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Removal and Recovery of Organic Pollutants from the Aquatic Environment. VII. Adsorption of Phenol and Carboxylic Acids on Crosslinked Poly(4-vinylpyridine)

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Molecular adsorptions of phenols and carboxylic acids on crosslinked poly(4-vinylpyridine) were studied in comparison with those on various polymeric adsorbents. Enthalpies for the adsorption of phenol on various polymeric adsorbents were evaluated based upon the temperature dependence of the phenol adsorption isotherms. The enthalpy on crosslinked poly(4-vinylpyridine) was close to that on porous poly(styrene-divinylbenzene) resin with no ion exchange functional group, and was much smaller than that on commercial weak base anion exchange resin. The relative adsorption capacities of various polymeric adsorbents for carboxylic acids and substituted phenols indicated that the acid-base interaction as well as hydrophobic interaction between these organic acids and crosslinked poly(4-vinylpyridine) was an important factor in the adsorption.

In previous papers of this series, crosslinked poly(vinylpyridine) was reported to be an excellent polymeric adsorbent for removal and recovery of phenol[1] and carboxylic acids[2] from aqueous solution. The capacities of crosslinked poly(vinylpyridine) for the adsorption of these organic acids were scarcely affected by the presence of inorganic salts. On the contrary, the capacities of commercial strong base and weak base anion exchange resins for the adsorption of these organic acids were conspicuously reduced in the presence of inorganic salts. Elution of the adsorbed organic acids from crosslinked poly(vinylpyridine) was easily accomplished by a simple treatment with organic solvents such as acetone and methanol, which was notably easier than those from anion exchange resins, and crosslinked poly(vinylpyridine) was efficiently regenerated. These observations showed that an ion exchange mechanism could not explain the adsorption of these organic acids by crosslinked poly(vinylpyridine). On the other hand, the capacities of crosslinked poly(vinylpyridine) for the adsorption of these organic acids were remarkably higher than those observed with porous poly(styrene-divinylbenzene) resin with no ion exchange functional group, in spite of the fact that the crosslinked poly(vinylpyridine) in the pulverized form was used. Therefore, a simple physical interaction between these organic acids and crosslinked poly(vinylpyridine) could not wholly explain the ability of the polymer for the adsorption of these organic acids. In this work, we have investigated the mechanism of the adsorption of phenol and carboxylic acids on crosslinked poly(vinylpyridine).

Experimental

Materials. Crosslinked poly(4-vinylpyridine) containing 72 mol% 4-vinylpyridine was prepared by a copolymerization of 4-vinylpyridine with divinylbenzene followed by griding and sifting to 60—80 mesh as was described previously.[1] The mean particle diameter was 0.20 mm in the wet state. For comparison, three commercial resins supplied by Rohm and Haas Co., Philadelphia, Pa., U. S. A., were used in this work. Amberlite IRA-400 was used as a strong base anion exchange resin, which had a styrene-divinylbenzene matrix with quarternary ammonium group. The particle size of this resin in the chloride form was 0.38—0.45 mm. This resin was used in the hydroxide form. Amberlite IRA-45 was used as a weak base anion exchange resin, which had a styrene-divinylbenzene matrix with primary, secondary, and tertiary amino groups. This resin was used in the free base form. The particle size was 0.36—0.46 mm. Amberlite XAD-4 was used as a porous poly(styrene-divinylbenzene) resin with no ion exchange functional group, which had a styrene-divinylbenzene matrix. The supplier claimed that the surface area of the resin was 784 m^2/g. These resins were preconditioned as was described previously.[1] Commercial products of phenol, *p*-cresol, *p*-nitrophenol, carboxylic acids, and other chemicals were used without further purification. Deionized water was used throughout the experiments.

