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Selective Adsorption of Alkylbenzenesulfonates on Quaternized Crosslinked Poly(4-vinylpyridine)

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Selective ion-exchange adsorption of a series of alkylbenzenesulfonate ions (C_nBS^-) on a series of crosslinked poly(*N*-alkyl-4-vinylpyridinium bromide) (C_mVP) and crosslinked poly(*N*-benzyl-4-vinylpyridinium bromide) (BVP) was investigated based upon the selectivity coefficient of the resins for C_nBS^- relative to Br^- which was expressed as $K_{Br}^{C_nBS^-}$. In the adsorption of C_nBS^- of $n<8$, the selectivity coefficient linearly increased with the number of carbon atoms of the alkyl chain, n, of C_nBS^-, which was ascribed to the hydrophobic interaction between the alkyl chain of C_nBS^- and the resin. In the adsorption of C_nBS^- of $n>8$, however, the selectivity coefficient did not increase with n, which was explained in terms of a steric effect. The selectivity coefficient also increased with the number of carbon atoms of the alkyl chain, m, of C_mVP, but saturation was also observed for the adsorption on C_mVP of $m>12$. In the adsorption of C_nBS^- of $n<8$ on BVP, significant influence of the degree of quaternization was not observed. In the adsorption of $C_{12}BS^-$, however, BVP of lower degree of quaternization showed a much larger selectivity than that of BVP of higher degree of quaternization. The observation indicated that steric repulsion between C_nBS^- ions adsorbed on the surface of the resin played a crucial role.

Adsorption of organic materials by polymeric adsorbents is of considerable interest.[1] In a previous paper,[2] crosslinked poly(*N*-benzyl-4-vinylpyridinium bromide) (BVP) was reported to be an excellent polymeric adsorbent for removal of sodium dodecylbenzenesulfonate from aqueous solution. Although the adsorption proceeded by ion-exchange mechanism, the adsorption capacity was scarcely affected by the presence of inorganic anions such as chloride, sulfate, and hydroxide ions. Extremely high selectivity of BVP for alkylbenzenesulfonate ion provided strong motivation for understanding of the nature of such adsorption. In this study, selectivities of BVP and a series of crosslinked poly(*N*-alkyl-4-vinylpyridinium bromide) (C_mVP, here m is the number of carbon atoms of the alkyl group) for a series of alkylbenzenesulfonate ions (C_nBS^-, here n is the number of carbon atoms of the alkyl group) were determined, and an attempt has been made to indicate which factors operate in determining the selectivity.

Experimental

Materials. Sodium dodecylbenzenesulfonate ($C_{12}BS$) of high purity (special grade for the test of synthetic detergent) was supplied from Wako Pure Chemical Industries, Japan. Sodium benzenesulfonate (C_0BS) was supplied from Nakarai Chemicals, Japan. Sodium ethylbenzenesulfonate (C_2BS) was supplied from Tokyo Kasei Kogyo Co., Japan. These sodium alkylbenzenesulfonates (C_nBS) were used without further purification. Sodium butylbenzenesulfonate (C_4BS), sodium hexylbenzenesulfonate (C_6BS), and sodium octylbenzenesulfonate (C_8BS) were prepared according to the literature procedure[3] with minor modifications, and purified by recrystallization from hot methanol before use.

^1H NMR spectra of these C_nBS were obtained with a Varian T-60A spectrometer in dimethyl-d_6 sulfoxide using tetramethylsilane as an internal standard. Aromatic protons showed distinct AB-type quartets. This result indicated that para isomers were predominant and the presence of ortho and meta isomers was not significant. Aliphatic protons showed the presence of only one methyl group in each C_nBS. This result indicated that the normal alkyl groups were predominant and the presence of branched alkyl groups was not significant. Relative amounts of aromatic and aliphatic protons were also consistent with the prescribed structure.

TABLE 1. DEGREE OF QUATERNIZATION AND ION EXCHANGE CAPACITY OF RESINS

Resin	Degree of quaternization/%	Ion exchange capacity/mequiv. g^{-1}
BVP	89	2.85
BVP′	32	1.51
C_4VP	71	2.77
C_8VP	55	2.09
$C_{12}VP$	36	1.44
$C_{16}VP$	20	0.92

Crosslinked poly(4-vinylpyridine) containing 72 mol% of 4-vinylpyridine was prepared by a copolymerization of 4-vinylpyridine with divinylbenzene followed by grinding and sifting to 60—80 mesh as described previously.[4] Quaternization of the copolymer with benzyl bromide in benzene (60 °C 4 h) yielded crosslinked poly(*N*-benzyl-4-vinylpyridinium bromide) (BVP).[2] Quaternization of the copolymer with a series of alkyl bromides was carried out in a similar fashion (60 °C, 40 h) to yield crosslinked poly(*N*-alkyl-4-vinylpyridinium bromide) (C_mVP). The resins thus obtained were washed with benzene, methanol, and water before the adsorption test. Degree of quaternization and ion exchange capacities of the resins were determined by titration with standard $AgNO_3$ solution using eosin as the indicator, after the reaction with excess aq $NaNO_3$ (Table 1).

