectively, and R the gas constant. Accordingly, the abscissa in Fig. 4 is considered to have relation to ΔH_M and the correlation of a with P_x suggested the following matters.

Based on the assumption of the surface layer in Fig. 5, $(\Delta H_M^s - \Delta H_M)$ is considered to correspond to the free energy of transfer of phenols from the bulk phase to the surface layer, *i.e.*, the escaping tendency from the bulk phase, by the similar expression to equation (4), and then it seems to have relation to ΔH_M or π . On the other hand, a is related to the number of adsorption sites. Therefore, the result in Fig. 4 suggested that $(\Delta H_M^s - \Delta H_M)$ may be effective in an increase in the concentration of the adsorbate component in the surface layer or predominantly effective in an increase in the number of adsorption sites, though ΔG_B also may give the similar effect. In other words, $(\Delta H_M^s - \Delta H_M)$ or π is considered to form a factor in determining the mode of orientation of phenols on the carbon black.

Conclusively, the surface layer on carbon black is considered to play the similar role to *n*-octanol layer in the partition experiment, while the adsorption takes place according to Langmuir equation.

Free Energy of Transfer of Phenols to the Adsorption Sites on Carbon Black

Since Langmuir constant b in equation (1) is considered to be a mean equilibrium constant for the transfer of many solute molecules to adsorption (or binding) sites on the adsorbent, it is derived that $C=1/b$ and thus $\Delta S_M = R \ln b$ at $M/a = \theta = 1/2$, where θ is the binding fraction.

Plotting $-RT \ln b$ against $\pi = \log (P_x/P_H)$ in Fig. 6, there was found no correlation, contrary to the result shown in Fig. 4. Therefore, it was suggested that $(\Delta H_M^s - \Delta H_M)$ may be reduced with $-T\Delta S_M^s$ ($M=a/2$) which increases positively as $(\Delta H_M^s - \Delta H_M)$ increases negatively, or that ΔG_B may be the predominant factor in the increase in $-RT \ln b$. The details of ΔG_B will be discussed later.

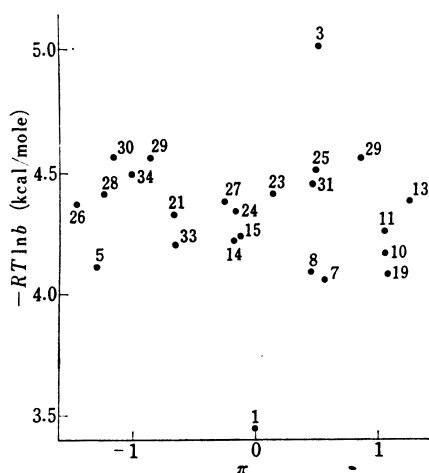


Fig. 6. Relationship between Apparent Free Energy of Adsorption at 30°, $-RT \ln b$, and Logarithm of Partition Coefficient, $\pi = \log P_x/P_H$, where P_x and P_H are the Partition Coefficients to *n*-Octanol of Each Phenol Derivatives and Phenol Itself, respectively, represented by the Same No. as in Table I

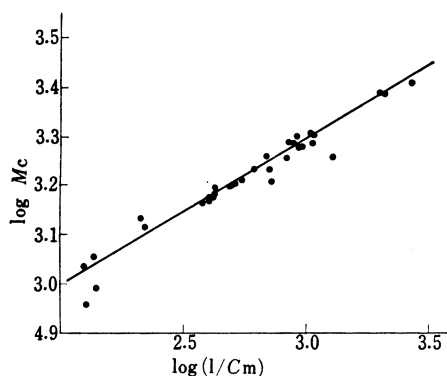


Fig. 7. Relationship of Phenols between Adsorbed Amount at Equilibrium Concentration $2 \times 10^{-3} M$, M_c , and Equilibrium Concentration at Adsorbed Amount 1.6×10^{-3} mole/g, C_m

In this connection, the quantity of $-RT \ln b$ treated above should not correspond to the intrinsic free energy of adsorption, ΔG_A , which might contain the quantity dependent on the adsorbed amount, *i.e.*, $T\Delta S_M^s$ ($M=a/2$), and thus ΔG_A should be expressed as follows:

$$\Delta G_A = -RT \ln b + T\Delta S_M^s (M=a/2) \quad (5)$$

This concept is considered similar to that described by Kipling as:¹²⁾ $\Delta G_A = -RT \ln(b/A_0\tau)$, where A_0 is the limiting area of the adsorbed molecule and τ the thickness of the adsorbed layer.

Relationship of Phenols between Adsorbed Amount at an Identical Equilibrium Concentration, M_c , and Mole Fraction in the Surface Layer, X^s

Plotting the adsorbed amount at an identical equilibrium concentration, M_c , against the equilibrium concentration at identical adsorbed amount, C_m , both on logarithmic scale, a linear relationship was observed as shown in Fig. 7, suggesting the following matters.

Expressing the left hand of equation (3) by ΔJ , the following equation is given for each compound.

$$\Delta J = -T\Delta S_M + T\Delta S_M^s \quad (6)$$

At an identical equilibrium concentration, the quantity of ΔS_M for every compound is considered identical. Then the following equation is given.

$$\Delta J(c) = -T k(c) + T\Delta S_M^s(c) \quad (7)$$

where $k(c)$ is the constant.