Procedure. Column studies were conducted using a 1.0-cm diameter glass column with a fritted glass filter connected with a dropping funnel in a down-flow fashion at room temperature as was described in a previous paper.[1] The adsorption capacity of resins was evaluated in two ways: (i) the breakthrough capacity, which was based upon the total amount of adsorbed organic acids until the effluent concentration reached 1 mg dm^{-3} (in the adsorption of substituted phenols), or until the effluent solution became acidic using Methyl Red as the indicator (in the adsorption of carboxylic acids); (ii) the total capacity, which was based upon the total amount of adsorbed organic acids until the effluent concentration reached the influent concentration. The concentrations of phenol, *p*-cresol, and *p*-nitrophenol were determined based upon the adsorptivities at 275, 279, and 318 nm, respectively, or with aid of 4-aminoantipyrine[3] using a Shimadzu UV-200S, UV-100-01 or UV-100-02 spectrophotometer. The concentrations of carboxylic acids were determined by titration with a standard 0.1 mol dm^{-3} sodium hydroxide solution using phenolphthalein as the indicator.

Equilibrium adsorption tests were conducted by placing weighed quantities of polymeric adsorbent and samples of aqueous solution of organic acids in a 300-cm^3 Erlenmeyer flask sealed by a rubber stopper with magnetic stirring at the prescribed temperature. After the mixture reached equilibrium, the concentration of organic acids was determined.

Results and Discussion

Enthalpies for Phenol Adsorption. The experimental isotherms of phenol adsorption on crosslinked poly(4-vinylpyridine), porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (Amberlite XAD-4), and weak base anion exchange resin in the free base form (Amberlite IRA-45) are shown in Figs. 1, 2, and 3, respectively. The linear relationship of Figs. 1, 2, and 3 indicates that the adsorption isotherms of phenol on these polymeric adsorbents follow the Freundlich equation. The type of adsorption of phenol on crosslinked poly(4-vinylpyridine) appears to be not unusual but commonly observed in most of liquid-phase adsorptions. The temperature dependence of isotherms was large in the adsorption of phenol on weak base anion exchange resin in the free base form (Fig. 3), when compared with that on crosslinked poly(4-vinylpyridine) (Fig. 1) and that on porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (Fig. 2).

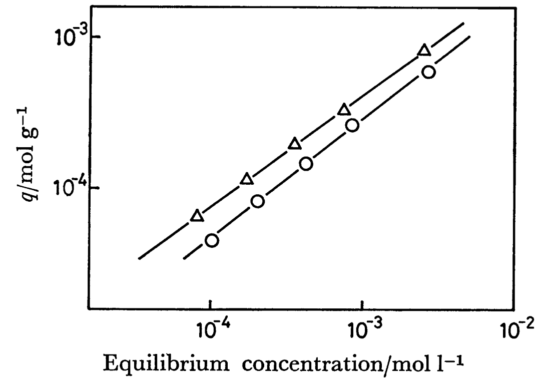


Fig. 1. Phenol adsorption isotherms on crosslinked poly(4-vinylpyridine).
△: 20 °C, ○: 50 °C.

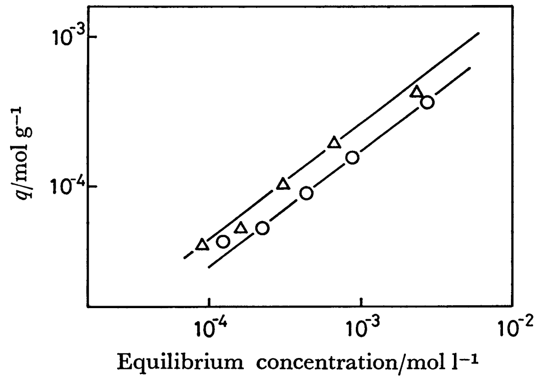


Fig. 2. Phenol adsorption isotherms on porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (Amberlite XAD-4).
△: 20 °C, ○: 50 °C.

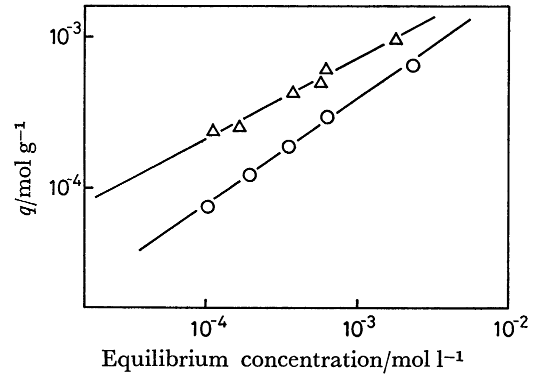


Fig. 3. Phenol adsorption isotherms on weak base anion exchange resin (Amberlite IRA-45) in the free base form.
△: 20 °C, ○: 50 °C.

