

Effect of Inorganic Salt on Adsorption of Sodium Alkyl Sulfates and Fatty Acid Sodium Salts from Aqueous Solution onto Ion Exchange Resins

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Synopsis

The adsorption isotherms of sodium salts of alkyl sulfonic acid and fatty acid with various carbon numbers onto ion exchange resins were measured in the absence and in the presence of sodium chloride in aqueous solutions. In the absence of the inorganic salt, the amount of adsorption remarkably increased with an increase in the length of alkyl groups in the adsorbates. Furthermore, the amount of adsorption apparently decreased with addition of sodium chloride into the solutions and almost reached a constant value at high concentrations of NaCl. This behavior strongly suggested that the electrostatic interaction on the adsorption decreased with increasing salt concentration and that the effect of hydrophobic interaction seems to play an important role on adsorption.

INTRODUCTION

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 papers,^{5,6} the adsorption of sodium alkyl sulfates or fatty acid sodium salts from aqueous solution onto ion exchange resins such as Amberlite IRA94 and IRA68, and 4-vinylpyridine was studied. This paper describes the detailed results of adsorption equilibrium of sodium alkyl sulfates and fatty acid sodium salts with various carbon numbers onto ion exchange resins (IRA94 and IRA68) in the presence and in the absence of sodium chloride to obtain precise information about the treatment of wastewaters containing detergents, and also to gain further insight into the adsorption mechanism.

EXPERIMENTAL

Materials

The ion exchange resins used in this experiment were a styrene type copolymer and an acrylamide type copolymer known as Amberlite IRA 94 and IRA 68 (Rohm and Hass Co.). Both are weakly basic resins and the exchange capacities are 4.6 (IRA94) and 5.6 (IRA68) meq/g of dried resins, respectively. The resins were purified by standard methods and used as HBr salts. The adsorbates studied were five sodium alkyl sulfates and four fatty acid sodium salts from commercial sources (stated minimum assay 98%) and were used

TABLE I
Sodium Alkyl Sulfates and Fatty Acid Sodium Salts

<i>n</i>	CH ₃ (CH ₂) _{<i>n</i>} SO ₃ Na	Abbreviation	CH ₃ (CH ₂) _{<i>n</i>} COONa	Abbreviation
4	1-Pentanesulfonic acid	S5	Hexanoic acid	C6
6	1-Heptanesulfonic acid	S7	Octanoic acid	C8
8	1-Nonanesulfonic acid	S9	Decanoic acid	C10
10	1-Undecanesulfonic acid	S11	Dodecanoic acid	C12
12	1-Tridecanesulfonic acid	S13		

without further purification. The structure of these materials were listed in Table I.

Adsorption Procedure

In a typical adsorption experiment, 0.02–0.1 g of resin was immersed in 10 mL of proper concentration of adsorbates in the absence or presence of sodium chloride in an aqueous solution. Equilibration took place in 20-mL stoppered tubes, which were shaken for 24–48 h in a thermostatted 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

The adsorption isotherms of sodium alkyl sulfates (S5–S13) on IRA94 and IRA68 at 25°C in the absence of sodium chloride are shown in Figures 1 and 2, where the degree of adsorption is represented as the moles of adsorbed sodium alkyl sulfates per gram of resin, *r* vs. the equilibrium concentration of the adsorbates, *C* (mol/L). Figures 1 and 2 illustrate that the amount of the adsorbates adsorbed on both resins increases as the carbon number of the adsorbates increases, in the order S13 > S11 > S9 > S7 > S5. IRA94 shows greater adsorbability than IRA68 for all the adsorbates used. The similar results have been observed with adsorption of fatty acid sodium salts on IRA94 and IRA68 as described in previous article.⁵

In the adsorption of sodium alkyl sulfate on these resins the electrostatic interaction between the positively charged amino group in the adsorbent and negatively charged sulfonate group on adsorbates makes predominant role in binding. In the present system, therefore, the adsorption isotherms could be approximated by the Langmuir type equation. Klotz et al.⁷ have derived an equation, eq. (1), 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 free small molecule:

