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Adsorption of Solute from the Solutions. IV.[1] Adsorption of Benzoic Acids on Graphite

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The adsorption of 14 monosubstituted benzoic acids, together with 1-naphthoic acid and cyclohexanecarboxylic acid, on graphite from aqueous solutions at 5° was investigated. The adsorption isotherms apparently fitted the Langmuir equation. The logarithmic value of the first equilibrium constant per unit weight of graphite was significantly correlated with plane size of adsorbate molecule, and not with its $\mathrm{p}K_a$ and π, the Hansch–Fujita substituent constant. Furthermore, decreasing order of the affinity to graphite was as follows: 1-naphthoic acid>benzoic acid>cyclohexanecarboxylic acid. These results may indicate that adsorbed acids are mostly oriented flat on graphite surface, and plane-to-plane stacking between acid molecule and fused benzene ring plane of graphite seems to be dominant among possible adsorption forces.

Graphite, with its very small adsorption capacity among the coal series,[3] has been reported to adsorb various compounds[4] such as phenols and sulfonated aromatic compounds from solutions, and also known to be useful for separation of aromatic hydrocarbons, especially those having carcinogenic activity.[5] Systematic studies, however, have been scarcely presented on the adsorption in the liquid phase. In this work the adsorption of monosubstituted benzoic acids, together with 1-naphthoic acid and cyclohexanecarboxylic acid, from aqueous solutions was investigated for revealing the adsorption features of graphite.

Experimental and Calculation

Materials——Graphite was purchased from Junsei Pure Chemicals and Co., Ltd. (Lot No. 210252). All other reagents were of JIS special grade or the like, and their melting points and ultraviolet spectra were checked.

Adsorption Experiments——Usually about 200 mg of graphite was suspended in 20 ml of adsorbate solutions (in 0.2 M phosphate buffer of pH 6.0, 7.0, and 8.0, or in distilled water) of various concentrations (usually between 3.3×10^{-5} M and 2.0×10^{-4} M), and shaken at 5°. After equilibration the supernatant liquid was isolated, and the concentration was determined. The equilibration period was from 1 to 2 days.

Measurements of Adsorbates——The concentration of adsorbates was spectrophotometrically determined by utilizing their optical absorption in the ultraviolet region. A Hitachi–Perkin Elmer model 139 spectrophotometer with 1-cm cells was employed for the measurements.

Plane Size of Molecules——Approximate plane size difference, ΔA, between substituted and unsubstituted benzoic acids was calculated from van der Waals radii of atoms[6] and reasonable values of bond length and bond angle.[7] For simplifying the calculation, it was assumed that all the atoms in a molecule were located on the same plane.

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[1] Part III: I. Moriguchi and N. Kaneniwa, *Chem. Pharm. Bull.* (Tokyo), **17**, 961 (1969).

[2] Location: *Hatanodai, Shinagawa-ku, Tokyo.*

[3] See, for instance, I.L. Ettinger, *Dokl. Akad. Nauk SSSR*, 142, 196 (1962).

[4] *a*) C.H. Giles and A.S.A. Hassan, *J. Soc. Dyers and Colourists*, **74**, 846 (1958); J.W. Galbraith, C.H. Giles, A.G. Halliday, A.S.A. Hassan, D.C. McAllister, N. Macaulay, and N.W. Macmillan, *J. Appl. Chem.* (London), **8**, 416 (1958); *b*) I.A. Easton, C.H. Giles, and P.B. McKay, *Chem. Ind.* (London), **1964**, 1863.

[5] W. Rochus and R. Kikuth, Ger. Patent 1021840 (1958).

[6] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1960, Chapter VII.

[7] "Kagaku Benran," ed. by Chemical Society of Japan, Maruzen Co., Ltd., Tokyo, 1966, pp. 1209—1225.