In order to evaluate the temperature dependence of isotherms more quantitatively, we calculated the enthalpies for phenol adsorption on these three polymeric adsorbents. The enthalpy of adsorption on polymeric adsorbents is generally calculated from isotherms for adsorptions at two different temperatures by use of the following relationship:[4]

$$\Delta H^0 = \frac{2.303RT_1T_2}{T_2-T_1}(\log C_1-\log C_2).$$

Here, ΔH^0 is the enthalpy of adsorption, R is the gas constant, C_1 and C_2 are the equilibrium concentrations of solute in moles per liter at the absolute temperatures T_1 and T_2, respectively. Enthalpies of phenol adsorption were calculated based upon the isotherms at 20 and 50 °C. The enthalpy of adsorption calculated by use of the above relationship depends upon the value of q, which is the number of moles of solute adsorbed per gram of dry adsorbent, and we calculated the enthalpy at four different values of q. Results are given in Table 1.

The enthalpy of phenol adsorption on weak base anion exchange resin (IRA-45) was large, and that on crosslinked poly(4-vinylpyridine) was close to that on porous poly(styrene-divinylbenzene) resin with no ion exchange functional group. These results show that the adsorption of phenol on crosslinked poly(4-

TABLE 1. ENTHALPIES FOR PHENOL ADSORPTION

	$\frac{q}{\text{mol g}^{-1}}$	$\frac{-\Delta H^0}{\text{kcal mol}^{-1}}$
Crosslinked poly(4-vinylpyridine)[a]	8.0×10^{-5}	3.8
	2.0×10^{-4}	3.4
	6.0×10^{-4}	2.7
	1.0×10^{-3}	1.9
Amberlite XAD-4[b]	8.0×10^{-5}	3.4
	2.0×10^{-4}	3.4
	6.0×10^{-4}	3.4
	1.0×10^{-3}	3.4
Amberlite IRA-45[c]	8.0×10^{-5}	11.0
	2.0×10^{-4}	8.6
	6.0×10^{-4}	5.0
	1.0×10^{-3}	4.4

a) Pulverized copolymer of 4-vinylpyridine with divinylbenzene containing 72 mol% 4-vinylpyrine. b) Porous poly(styrene-divinylbenzene) resin with no ion exchange functional group. Claimed to have a surface area of 784 m^2 g^{-1}. c) Weak base anion exchange resin in the free base form.

vinylpyridine) occurs through a different mechanism from that on anion exchange resin, and that the adsorption is rather close to physical adsorption.

Capacities for the Adsorption of Carboxylic Acids. Column studies were also performed in order to obtain detailed information concerning the nature and mechanism of the adsorption of phenol and carboxylic acids on crosslinked poly(4-vinylpyridine). Since the crosslinked poly(4-vinylpyridine) was developed as a polymeric adsorbent for removal and recovery of organic pollutants from waste water, the column studies were much more important and practical than the studies of adsorption equilibrium for this purpose. Relative adsorption capacities of these organic acids on the polymeric adsorbents were compared.

Effects of two factors, *i.e.*, hydrophobic interaction and acid-base or electrostatic interaction between the polymeric adsorbents and the organic acids, were evaluated on the basis of the relative adsorption capacites. The hydrophobic interaction between the polymeric adsorbents and the organic acids were evaluated in terms of the effect of the length of hydrocarbon chain. The acid-base or electrostatic interaction between the polymeric adsorbents and the organic acids were evaluated in terms of the effect of $\mathrm{p}K_a$ of the organic acids.

