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Adsorptions of Organic Compounds in Basic Solutions

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The adsorption isotherms of various aromatic compounds on an activated carbon or a polystyrene adsorbent in aqueous solutions and basic solutions were investigated. The adsorption isotherms of nonionic compounds and strong anionic electrolytes in the basic solutions were equal to the isotherms in the aqueous solutions. However, the adsorbed amounts of weak anionic electrolytes decreased with ionization in the basic solutions, and the adsorption isotherms of the non-ionized form and the ionized form of all these compounds except phenol could be expressed by the Freundlich equations with the same values of n. The amounts of those weak anionic electrolytes adsorbed at a desired pH could be calculated from the adsorption isotherms of the non-ionized form and the ionized form and the ionization constants.

Applications of adsorption from solutions on solid adsorbents have been considerably developed and become very important in many fields, such as in purification processes, water-treatment processes, and analytical methods.[1]

Adsorptions are now carried out at various pH values in those adsorption processes, and regenerations by desorption with a basic solution are applied in several processes. However, the influence of the pH on the adsorptions of organic compounds in water has not been made clear.[2] In this study, the adsorption isotherms of 7 aromatic compounds on an activated carbon or a polystyrene adsorbent were obtained in basic solutions, and they were compared with the isotherms in aqueous solutions.

Experimental

Three nonionic and four anionic compounds, whose properties are shown in Table 1, were tested as adsorbates in this study. A granular activated carbon and a polystyrene adsorbent whose properties are shown in Table 2 were used as adsorbents.

The adsorption isotherms at 25 °C were obtained by means of a batch-adsorption method as same in the previous paper.[3]

Results and Discussion

The adsorption isotherms in the aqueous solutions are shown in Figs. 1 and 2 as the Freundlich expression, logarithmic relationships between the adsorbed amount Q(mol g^{-1}) and the equilibrium concentration C(mol dm^{-3}). Most of them show linearity, and most could be expressed by the Freundlich equation; $Q = kC^{1/n}$. However, the isotherms for several anionic compounds, such as benzoic acid and nitrobenzoic acid fell lower in the concentration range than about 10^{-4} mol dm^{-3}. Further, the amount of the benzenesulfonic acid adsorbed for the activated carbon was much smaller than those of the other compounds, and it was negligibly small for the polystyrene adsorbent. Since benzoic acid and nitrobenzoic acid are ionized partially in the concentration range lower than about 10^{-4} mol dm^{-3} and since benzensulfonic acid is ionized completely throughout the concentration range, it can be presumed that the adsorbed amounts decrease with the ionization of the adsorbates.

TABLE 1. PROPERTIES OF THE ADSORBATES TESTED

Adsorbate	Molecular weight	Solubility mol dm^{-3}	Ionization constant K_a
Nitrobenzene	123.1	1.6×10^{-2}	—
Benzaldehyde	106.1	2.8×10^{-2}	—
Benzonitrile	103.1	2.1×10^{-2}	—
Benzoic acid	122.1	2.8×10^{-2}	6.1×10^{-5}
m-Nitrobenzoic acid	167.1	2.1×10^{-2}	3.6×10^{-4}
Phenol	94.1	9.2×10^{-1}	1.0×10^{-10}
Benzenesulfonic acid	158.2	∞	2×10^{-1}

Then the adsorption isotherms in sodium hydroxide solutions were obtained. The adsorption isotherms of the nonionic compounds and benzenesulfonic acid in the 1 mol dm^{-3} sodium hydroxide solution are shown

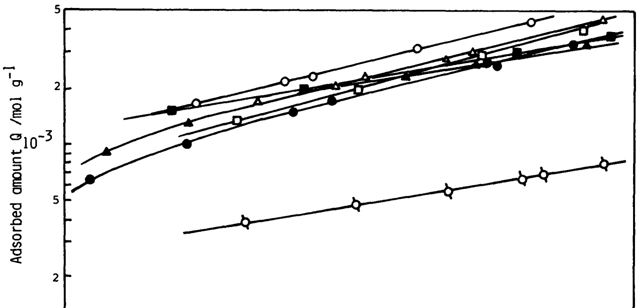

Fig. 1. Adsorption isotherms of organic compounds on activated carbon in aqueous solutions at 25 °C. ○: Nitrobenzene, △: benzaldehyde, □: benzonitrile, ●: benzoic acid, ▲: *m*-nitrobenzoic acid, ■: phenol, Q: benzenesulfonic acid.