Results and Discussion

The adsorption of 14 *para*- and *meta*-monosubstituted benzoic acids[8] from aqueous solutions of pH 6.0, 7.0, and 8.0 was measured on graphite at 5°. Fig. 1 shows some examples of the adsorption isotherms. The isotherms for all the compounds apparently fit the Langmuir equation,

$$1/x = 1/n + 1/cnK \qquad (1)$$

where x represents the amount of adsorbate adsorbed on a unit weight of graphite, n the maximum of x, K the intrinsic affinity constant between the adsorbate and binding site on graphite, and c the equilibrium concentration of the adsorbate in the solution.

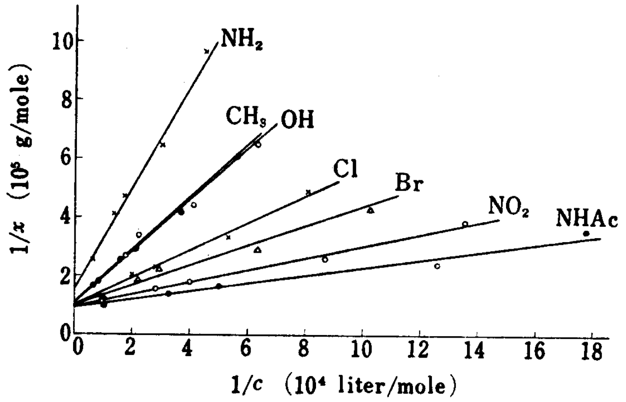

Fig. 1. Langmuir Plots for Adsorption of *meta*-Substituted Benzoic Acids on Graphite at pH 7.0 and 5°

The multiple equilibria in which a unit weight of graphite, G, may adsorb many molecules of solute, A, are expressed as the following general form

$$GA_{i-1} + A \rightleftharpoons GA_i, \qquad i=1, 2, \cdots\cdots, n \qquad (2)$$

The i-th equilibrium constant, K_i, was shown by Klotz and his coworkers[9] for the ideal situation of no other interaction such as the Langmuir-type binding, as

$$K_i = \{(n-i+1)/i\}K \qquad (3)$$

where n and K are identical with those of the Langmuir equation. From Eq. (3), the first equilibrium constant may be given as

$$K_1 = nK \qquad (4)$$

The apparent value of nK can be obtained with considerable accuracy as the reciprocal of the slope of Langmuir's plot (see Fig. 1). On the other hand, the estimation of the individual values of n and K seems to be less accurate, especially in the case of weak adsorbent such as graphite. Furthermore, the meaning of n evaluated from isotherms for adsorption from the solution does not seem to be so simple as that in the case of gaseous adsorption. By inspection of the isotherms (see Fig. 1), a tendency was recognized that the value of n increased with an increase of nK. This tendency is contrary to the expectation from the approximate plane size of solute molecules (see Table I). This discrepancy may be ascribed to competition of solutes with solvent molecules and buffering agents in the adsorption on graphite. This problem will be discussed further in later papers.

The logarithmic values of nK for 14 benzoic acids are listed in Table I, together with values of ΔA, pK_a,[10] and the Hansch–Fujita substituent constant, π.[11] The constant π has been defined as

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[8] The adsorption of benzoic acid and *p*-hydroxybenzoic acid could not be measured because the reproducibility of their optical absorbances was very poor probably owing to some interaction with buffering agents.

[9] I.M. Klotz, F.M. Walker, and R.B. Pivan, *J. Am. Chem. Soc.*, **68**, 1486 (1946); I.M. Klotz, "The Proteins," Vol. I, Academic Press, New York, 1953, p. 727.

[10] A. Albert and E.P. Serjeant, "Ionization Constants of Acids and Bases," Methuen & Co., Ltd., London, 1962.