Breakthrough and total capacities of polymeric adsorbents for the adsorption of various carboxylic acids were determined by the continuous flow column method. In Table 2 are given the capacities of the porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (Amberlite XAD-4). The adsorption capacity increased with the hydrocarbon chain length of the carboxylic acid, *i.e.*, in the order: formic $<$ acetic $<$ propionic $<$ butyric $<$ valeric acid. Similar tendency has been reported in the adsorption of carboxylic acids on a porous poly(styrene-divinylbenzene) resin,[5] although the results were obtained using the batch method.

The acidity of carboxylic acid did not affect significantly the adsorption capacity. For example, the adsorption capacities for valeric acid were 20—30 times larger than those for acetic acid, although $\mathrm{p}K_a$ values of these carboxylic acids are similar in magnitude. The adsorption capacities for formic and trifluoroacetic acid were much smaller than those for butyric and valeric acid, although the former carboxylic acids are more acidic.

In order to obtain a quantitative information about the effect of the structure of carboxylic acid on the adsorption capacity of the resin, the logarithm of the adsorption capacity was plotted against the number of carbon atoms in the carboxylic acid. The result is shown in Fig. 4. The straight line in Fig. 4 indicates that the logarithm of the adsorption capacity varies in proportion to the number of carbon atoms of the carboxylic acid.

It is widely held that the standard free energy change for transfer of hydrocarbon chains from aqueous solution to other phase varies in proportion to the num-

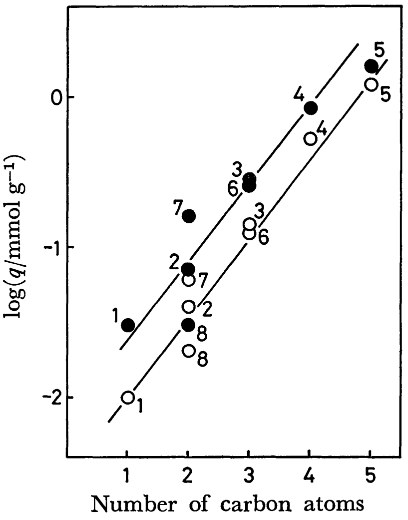


Fig. 4. Capacities of porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (Amberlite XAD-4) for the adsorption of carboxylic acids as a function of the number of carbon atoms of the carboxylic acids.

●: Total adsorption capacity, ○: breakthrough capacity. 1: HCOOH, 2: CH_3COOH, 3: CH_3CH_2COOH, 4: $CH_3(CH_2)_2COOH$, 5: $CH_3(CH_2)_3COOH$, 6: $CH_2{=}CHCOOH$, 7: $ClCH_2COOH$, 8: CF_3COOH.

Table 2. Capacities of porous poly(styrene-divinylbenzene) resin with no ion exchange functional group for the adsorption of carboxylic acids from aqueous solution[a)]

Run	Carboxylic acid	$\mathrm{p}K_a$	Breakthrough capacity[b)] mmol g^{-1}	Total adsorption capacity[c)] mmol g^{-1}
1	HCOOH	3.75 (25 °C)	0.01	0.03
2	CH_3COOH	4.76 (25 °C)	0.04	0.07
3	CH_3CH_2COOH	4.87 (25 °C)	0.14	0.28
4	$CH_3(CH_2)_2COOH$	4.82 (25 °C)	0.52	0.83
5	$CH_3(CH_2)_3COOH$	4.84 (25 °C)	1.20	1.55
6	$CH_2{=}CHCOOH$	4.26 (25 °C)	0.12	0.25
7	$ClCH_2COOH$	2.87 (25 °C)	0.06	0.16
8	CF_3COOH	0.25 (25 °C)	0.02	0.03

a) Determined by the continuous flow column method using 10 mmol dm^{-3} aqueous solution of carboxylic acids. Amberlite XAD-4 was used as the adsorbent. The flow rate was 3 bed volumes per hour. b) The total amount of adsorbed carboxylic acid until the effluent solution became acidic using Methyl Red as the indicator. c) The total amount of adsorbed carboxylic acid until the effluent concentration reached the influent concentration.

ber of carbon atoms.[6] For example, the standard free energy change for transfer of hydrocarbons from aqueous solution to pure liquid hydrocarbon was shown to be a linear function of the length of the hydrocarbon chain.[6,7] The free energy change for transfer of undissociated fatty acids from a dilute aqueous buffer solution to liquid heptane was also found to be proportional to the number of carbon atoms.[6,8] These relationships were explained in terms of hydrophobic interactions of the hydrocarbon chain.