TABLE 2. PROPERTIES OF THE ADSORBENTS USED

Adsorbent	Name	Surface area m^2 g^{-1}	Pore volume/cm^3 g^{-1} Total	Pore volume/cm^3 g^{-1} <20 nm
Activated Carbon	Filtrasorb 400	1030	0.84	0.52
Polystyrene	XAD-4	640	1.48	1.07

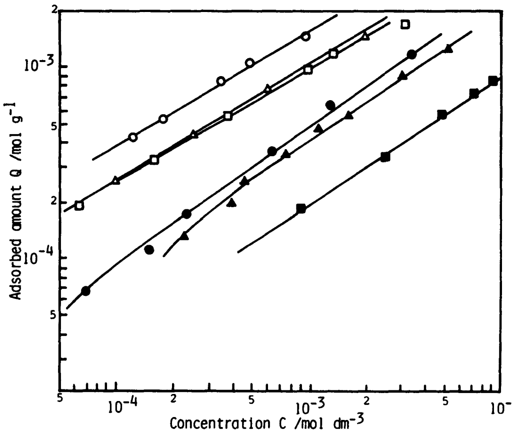

Fig. 2. Adsorption isotherms of organic compounds on polystyrene adsorbent in aqueous solutions at 25 °C.
(Symbols are same as in Fig. 1)

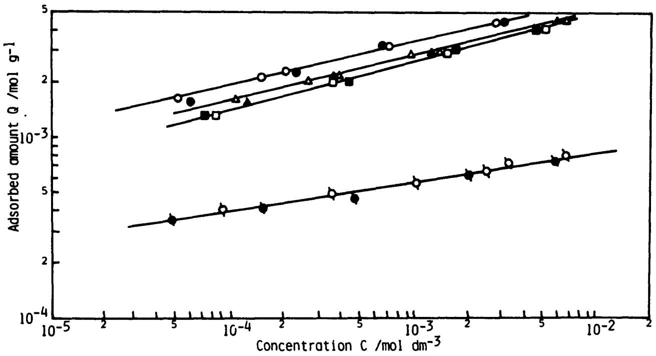

Fig. 3. Adsorption isotherms of nonionic compounds and benzenesulfonic acid on activated carbon in sodium hydroxide solutions at 25 °C.
○ △ □ ϙ: Aqueous solution, ● ▲ ■ ϙ: 1 mol dm^{-3} NaOH solution, ○ ●: nitrobenzene, △ ▲: benzaldehyde, □ ■: benzonitrile, ϙ ϙ: benzenesulfonic acid.

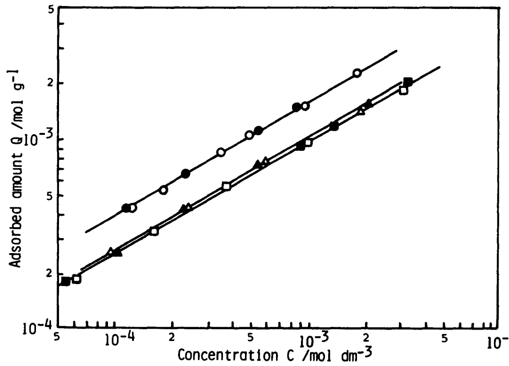

Fig. 4. Adsorption isotherms of nonionic compounds on polystyrene adsorbent in sodium hydroxide solutions at 25 °C.
○ △ □: Aqueous solution, ● ▲ ■: 1 mol dm^{-3} NaOH solution ○ ●: nitrobenzene, △ ▲: benzaldehyde, □ ■: benzonitrile.

in Figs. 3 and 4. The adsorption isotherms for these compounds in the basic solutions were almost equal to those in the aqueous solutions. Therefore, sodium hydroxide did not influence the adsorptions of the nonionic compounds and the strong anionic electrolytes.