[11] C. Hansch and T. Fujita, *J. Am. Chem. Soc.*, **86**, 1616 (1964).

$$\pi = \log P_X/P_H \quad (5)$$

where P_H is the partition coefficient of a parent compound between octanol and water and P_X is that of the derivative X,[11)] and used as a parameter for hydrophobic binding.[12)]

Table I. Adsorption Constant and Other Properties of Monosubstituted Benzoic Acids

Substituent	log $nK^{a)}$						ΔA (Å^2)	p$K_a$$^{9)}$		$\pi^{10)}$
	meta			*para*				*meta*	*para*	*para*
	pH 6.0	pH 7.0	pH 8.0	pH 6.0	pH 7.0	pH 8.0				
$NHCOCH_3$	0.03	$\bar{1}.88$	$\bar{1}.97$	0.39	0.24	$\bar{1}.97$	18.30	4.07	4.28	−0.98
NO_2	$\bar{1}.77$	$\bar{1}.69$	$\bar{1}.77$	$\bar{1}.95$	$\bar{1}.81$	$\bar{1}.53$	8.68	3.49	3.43	0.04
OCH_3				$\bar{1}.75$	$\bar{1}.54$	$\bar{1}.25$	10.30		4.47	0.11
Br	$\bar{1}.62$	$\bar{1}.47$	$\bar{1}.33$	$\bar{1}.62$	$\bar{1}.50$	$\bar{1}.24$	7.55	3.81	3.97	1.01
Cl	$\bar{1}.44$	$\bar{1}.34$	$\bar{1}.16$	$\bar{1}.44$	$\bar{1}.40$	$\bar{1}.12$	5.85	3.83	3.98	0.80
CH_3	$\bar{1}.29$	$\bar{1}.05$	$\bar{1}.06$	$\bar{1}.32$	$\bar{1}.35$	$\bar{2}.86$	8.04	4.27	4.37	0.43
OH	$\bar{1}.24$	$\bar{1}.07$	$\bar{2}.91$				3.68	4.08		
NH_2	$\bar{2}.91$	$\bar{2}.75$	$\bar{2}.51$	$\bar{1}.21$	$\bar{2}.89$	$\bar{2}.54$	5.38	4.74	4.85	−1.52

a) dimension of nK: liter/g

Fig. 2, 3, and 4 show the correlations of log nK with ΔA, pK_a, and π at pH 7.0. The correlation coefficients together with those at other pH's are tabulated in Table II, indicating that log nK is significantly correlated only with ΔA. This may suggest that the adsorption mainly depends on the plane size of adsorbate molecule and does not on its ionic or lipophilic character. Although Easton and his coworkers[4b)] have reported that the adsorption of aromatic sulfonic acids and cationic and anionic dyes on graphite is related directly to molecular weight of the adsorbate, the adsorption does not seem ascribable to the simple van der Waals attraction or the like. In a preliminary experiment, it had been observed that graphite adsorbed much smaller amount of benzoic acids in ethanol than in water. Moreover, graphite has been known to have a complete layered crystal lattice.[3)] Therefore, it is seemed that the