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

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

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

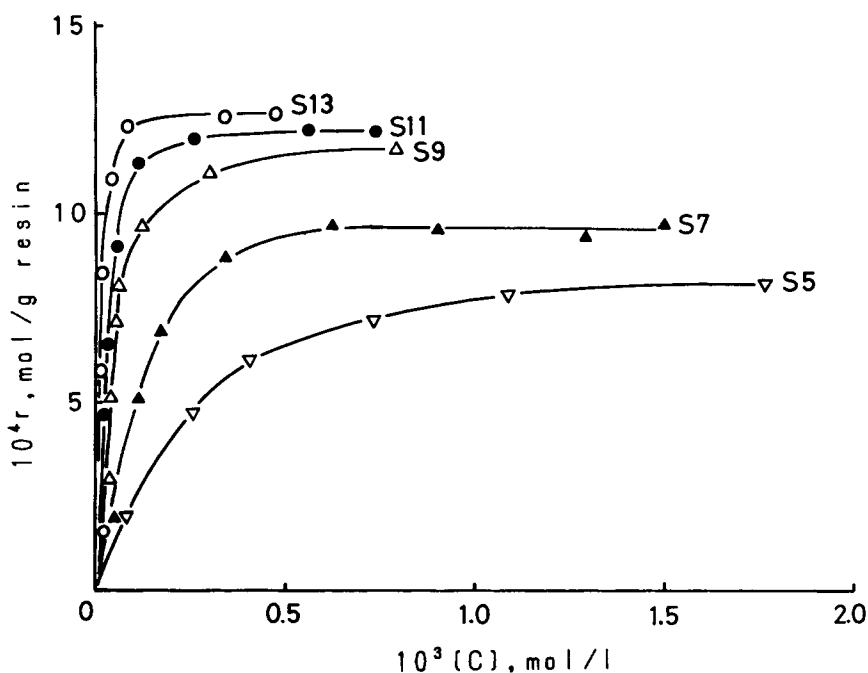


Fig. 1. Adsorption isotherms of sodium alkyl sulfates on IRA94 at 25°C in the absence of sodium chloride.

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 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, together with the previous results of fatty acid sodium salts.⁵ As shown in Table II, the nK values of sodium alkyl sulfates as well as fatty acid sodium salts for each resin increase with increasing carbon number of the adsorbates. IRA94 exhibits

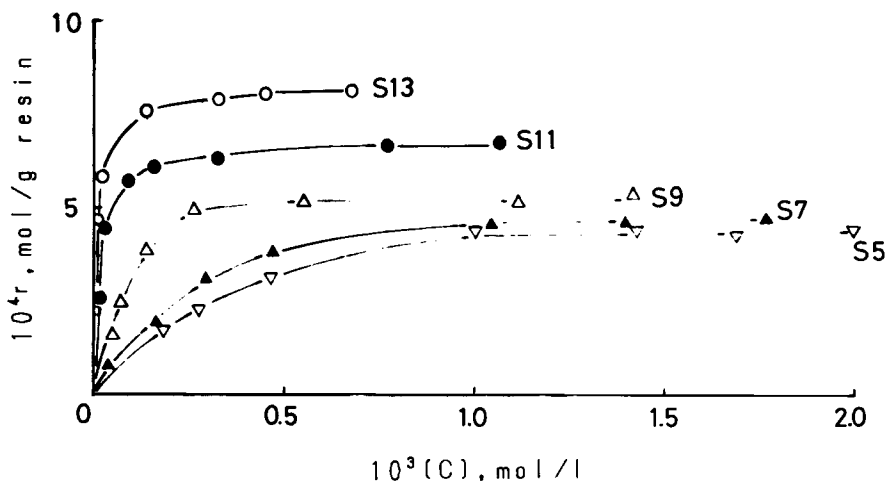


Fig. 2. Adsorption isotherms of sodium alkyl sulfates on IRA68 at 25°C in the absence of sodium chloride.

TABLE II
 Values of nK of the Sodium Alkyl Sulfates and Fatty Acid Sodium Salts
 for Each Resin in Aqueous Solution at 25°C

Adsorbates	nK (l/g resin)	
	IRA94	IRA68
S5	3.45	0.928
S7	15.1	2.26
S9	44.4	4.83
S11	162	9.72
S13	551	21.0
C6	1.37	0.386
C8	8.14	0.806
C10	36.3	3.08
C12	179	7.22

larger adsorption affinities than IRA68 does. Moreover, the nK is found to be related to the carbon number (N) of the adsorbate. Figure 3 shows a linear relation of $\log nK$ and N for both resins. Similar relations have been found in the adsorption of fatty acid sodium salts on activated carbons,⁸ and that of sodium alkyl sulfates on ion exchange resins derived from 4-vinylpyridine.⁶