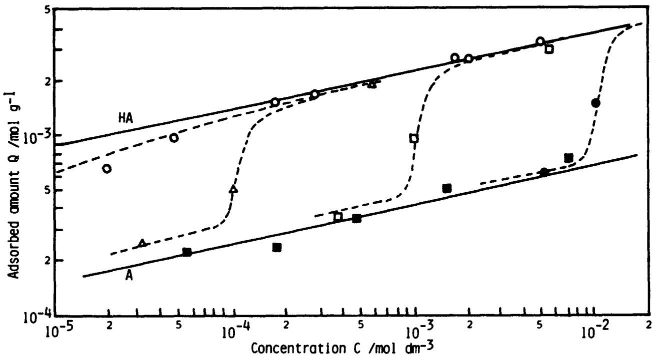

Fig. 5. Adsorption isotherms of benzoic acid on activated carbon in sodium hydroxide solutions at 25 °C.
○: Aqueous solution, △: 10^{-4} mol dm^{-3} NaOH solution, □: 10^{-3} mol dm^{-3} NaOH solution, ●: 10^{-2} mol dm^{-3} NaOH solution, ■: 1 mol dm^{-3} NaOH solution.

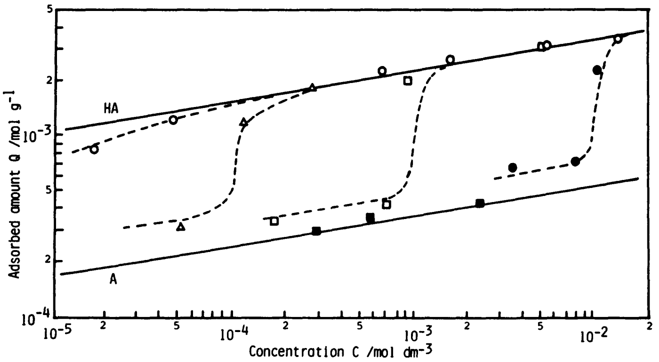

Fig. 6. Adsorption isotherms of nitrobenzoic acid on activated carbon in sodium hydroxide solutions at 25 °C.
(Symbols are same as in Fig. 5)

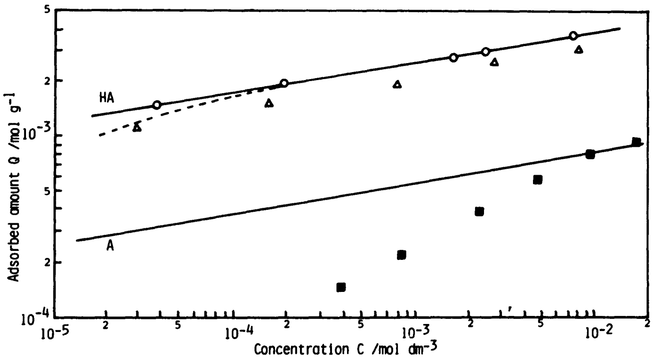

Fig. 7. Adsorption isotherms of phenol on activated carbon in sodium hydroxide solutions at 25 °C.
(Symbols are same as in Fig. 5)

The adsorption isotherms of the weak anionic electrolytes in sodium hydroxide solutions from 10^{-4} to 1 mol dm^{-3} are shown in Figs. 5—10. The amounts of these weak anionic electrolytes adsorbed in the 1 mol dm^{-3} sodium hydroxide solutions, in which those compounds were completely ionized, were much smaller than those in the aqueous solutions for the activated carbon. Their amounts adsorbed on the polystyrene adsorbent were negligibly small in the solutions of 1 mol dm^{-3} sodium hydroxide.

However, the adsorption isotherms of the completely ionized form for the activated carbon were parallel to their isotherms of the non-ionized form in the aqueous solutions, except for phenol. That, the values of n of the Freundlich equation were equal to one another. Urano *et al.*[3] reported that the distribution function of the adsorption energy could be obtained from the modified Freundlich isotherm equation; $Q = k'(C/C_s)^{1/n}$, and that the values of k' and n related, respectively, to adsorption space and mechanism, where C_s is the saturated concentration of the adsorbate. The fact that the values of n for the non-ionized form and the ionized form were equal to one another shows that the adsorption mechanisms of both forms are equal and that only the solubilities C_s are different. That, it can be thought that the adsorption amounts for those compounds except phenol decrease with the ionization in the basic solutions, because the apparent solubilities C_s of the ionized forms increase much more than those of the non-ionized forms.

