Adsorption of Sodium Alkyl Sulfates on Ion Exchange Resins Derived from 4-Vinylpyridine

In recent years many adsorbents have been investigated for the purpose of use for treatment of wastewaters.[1] Adsorption on ion exchange resins provides a technique for purification of municipal and industrial wastewaters.[2-4] In the preceding paper,[5] the adsorption of fatty acid sodium salts from aqueous solution onto ion exchange resins such as Amberlite IRA94 and IRA68 was studied. The present study describes the adsorption equilibrium of sodium alkyl sulfates with various carbon numbers onto ion exchange resins (PVP and PVPC8) derived from 4-vinylpyridine in aqueous solution to obtain precise information about the treatment of wastewaters containing detergents.

EXPERIMENTAL

Materials

The ion exchange resin (PVP) used in this experiment was 4-vinylpyridine and divinylbenzene copolymer purchased from Kouei Chemicals, Japan. The exchange capacity was 6.0 meq/g of dried resin. PVP was purified by standard methods and used as the HBr salt. PVPC8 was prepared by N-alkylation of PVP with octyl bromide. Thus, octyl bromide (9.18 g) was added dropwise into a suspension of PVP (5 g) in 100 mL of N,N-dimethylformamide. The suspension was kept at 100°C for 24 h under nitrogen atmosphere. After reaction, the resin was filtered out and washed first with ethanol and several times with water. The exchange capacity determined from the bromide ion analysis (Volhard method) was 4.7 meq/g resin. The adsorbates studied were five alkyl sulfonic acid sodium salts (see Table I) from commercial sources (stated minimum assay 98%) and were used without further purification.

ADSORPTION EXPERIMENTS

In a typical adsorption experiment, 0.02–0.1 g of resin was immersed in 10 mL of proper concentration of adsorbates in an aqueous solution. Equilibration took place in 20 mL stoppered tubes, which were shaken 24–48 h in a thermostated bath. After equilibration, the resin was removed, and the amount of bound adsorbates was measured by determining the total organic carbon in a Shimadzu Model TOC-10B analyzer.

RESULTS AND DISCUSSION

Adsorption isotherms of sodium alkyl sulfates (S5–S13) on PVP and PVPC8 at 25°C are shown in Figures 1 and 2. The degree of adsorption is represented as the moles of adsorbates per gram of

TABLE I
Sodium Alkyl Sulfates

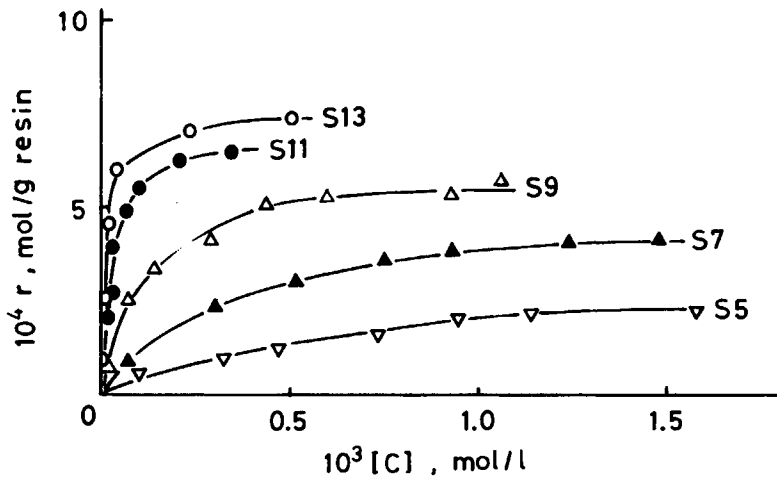| n	$CH_3(CH_2)_nSO_3Na$	Abbreviation
4	1-Pentanesulfonic acid	S5
6	1-Heptanesulfonic acid	S7
8	1-Nonanesulfonic acid	S9
10	1-Undecanesulfonic acid	S11
12	1-Tridecanesulfonic acid	S13

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Fig. 1.   Adsorption isotherms of sodium alkyl sulfates on PVP at 25°C.
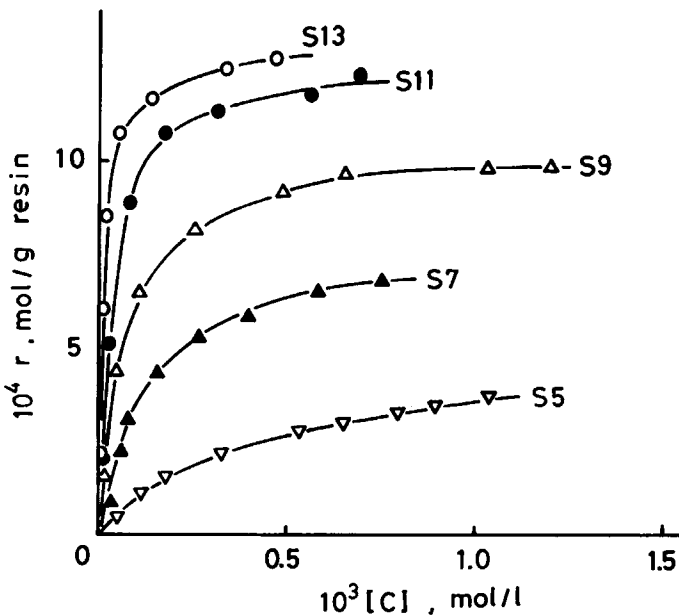