The adsorption capacity obtained in column studies depends upon the diameter of the column, the flow rate, and other experimental factors. However, such factors were almost constant throughout the present study. Therefore, the relative adsorption capacity may closely relate to the thermodynamic adsorption equilibrium constant and its logarithm may correlate to the free energy change of transfer of a carboxylic acid from aqueous solution to the resin. The straight line in Fig. 4 suggests that such free energy change varies in proportion to the number of carbon atoms in the carboxylic acid.

On the basis of these arguments, it is reasonably considered that hydrophobic interactions between the hydrocarbon chain of the carboxylic acid and the resin matrix are responsible for the increase in adsorption capacity with the chain length of the carboxylic acid.

In Tables 3 and 4 are given the capacities of the weak base anion exchange resin (Amberlite IRA-45) in the free base form and those of strong base anion exchange resin (Amberlite IRA-400) in the hydroxide form for the adsorption of carboxylic acids. The adsorption capacities were not significantly affected by the chain length of the carboxylic acid. However, the adsorption capacities decreased with an increase in pK_a of the carboxylic acid. Thus, it was felt that the ion exchange or acid-base interaction between the carboxylic acid and the resin played an important role in the adsorption of carboxylic acid on these anion exchange resins.

In Table 5 are given the capacities of crosslinked poly(4-vinylpyridine) for the adsorption of carboxylic acids. The adsorption capacity for a series of saturated aliphatic carboxylic acids increased in the order: acetic<propionic<butyric<valeric acid. However, pK_a values indicate the similar acidity of these carboxylic acids. The relation between the logarithm of the adsorption capacity and the number of carbon atoms of the carboxylic acid is shown in Fig. 5. The figure shows a linear relationship for this series of saturated aliphatic carboxylic acids of similar pK_a. Therefore, hydrophobic interaction between the hydrocarbon chain of the carboxylic acid and the resin matrix seems to play an important role in the adsorption on the crosslinked poly(4-vinylpyridine).

TABLE 3. CAPACITIES OF WEAK BASE ANION EXCHANGE RESIN IN THE FREE BASE FORM FOR THE ADSORPTION OF CARBOXYLIC ACIDS FROM AQUEOUS SOLUTION[a)]

Carboxylic acid	pK_a	Breakthrough capacity[b)] mmol g^{-1}	Total adsorption capacity[c)] mmol g^{-1}
HCOOH	3.75 (25 °C)	4.00	4.98
CH_3COOH	4.76 (25 °C)	3.13	4.08
CH_3CH_2COOH	4.87 (25 °C)	3.02	4.36
$CH_3(CH_2)_2COOH$	4.82 (25 °C)	3.25	4.91
$CH_3(CH_2)_3COOH$	4.84 (25 °C)	4.64	5.99
CH_2=CHCOOH	4.26 (25 °C)	3.44	5.15
$ClCH_2COOH$	2.87 (25 °C)	4.29	5.37
CF_3COOH	0.25 (25 °C)	4.29	5.45

a) Determined by the continuous flow column method using 100 mmol dm^{-3} aqueous solution of carboxylic acids. Amberlite IRA-45 was used as the adsorbent. The flow rate was 3 bed volumes per hour. b) See footnote (b) in Table 2. c) See footnote (c) in Table 2.

TABLE 4. CAPACITIES OF STRONG BASE ANION EXCHANGE RESIN IN THE HYDROXIDE FORM FOR THE ADSORPTION OF CARBOXYLIC ACIDS FROM AQUEOUS SOLUTION[a)]

Carboxylic acid	pK_a	Breakthrough capacity[b)] mmol g^{-1}	Total adsorption capacity[c)] mmol g^{-1}
HCOOH	3.75 (25 °C)	3.15	3.87
CH_3COOH	4.76 (25 °C)	2.78	3.67
CH_3CH_2COOH	4.87 (25 °C)	2.75	3.74
$CH_3(CH_2)_2COOH$	4.82 (25 °C)	2.73	3.99
CH_2=CHCOOH	4.26 (25 °C)	2.95	3.88
$ClCH_2COOH$	2.87 (25 °C)	3.37	4.01
CF_3COOH	0.25 (25 °C)	3.01	3.35

a) Determined by the continuous flow column method using 100 mmol dm^{-3} aqueous solution of carboxylic acids. Amberlite IRA-400 was used as the adsorbent. The flow rate was 3 bed volumes per hour. b) See footnot (b) in Table 2. c) See footnote (c) in Table 2.