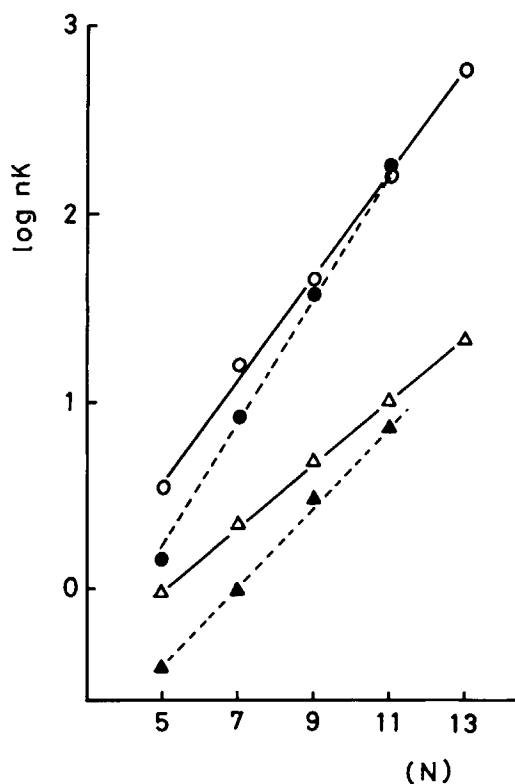


Fig. 3. Relationship between nK and N at 25°C. Adsorption systems: (○) sodium alkyl sulfate-IRA94; (●) fatty acid sodium salt-IRA94; (△) sodium alkyl sulfate-IRA68; (▲) fatty acid sodium salt-IRA68.

These results strongly suggest that the effect of hydrophobic interaction seems to play an important role on adsorption. This effect is more favorable for IRA94 which has hydrophobic phenyl groups in the resin. The $\log nK-N$ profiles also show that there are significant differences in adsorption affinities between sodium alkyl sulfates and fatty acid sodium salts which have a relatively short length of alkyl groups because of their pKa differences between the sulfonate and carboxylate groups. However, no differences are observed between the adsorbates which have long alkyl chains. These results also suggest that the adsorption of long chain adsorbates mostly depends on the hydrophobic interaction rather than the electrostatic interaction in the present systems. Thus, it might be considered that, in the adsorption of adsorbates on the resins, the electrostatic interaction between the positively charged amino group in the resin and negatively charged sulfonate or carboxylate groups on the adsorbate molecule only helps to bring the adsorbate molecule close to resin surface, and that the principal contribution to the affinity of the adsorbates for resins arises from the nonpolar van der Waals' force exerted between the hydrophobic parts of both the adsorbate and resin.

In order to gain further insight into the adsorption mechanism, a study is undertaken in the presence of sodium chloride. Figure 4 shows adsorption isotherms of S5 on IRA94 in various concentrations of NaCl. Calculated nK values are listed in Table III. It is found that the nK decreases with an increase in the salt concentration. Similar results are observed in the other adsorption systems. Thus, the effect of adding salt on adsorption is summarized in Figures 5 and 6, where the extent of adsorption is expressed in terms of a ratio of nK based on the absence of the salt. As can be seen in these figures, the ratios of nK decrease with an increase in the salt concentration and almost reach a constant value above 0.1 mol/L NaCl with all the adsorbates used in this study, although the degree of decreasing ratio depends on the adsorbate-resin systems used. This effect is probably due to the