Deionized water was used throughout the experiments. Other chemicals were used as obtained commercially.

Equilibrium Adsorption Test. Equilibrium adsorption tests were conducted by placing weighed quantities of the resin and an aqueous solution of sodium alkylbenzenesulfonate and sodium bromide (total concentration 0.1 M) in a 100-cm^3 Erlenmeyer flask equipped with a mechanical stirrer at 30 ± 1 °C. After the mixture reached equilibrium, the concentration of alkylbenzenesulfonate ion was determined based upon the absorptivities at 260 nm using Shimadzu UV-100-02 spectrophotometer. Concentration of bromide ion was determined by titration with standard $AgNO_3$ solution using eosin as the indicator.

Results and Discussion

Selectivities of several quaternized crosslinked poly(4-vinylpyridine) (BVP and C_mVP) for a series of alkylbenzenesulfonate ions (C_nBS^-) were determined by equilibrium adsorption tests. The selectivities were determined relative to bromide ion because of the following reasons. The bromide form of the quaternized crosslinked poly(4-vinylpyridine) can be obtained more easily than the corresponding chloride form since the quaternization with alkyl bromide proceeds more smoothly than that with alkyl chloride. Although the bromide form of the polymer can be transformed into the chloride form or sulfate form by ion-exchange process, it is difficult to confirm the completeness of the transformation. Incomplete transformation might result in a large experimental error in determination of selectivities. The selectivity coefficients, $K_{Br^-}^{C_nBS^-}$, were calculated by use of the following relationship.[5]

$$K_{Br^-}^{C_nBS^-} = \frac{(\text{mmol } C_nBS^- \text{ in resin})}{(\text{mmol } Br^- \text{ in resin})} \times \frac{[Br^-]}{[C_nBS^-]}, \qquad (1)$$

where $[Br^-]$ is the molar concentration of bromide ion in the solution and $[C_nBS^-]$ is the molar concentration of alkylbenzenesulfonate ion. The selectivity coefficients somewhat varied with the molar fraction of alkylbenzenesulfonate ion in the resin, x, which was defined as follows:

$$x = \frac{(\text{mmol } C_nBS^- \text{ in resin})}{(\text{mmol } C_nBS^- \text{ in resin}) + (\text{mmol } Br^- \text{ in resin})}. \qquad (2)$$

The dependency of $K_{Br^-}^{C_nBS^-}$ on x is illustrated in Fig. 1. Therefore, discussions were made based on the values of $K_{Br^-}^{C_nBS^-}$ at $x=0.5$, which were determined from the plots of $\log K_{Br^-}^{C_nBS^-}$ *vs.* x.

Influence of Alkyl Chain Length of Alkylbenzenesulfonates. With increasing alkyl chain length of alkylbenzenesulfonate ions, *i.e.*, when the value of n of C_nBS^- increased, the competition between alkylbenzenesulfonate ion and bromide ion for the ion-exchange sites strongly favored the adsorption of the former. In order to evaluate the influence of alkyl chain length more quantitatively, $\log K_{Br^-}^{C_nBS^-}$ of BVP was plotted against the number of carbon atoms, n, of the alkyl chain of C_nBS^-. In the cases where $n<8$, $\log K_{Br^-}^{C_nBS^-}$ of BVP increased linearly with n as shown in Fig. 2. It holds widely that the standard free energy change for transfer of hydrocarbon chains from aqueous solution to other phase varied in proportion to the number of carbon atoms. This relationship has been explained in terms of hydrophobic interactions of the hydrocarbon chain.[6] On this basis, it may be reasonably considered that hydrophobic interaction between the resin and the alkyl chain of C_nBS^- is responsible for the increase in selectivity with the length of alkyl chain.