Table 5. Capacities of crosslinked poly(4-vinylpyridine) for the adsorption of carboxylic acids from aqueous solution[a]

Run	Carboxylic acid	pK_a	Breakthrough capacity[b)] mmol g^{-1}	Total adsorption capacity[c)] mmol g^{-1}
1	HCOOH	3.75 (25 °C)	2.61	3.03
2	CH_3COOH	4.76 (25 °C)	1.00	1.33
3	CH_3CH_2COOH	4.87 (25 °C)	1.75	2.02
4	$CH_3(CH_2)_2COOH$	4.82 (25 °C)	2.72	2.95
5	$CH_3(CH_2)_3COOH$	4.84 (25 °C)	4.21	4.70
6	$CH_2{=}CHCOOH$	4.26 (25 °C)	2.36	—
7	$ClCH_2COOH$	2.87 (25 °C)	2.45	4.78
8	CF_3COOH	0.25 (25 °C)	6.66	6.72

a) Determined by the continuous flow column method using 100 mmol dm^{-3} aqueous solution of carboxylic acids. The flow rate was 3 bed volumes per hour. Crosslinked poly(4-vinylpyridine) containing 72 mol% 4-vinylpyridine in the pulverized form was used as the adsorbent. b) See footnote (b) in Table 2. c) See footnote (c) in Table 2.

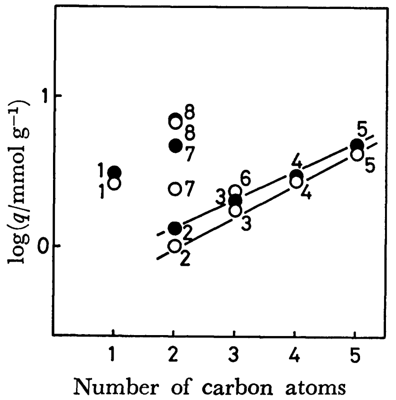
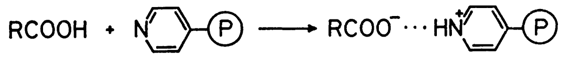
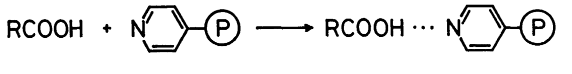


Fig. 5. Capacities of crosslinked poly(4-vinylpyridine) containing 72 mol% 4-vinylpyridine for the adsorption of carboxylic acids as a function of the number of carbon atoms of the carboxylic acids.
●: Total adsorption capacity, ○: breakthrough capacity. 1: HCOOH, 2: CH_3COOH, 3: CH_3CH_2COOH, 4: $CH_3(CH_2)_2COOH$, 5: $CH_3(CH_2)_3COOH$, 6: $CH_2{=}CHCOOH$, 7: $ClCH_2COOH$, 8: CF_3COOH.