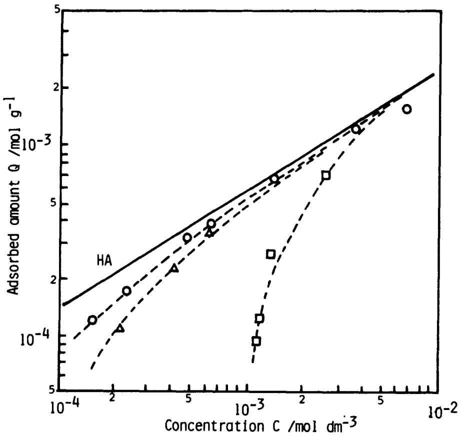

Fig. 8. Adsorption isotherms of benzoic acid on polystyrene adsorbent in sodium hydroxide solutions at 25 °C.
(Symbols are same as in Fig. 5)

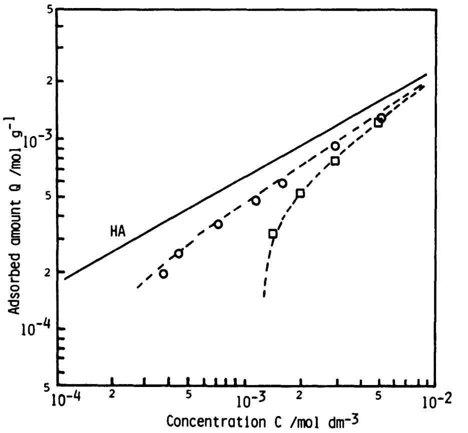

Fig. 9. Adsorption isotherms of nitrobenzoic acid on polystyrene adsorbent in sodium hydroxide solutions at 25 °C.
(Symbols are same as in Fig. 5)

The adsorptions of those weak anionic electrolytes in a basic solution seem to be examples of the adsorption of the dual-components, the non-ionized form (HA) and the ionized form (A). Getzen and Ward[4] reported a method of estimating the adsorption of several substituted benzoic acids by the application of the Langmuir equation for dual-components. However, it is difficult to determine the parameters of the Langmuir equation for application over a wide concentration range. Radke and Prausnitz[5] also proposed a method of predicting the adsorption of multi-components by means of a thermodynamic consideration. The total amounts Q of benzoic acid adsorbed under several conditions were calculated by the Radke-Prausnitz method for the forms of HA and A; they are compared with the observed data in Table 3. The calculated values are different from the observed data. Therefore, the Radke-Prausnitz method cannot be applied for the adsorption of the ionic compounds.

Now, assuming that the adsorptions of the non-ionized and the ionized forms are independent of one another, the total adsorbed amounts Q can be calculated as follows from the sum of the two Freundlich equations for HA and A;

$$Q = Q_{\mathrm{HA}} + Q_{\mathrm{A}} = k_{\mathrm{HA}} C_{\mathrm{HA}}^{1/n} + k_{\mathrm{A}} C_{\mathrm{H}}^{1/n} \tag{1}$$

The values of k_{HA}, k_{A}, and n can be obtained from the adsorption isotherms in aqueous solutions and sodium hydroxide solutions of 1 mol dm^{-3}; they are summarized in Table 4. The concentrations of the non-ionized and the ionized forms, C_{HA} and C_{A}, can be calculated from

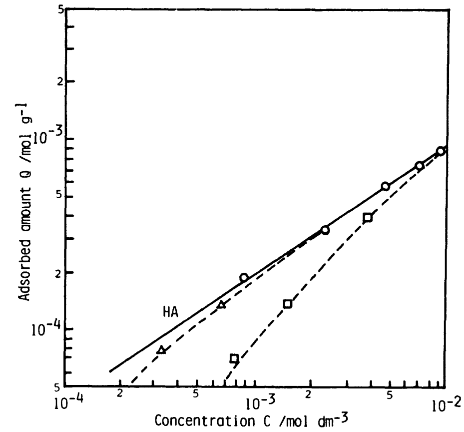

Fig. 10. Adsorption isotherms of phenol on polystyrene adsorbent in sodium hydroxide solutions at 25 °C.
(Symbols are same as in Fig. 5)