Next, at an identical adsorbed amount, assuming that the total number of all kinds of molecules and the activity coefficient of adsorbate component in the surface layer do not vary with the adsorbates, the quantity of ΔS_M^s for every compound is considered identical. Then, equation (6) is expressed as follows.

$$\Delta J(m) = -T\Delta S_M(m) + T k(m) \quad (8)$$

where $k(m)$ is the constant.

ΔJ is independent of C_m and M_c , and thus it is considered that $\Delta J(c) = \Delta J(m)$. Therefore, equations (7) and (8) give the following equation.

$$\begin{aligned} k(c) + k(m) &= \Delta S_M^s(c) + \Delta S_M(m) \\ &= R(\ln X^s + \ln X) \end{aligned} \quad (9)$$

where X^s and X are the mole fractions of adsorbate component in the surface layer and in the bulk phase, respectively.

X is considered proportional to C_m , but X^s is not to M_c because the property of water in the surface layer may be different from that in the bulk phase. Actually, the slope of the plot in Fig. 7 is not the unity, but is 0.302. Therefore, X^s should be expressed as follows

$$X^s = (M_c)^\lambda \quad (10)$$

where λ is the constant.

Accordingly, equation (9) is modified as follows.

$$\log M_c = (1/\lambda) \log (1/C_m) + k \quad (11)$$

where k is the constant determined by $k(c)$, $k(m)$, the activity coefficient of the component and the total numbers of molecules in the bulk phase and the surface layer.

Finally, the linear relationship in Fig. 4 seemed to be explained reasonably by equation (11) and thus the relationship of phenols between the adsorbed amount at an identical equilibrium concentration, M_e , and the mole fraction in the surface layer, X^s , could be expressed by equation (10), the value of being 3.31.

Relationship of Phenols between Binding Energy on Carbon Black and Hydrophobic Bonding

Plotting the adsorbed amount at an identical equilibrium concentration, M_e , against the partition coefficient in *n*-octanol/water system, P_x , of phenols, there was not found a simple correlation, as shown by groups I and II in Fig. 8.

Since the ordinate in Fig. 8 is considered to correspond to $-T\Delta S_M^s$ (c) in equation (7) as discussed already, the above result suggested that $(\Delta H_M^s - \Delta H_M)$ or π alone is not the factor in determining the quantity of $-T\Delta S_M^s$ (c) for phenols, contrary to the case shown in Fig. 4.

Regarding group I, these phenols are considered to have substituents containing hydrophobic and van der Waals forces, *e.g.*, such as methyl and ethyl groups, and the effect of the charge-transfer interaction on the increase in the adsorption of these phenols by carbon black shown in Fig. 8 might be little compared with that of the hydrophobic bonding on the consideration that their formation constants of charge-transfer complex with chloranyl¹³⁾ had no relation to the increase in M_e . Therefore, $(\Delta H_M^s - \Delta H_M)$ may be predominantly effective in an increase in $-T\Delta S_M^s$ (c), or the increase in adsorption may be predominantly due to the tendency of the in hydrophobic bonding.

Regarding group II, in addition to $(\Delta H_M^s - \Delta H_M)$, ΔG_B should be taken into consideration, which makes the left hand of equation (3) more negative. ΔG_B is considered to take to its source from various interaction forces in addition to the charge-transfer one. Although Mattson, *et al.*,⁸⁾ described the adsorption of *p*-nitrophenol on active carbon was a physical one, some interaction like a chemical reaction, which does not make so a great deviation from the physical adsorption, might give effect on ΔG_B . For example, the adsorbed amounts of *p*-methoxyphenol, *m*-aminophenol, *o*-hydroxyphenol, and *p*-hydroxyphenol increased with temperature, as shown in Table I, and Boehm reported that 18% of oxygen on the carbon surface reacted as quinone.¹⁴⁾ Additionally, since the substituents of group II contain *pi*-electrons and dipoles, charge transfer and dipole interactions of these substituents are considered to give effect on ΔG_B , resulting in a deviation from group I.

Acknowledgement The authors gratefully acknowledge the award of Research Grants from Naito Foundation (to T.N.).

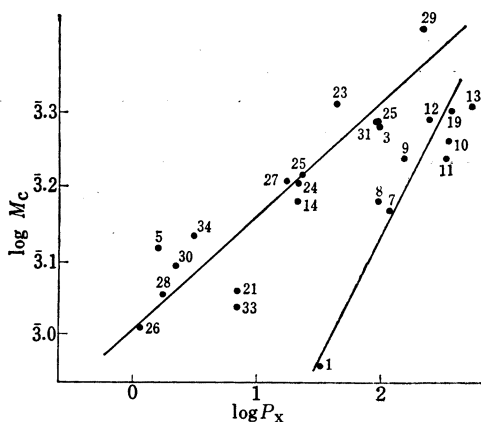


Fig. 8. Relationship of Phenols between Adsorbed Amount at Equilibrium Concentration $2 \times 10^{-3}M$, M_e , and Partition Coefficient to *n*-Oxtanol, P_x

13) H. Umeyama, S. Wada, T. Nagai, and H. Nogami, presented at the 91st Annual Meeting of Pharmaceutical Society of Japan, Fukuoka, April, 1971, No. 7F4-4.

14) H.P. Boehm, *Advance in Catalysis*, 16, 179 (1966).