The standard free energy change for the transfer of alkylbenzenesulfonate ion from aqueous solution to the resin phase (ΔG) is correlated to the selectivity coefficient as follows:[7]

$$-RT\delta(\ln K_{Br^-}^{C_nBS^-})/\delta n = \delta\Delta G/\delta n + \Pi\delta V_{C_nBS^-}/\delta n, \qquad (3)$$

where Π is the swelling pressure of the resin and $V_{C_nBS^-}$ is partial molar volume of C_nBS^-. The linear part of Fig. 2 gave a value for $RT\delta(\ln K_{Br^-}^{C_nBS^-})/\delta n$ of approximately 2400 J mol^{-1}. Similar values (*ca.* 2200 J mol^{-1}) were reported for the adsorption of aliphatic carboxylate anion on anion exchange resins.[7]

On the other hand, in the cases where $n>8$, $\log K_{Br^-}^{C_nBS^-}$ did not increase with n. Steric factor seemed to be responsible for the results, since hydrophobic interaction is expected to increase with further increase in the alkyl chain length. As the alkyl chain length of C_nBS^- increased, steric repulsion between the adsorbed sulfonate ions would increase, which might compensate for the increase in hydrophobic interaction. Steric repulsion between the polymer matrix and the sulfonate ions also seemed to be important.

As has been mentioned above, steric effect seemed to

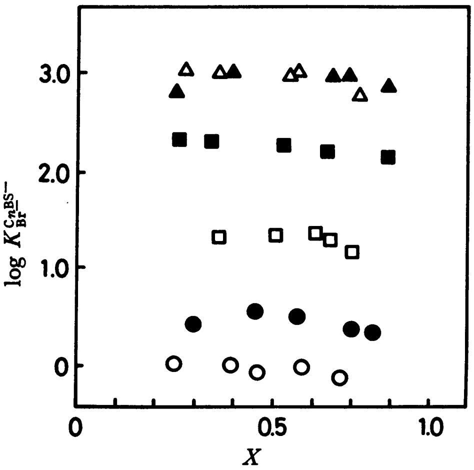

Fig. 1. Variation of selectivity coefficients of BVP resin for a series of alkylbenzenesulfonate ions (C_nBS^-) with molar fraction of C_nBS^- in resin.
○: C_0BS^-, ●: C_2BS^-, □: C_4BS^-, ■: C_6BS^-, △: C_8BS^- ▲: $C_{12}BS^-$. Degree of quaternization of BVP was 89%.

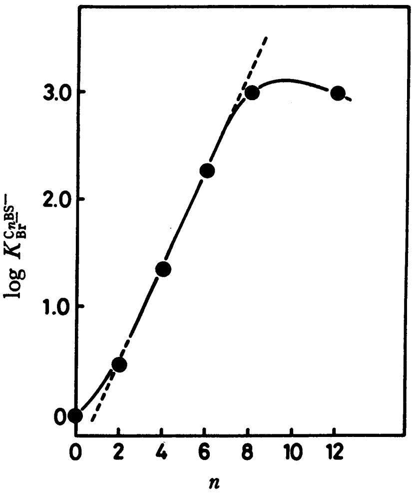

Fig. 2. Variation of selectivity coefficients of BVP resins for a series of alkylbenzenesulfonate ions (C_nBS^-) with a number of alkyl carbon atoms of C_nBS^-. Degree of quaternization of BVP was 89%.

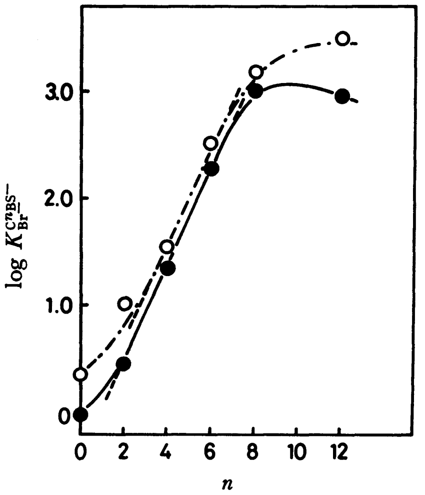

Fig. 3. Variation of selectivity coefficients of BVP resins for a series of alkylbenzenesulfonate ions (C_nBS^-) with a number of alkyl carbon atoms of C_nBS^-. Influence of degree of quaternization.
●: Degree of quaternization, 89%, ○: Degree of quaternization, 32%.