TABLE 3. COMPARISON OF Q CALCULATED BY THE RADKE-PRAUSNITZ METHOD AND OBSERVED DATA FOR BENZOIC ACID

C_{Na}	C	C_{HA}	C_{A}	Q/mol g^{-1}	
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	Calculated	Observed
1.0×10^{-2}	5.0×10^{-3}	6.0×10^{-10}	5.0×10^{-3}	2.0×10^{-4}	6.0×10^{-4}
1.0×10^{-2}	1.0×10^{-2}	1.2×10^{-6}	1.0×10^{-2}	7.4×10^{-4}	1.5×10^{-3}
1.0×10^{-2}	2.6×10^{-2}	1.6×10^{-2}	1.0×10^{-2}	1.4×10^{-3}	5.2×10^{-3}

TABLE 4. PARAMETERS OF FREUNDLICH EQUATION FOR THE NON-IONIZED FORM AND THE IONIZED FORM

	Activated Carbon			Polystyrene		
	k_{HA}	k_A	n	k_{HA}	k_A	n
Nitrobenzene	1.9×10^{-2}	—	4.0	9.1×10^{-2}	—	1.7
Benzaldehyde	1.6×10^{-2}	—	3.9	6.2×10^{-2}	—	1.7
Benzonitrile	1.7×10^{-2}	—	3.7	4.5×10^{-2}	—	1.8
Benzoic acid	9.4×10^{-3}	1.8×10^{-3}	4.8	6.7×10^{-2}	$<10^{-4}$	1.5
m-Nitrobenzoic acid	7.9×10^{-3}	1.2×10^{-3}	5.7	2.8×10^{-2}	$<10^{-4}$	1.8
Phenol	8.3×10^{-3}	—	5.7	1.9×10^{-2}	$<10^{-4}$	1.5
Benzenesulfonic acid	—	1.6×10^{-3}	6.7	—	$<10^{-4}$	—

the total concentration of the organic compound C, the concentration of the sodium ion C_{Na}, and the ionization constant K_a by means of the following equations;

$$C = C_{HA} + C_A \tag{2}$$

$$C_H + C_{Na} = C_A + C_{OH} = C_A + 10^{-14}/C_H \tag{3}$$

$$K_a = C_H C_A / C_{HA} \tag{4}$$

The adsorption isotherms in 10^{-4}, 10^{-3}, and 10^{-2} mol dm^{-3} of sodium hydroxide solutions were calculated by means of Eqs. 1—4; they all shown as broken lines in Figs. 5—10. The calculated lines approximately fit the observed plots for the various systems of a weak anionic compound and an adsorbent except for the adsorption of phenol on the activated carbon. Therefore, the adsorptions of the non-ionized form and the ionized form of those compounds seem to be practically independent of one another.

Consequently, the total adsorbed amount at a desired pH (or C_H) for the weak anionic electrolytes, except for several phenolic compounds,[6] can be predicted by the use of Eq. 1 from the adsorption isotherms of the non-ionized form and the ionized form and the ionization constant, because the concentrations of both forms, C_{HA} and C_A, can be given as Eqs. 5 and 6 from Eqs. 2—4 at the desired pH;

$$C_{HA} = 10^{-pH}C/(10^{-pH} + K_a) \tag{5}$$

$$C_A = K_a C/(10^{-pH} + K_a) \tag{6}$$

The amounts of phenol adsorbed on the activated carbon decreased much in the lower concentration ranges in basic solutions, as shown in Fig. 7. It was shown in previous papers[3,6] that several phenolic compounds combined with the carbon surface by means of the π-electron combination. Therefore, the deviation of phenol for the activated carbon may be due to the combination of the hydroxide ion with the electrophilic groups on the surface of activated carbon.[3,6]

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