However, marked deviations from the linear relationship of Fig. 5 were observed for formic acid (1), chloroacetic acid (7), and trifluoroacetic acid (8), in contrast to the relation shown in Fig. 4 for the adsorption on porous poly(styrene-divinylbenzene) resin with no ion exchange functional group. These carboxylic acids have much lower pK_a values than those of the saturated aliphatic carboxylic acids mentioned above. The effect of acidity on the capacity of crosslinked poly(4-vinylpyridine) for the adsorption of carboxylic acids is also demonstrated by a tendency that the adsorption capacity increased with the acidity in a series acetic<chloroacetic<trifluoroacetic acid. The larger capacity for the adsorption of acrylic acid than that for propionic acid can also be attributed to the difference in acidity of these carboxylic acids, since both of these carboxylic acids have a similar chain length. The larger adsorption capacity for formic acid than that for acetic acid cannot be explained in terms of the hydrophobic interaction, since such interaction seems to be smaller in the adsorption of formic acid as can be seen in Fig. 4. Higher acidity of formic acid may be responsible for the larger adsorption capacity. These observations clearly indicate the importance of acidity of the carboxylic acid in the adsorption on crosslinked poly(4-vinylpyridine). However, as was reported previously,[1,2)] ion exchange mechanism does not appear to be suitable for the adsorption of phenol or carboxylic acids on crosslinked poly(4-vinylpyridine). Thus, the effect of acidity on the above adsorption capacity may be ascribable to the contribution of the acid-base interaction between the pyridyl group of the crosslinked poly(vinylpyridine) and the carboxyl group of the carboxylic acid. Because pyridine is an organic base, it is reasonable to consider the following interaction, where the pyridyl group of the resin uptakes a proton from the carboxylic acid to form a complex with the carboxylate anion as the associated counterion:



The formation of hydrogen bond may also contribute to the interaction between the pyridyl group and the carboxylic acid:



Such acid-base interactions may increase with acidity of carboxylic acid, and may be responsible for the remarkably higher capacity of the crosslinked poly(vinylpyridine) for the adsorption of carboxylic acid than that of the resin with no ion exchange functional group as Amberlite XAD-4.

Capacities for the Adsorption of Substituted Phenols. Breakthrough capacities of polymeric adsorbents for the adsorption of substituted phenols were also determined by the continuous flow column method. Results are given in Table 6.

Adsorption capacities of the porous poly(styrene-divinylbenzene) resin with no ion exchange functional group (XAD-4) for substituted phenols were in the order: *p*-nitrophenol ≈ phenol < *p*-cresol. The larger adsorption capacity for *p*-cresol than that for phenol may be attributed to the higher hydrophobicity

TABLE 6. BREAKTHROUGH CAPACITIES OF POLYMERIC ADSORBENTS FOR THE ADSORPTION OF SUBSTITUTED PHENOLS FROM AQUEOUS SOLUTION[a)]

Substituted phenol	pK_a	Breakthrough capacity mmol g^{-1} b)		
		XAD-4[c)]	IRA-45[d)]	PVP[e)]
p-Cresol	10.26 (25 °C)	2.41	2.38	3.88
Phenol	10.00 (20 °C)	1.59	2.89	2.93
p-Nitrophenol	7.15 (25 °C)	1.58	3.60	5.39

a) Determined by the continuous flow column method using 35 mmol dm^{-3} aqueous solution of substituted phenols. The flow rate was 3 bed volumes per hour. b) The total amount of adsorbed phenols before the effluent concentration reached 1 mg dm^{-3}. c) See footnote (b) in Table 1. d) See footnote (c) in Table 1. e) See footnote (a) in Table 1.

of *p*-cresol. The capacity for *p*-nitrophenol adsorption was close to that for phenol adsorption in spite of large difference in pK_a of the two phenols. This result implies that the acidity of phenolic hydroxyl group did not significantly affect the adsorption capacity. In contrast, the adsorption capacity of weak base anion exchange resin (IRA-45) in the free base form for substituted phenols was in the order: *p*-cresol< phenol<*p*-nitrophenol. Thus, the adsorption capacity increased with the acidity of adsorbate in this case. This result suggests the importance of the ion exchange or acid-base interaction between the substituted phenols and the resin.

In the adsorption on crosslinked poly(4-vinylpyridine), the capacity for *p*-cresol adsorption was higher than that for phenol adsorption. This fact may be explained in terms of higher hydrophobicity of the former adsorbate. Adsorption capacity for *p*-nitrophenol was also higher than that for phenol. Higher acidity of *p*-nitrophenol than that of phenol seems to be responsible for this result. These observations may suggest that both hydrophobic interaction and acid-base interaction played important roles in the adsorption of substituted phenols on crosslinked poly(4-vinylpyridine) as well as in the adsorption of carboxylic acids.

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