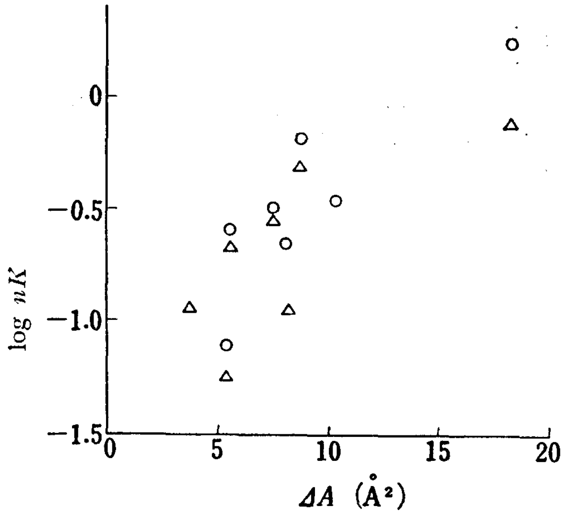

Fig. 2. Correlation of log nK with ΔA at pH 7.0

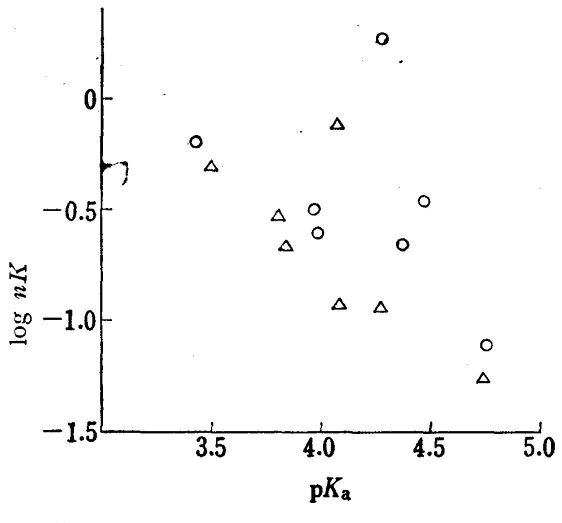

Fig. 3. Correlation of log nK with pK_a at pH 7.0

△: *meta*-substituted benzoic acid ○: *para*- substituted benzoic acid

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12) C. Hansch, K. Kiehs, and G.L. Lawrence, *J. Am. Chem. Soc.*, **87**, 5770 (1965).

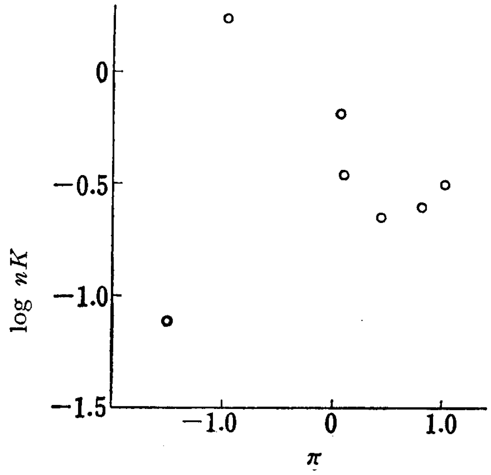

Fig. 4. Correlation of log nK with π for *para*-Substituted Benzoic Acids at pH 7.0

TABLE II. Correlation Coefficients of log nK with ΔA, pK_a, and π

	Correlation coefficient		
	With ΔA[a]	With pK_a[a]	With π[b]
pH 6.0	0.834[c]	−0.453	−0.095
pH 7.0	0.800[c]	−0.525	0.034
pH 8.0	0.802[c]	−0.605[d]	0.039

a) 14 samples
b) 7 samples
c) highly significant at $<$0.001 level
d) correlated at $<$0.05 level

adsorbates are mostly oriented flat on graphite surface, and that plane–to–plane stacking[13] between adsorbate molecule and fused benzene ring plane of graphite is dominant among possible adsorption forces.

For the further support of this mechanism, the adsorption of 1-naphthoic acid, benzoic acid, and cyclohexanecarboxylic acid was examined on graphite in distilled water at 5°. The values of nK evaluated from the Langmuir isotherms are shown in Table III. The decreasing order of nK is as follows: 1-naphthoic acid>benzoic acid>cyclohexanecarboxylic acid. This result may be affirmative for the plane–to–plane stacking: 1- naphthoic acid has a large naphthalene ring plane and benzoic acid a benzene ring plane, but cyclohexanecarboxylic acid has not a plane moiety. Thus it may be concluded that benzoic acids, or more generally carboxylic acids, are adsorbed from aqueous solutions dominantly by plane–to–plane stacking on the surface of graphite, and the affinity depends mainly on the plane size of the solute molecule to be adsorbed.

TABLE III. Adsorption Constant on Graphite in Water at 5°

Compound	Molecular weight	nK (liter/g)
1-Naphthoic acid	172.2	0.238
Benzoic acid	122.1	0.092
Cyclohexanecarboxylic acid	128.2	0.014

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13) O. Jardetzky, *Biopolymers Symposia*, 1, 501 (1964).