Fig. 2.   Adsorption isotherms of sodium alkyl sulfates on PVPC8 at 25°C.

resin, r vs. the equilibrium concentration of the adsorbates, C (mol/L). As shown in Figures 1 and 2, it is apparent that the amount of the adsorbates adsorbed on both resins increases as the carbon number of the adsorbates increases. Furthermore, PVPC8 shows greater adsorbability than PVP for all the adsorbates used.

The adsorption of sodium alkyl sulfate on these resins depends on the amount of basic sites in the adsorbent because of the ionic bonding between adsorbate anion and protonated basic site. In the present system, therefore, the adsorption isotherms could be approximated by the Langmuir type equation. Klotz et al.[6] have been derived an equation, in which r represents the moles of compounds bound per gram polymer, n is a total number of available binding sites on polymer, K

is the intrinsic binding constant, and C is the concentration of the free small molecule:

$$\frac{1}{r} = \frac{1}{nK}\frac{1}{C} + \frac{1}{n}$$ (1)

The relative values of the successive equilibrium constants can be determined solely by statistical factors. For this situation the equilibrium constants of the ith reaction is given by the relation:

$$k_i = \frac{n - (i - 1)}{i} K$$ (2)

for the first reaction ($i = 1$), the first equilibrium constant, k_1 is equal to nK in eq. (2). If we use nK as the degree of the adsorption, the nK is obtained from plots of $1/r$ vs. $1/C$ or nonlinear least squares fitting. The nK values of sodium alkyl sulfates for both resins are listed in Table II. As shown in Table II, the nK values for each resin increases with increasing carbon number of the adsorbate. Moreover, the nK is found to related to the carbon number (N) of the adsorbate. Figure 3 shows a linear relation of log nK and N. Similar relations have been found in

TABLE II
Values of nK of Sodium Alkyl Sulfates for Each Resin
in Aqueous Solution at 25°C

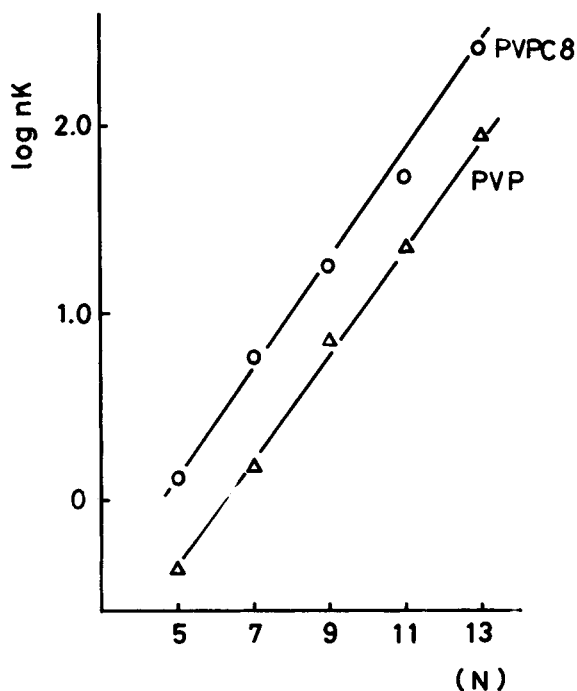| Resin	nK (l/g resin)				
	S5	S7	S9	S11	S13
PVP	0.401	1.50	6.93	23.4	89.3
PVPC8	1.30	5.77	17.7	51.3	260

Fig. 3. Relationship between nK and N at 25°C.

the adsorption of fatty acid sodium salts on activated carbons.[7] These results strongly suggest that the effect of hydrophobic interaction plays an important role in binding. This effect is more favorable for PVPC8, which has hydrophobic octyl groups in the polymer.

Finally, in the adsorption of sodium alkyl sulfates onto the resins, the amount of adsorption markedly increases with increasing alkyl side chains of the salts. Furthermore, the introduction of octyl groups in the resin increases the adsorbability in all cases. Therefore, it is clear that the increasing adsorptions result from the hydrophobic interaction in addition to the ionic adsorption.

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