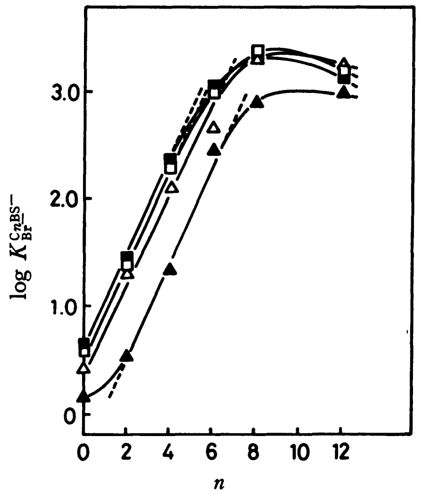

Fig. 4. Variation of selectivity coefficients of C_mVP resins for a series of alkylbenzenesulfonate ions (C_nBS^-) with a number of alkyl carbon atoms of C_nBS^-.
▲: C_4VP, △: C_8VP, □: $C_{12}VP$, ■: $C_{16}VP$.

play an important role in the adsorption. Since steric repulsion between the adsorbed alkylbenzenesulfonate ions was expected to be reduced if the ion exchange sites were separated by enough distances from each other, the influence of degree of quaternization of the resin was examined. Thus, the adsorption tests were carried out with BVP of lower degree of quaternization (32%) and that of higher degree of quaternization (89%). Figure 3 shows the selectivity coefficients obtained for these resins. No significant difference was observed between their selectivities for C_nBS^- of $4<n<8$. In these cases steric repulsion between the adsorbed alkylbenzenesulfonate ions seemed to be insignificant. However, in the case of the adsorption of $C_{12}BS^-$, the selectivity coefficient of BVP of lower degree of quaternization was much higher than that of BVP of higher degree of quaternization. In the latter case, the alkyl chain of $C_{12}BS^-$ was presumably long enough to cause steric repulsion between the adsorbed $C_{12}BS^-$ ions, whereas in the former case such steric repulsion might be reduced by separation of ion exchange sites on the surface of the resin.

Influence of alkyl chain length of alkylbenzenesulfonate ions was also examined in the case of the adsorption on a series of crosslinked poly(*N*-alkyl-4-vinylpyridinium bromide) (C_mVP). In Fig. 4 are shown the plots of log $K_{Br^-}^{C_nBS^-}$ of C_mVP against the number of carbon atoms, *n*, of C_nBS^-. In the cases where $n<8$, log $K_{Br^-}^{C_nBS^-}$ of each C_mVP also increased linearly with *n*, which was ascribed to the hydrophobic interaction between the alkyl chain of C_nBS^- and the resin. Although the degree of quaternization of these C_mVP was not equal, Fig. 3 shows that the linearity of the plot of log $K_{Br^-}^{C_nBS^-}$ *vs*. *n* was not influenced by the degree of the quaternization. The linearity of Fig. 4 gave a value of 2400 J mol^{-1} for $RT\delta(\ln K_{Br^-}^{C_nBS^-})/\delta n$.

Influence of Alkyl Chain Length of Resins. Since hydrophobic interaction between the alkyl chain of the C_nBS^- ion and the resin was suggested to play an important role in the adsorption, the influence of the hydrophobicity of the resin was then examined. Thus the selectivities of a series of crosslinked poly(*N*-alkyl-4-vinylpyridinium bromide) (C_mVP) were plotted against the number of carbon atoms, *m*, of the alkyl chain attached to the resin. As can be seen in Fig. 5, log $K_{Br^-}^{C_nBS^-}$ increased with *m*, which may be attributed to the hydrophobic interaction mentioned above. In the cases where $m>12$, however, saturation of the selectivity coefficients was observed. This may be ascribable to the steric effect as discussed above. It should be noted here that in the case of the adsorption of $C_{12}BS^-$, the selectivity coefficient did not vary appreciably with the value of *m*. Probably the alkyl chain of $C_{12}BS^-$ was long enough to cause significant steric repulsion even in the case of the resins having a short alkyl chain such as C_4VP and C_8VP.

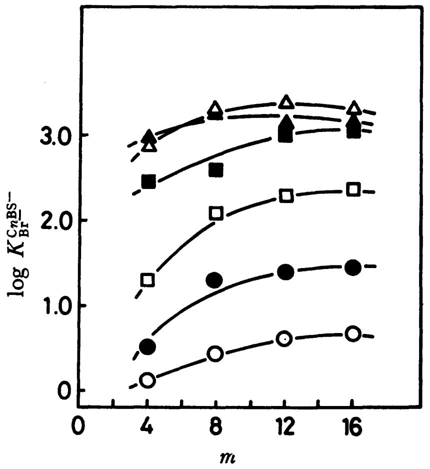

Fig. 5. Variation of selectivity coefficients of C_mVP resins for a series of alkylbenzenesulfonate ions (C_nBS^-) with a number of alkyl carbon atoms of C_mVP.
○: C_0BS^-, ●: C_2BS^-, □: C_4BS^-, ■: C_6BS^-, △: C_8BS^-, ▲: $C_{12}BS^-$.

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