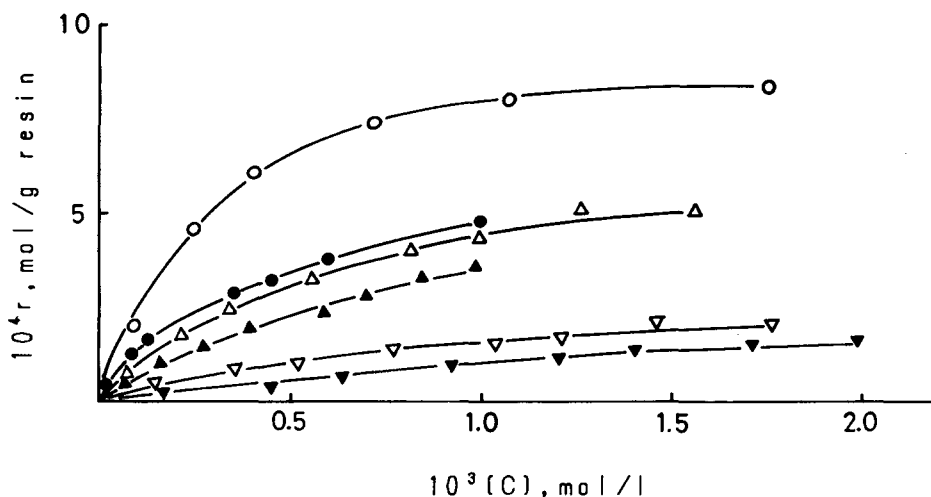


Fig. 4. Adsorption isotherms of S5 on IRA94 at 25°C in the presence of various concentrations of NaCl. Concentrations of NaCl: (○) without NaCl; (●) 0.002 mol/L; (Δ) 0.005 mol/L; (▲) 0.01 mol/L; (▽) 0.05 mol/L; (▼) 0.1 mol/L.

TABLE III
Values of nK for Adsorption of S5 with IRA94 in Various Concentrations
of NaCl at 25°C

Concn. of NaCl (mol/L)	nK (l/g resin)
0	3.45
0.002	1.96
0.005	1.25
0.01	0.636
0.05	0.232
0.1	0.127

shielding of the electric field around the adsorption system on addition of the salt and competition between the adsorbate anion and chloride ion to the positively charged sites on the resin. Therefore, it is likely that the electrostatic force in the adsorption decreases with increasing salt concentration and then disappears at higher concentration or above. However, the adsorption affinities still remain with high concentrations of NaCl. This result clearly indicates that the hydrophobic interactions are involved in the adsorption. Takagishi et al.⁹ have found the same phenomena as described above on the binding of methyl orange and its homologs with polycations containing various apolar groups in the presence of sodium chloride by the equilibrium dialysis method, and they strongly suggested that the hydrophobic interaction in addition to the electrostatic one seems to play an important role in the binding.

Finally, in the present study, it is clear that the adsorption of sodium alkyl sulfates and fatty acid sodium salts onto the resins involves hydrophobic interaction between apolar side groups of the adsorbates and resins, as well as electrostatic attraction of the charged groups between sulfonate or carboxylate groups in the adsorbates and dialkylamino groups in the resins.

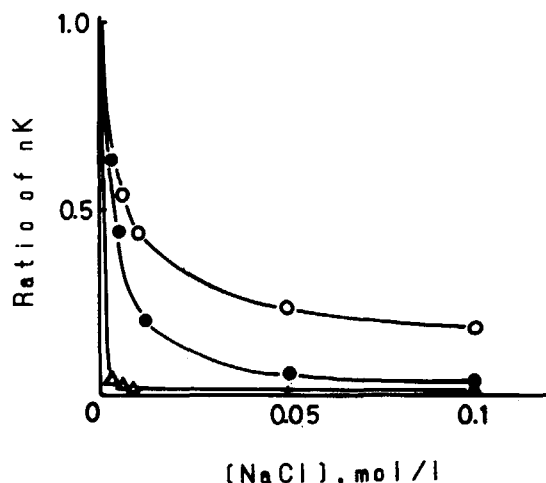


Fig. 5. Effect of sodium chloride concentration on adsorption of S5 and S9 by IRA94 and IRA68 at 25°C: (○) S9-IRA94; (●) S5-IRA94; (Δ) S5-IRA68.

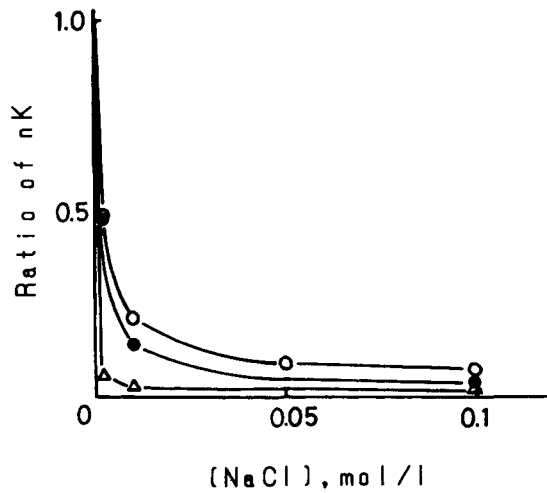


Fig. 6. Effect of sodium chloride concentration on adsorption of C6 and C10 by IRA94 and IRA68 at 25°C: (○) C10-IRA94; (●) C6-IRA94; (△) C6-IRA68.

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