Adsorption of Anionic Surfactants and Related Compounds from Aqueous Solution onto Activated Carbon and Synthetic Adsorbent

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SYNOPSIS

The adsorption isotherms of two anionic surfactants and sodium alkyl sulfonates with various carbon numbers onto activated carbon and synthetic adsorbent were measured in aqueous solutions. The adsorption affinities remarkably increased with an increase in the length of alkyl group in the adsorbates for both adsorbents. Furthermore, the amount of adsorption increases with addition of sodium chloride into the solutions. These behaviors suggested that the effect of hydrophobic interactions seem to play an important role on adsorption of both adsorbents.

INTRODUCTION

In recent years, many adsorbents have been investigated for the purpose of use for treatment of wastewaters.[1] Adsorption on activated carbon provides a technique for purification of municipal and industrial wastewaters.[2-7] In the preceding papers,[8-10] the adsorption of sodium alkyl sulfonates 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 results of adsorption equilibrium of sodium dodecylbenzene sulfonate (NaDBS), sodium dodecyl sulfate (SDS), and sodium alkyl sulfonates with various carbon numbers onto activated carbon (Diahope) and synthetic adsorbent (Amberlite XAD-7) to gain further insight into the adsorption behavior on various adsorbents and also to obtain precise information about the treatment of wastewaters containing detergents.

EXPERIMENTAL

Materials

The activated carbon used in this study was a commercially available type known as Diahope 006 (Mitsubishi Chemical Industries Ltd.). The specific surface area measured by the BET method was 1150 m^2/g. The iodine number was 1070 mg/g. The carbon was ground to 100–300 mesh, purified by standard methods, and used for the equilibrium adsorption experiment. The synthetic adsorbent used was an acrylic ester-type copolymer known as Amberlite XAD-7 (Rohm and Hass Co.). The specific surface area was 350–500 m^2/g. The mean pore diameter was very large (90 Å) compared to that of activated carbon. The adsorbates studied were sodium dodecylbenzene sulfonate (NaDBS), sodium dodecyl sulfate (SDS), and five sodium alkyl sulfonates (S5–S13) from commercial sources (stated minimum assay 98%) and were used without further purification. The structures of sodium alkyl sulfonates are listed in Table I.

Adsorption Procedure

In a typical equilibrium adsorption experiment, 0.02–0.1 g of the adsorbents 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 for 24–48 h in a thermostated bath at 25°C. After equilibration, the adsorbents were removed and the amount of bound adsorbates was measured by determining the total organic carbon in a Shimadzu Model TOC-10B analyzer. In the case of activated carbon, a membrane filter (pore size 1.0 mμ) was used for filtration.

Table I Sodium Alkyl Sulfonates

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

RESULTS AND DISCUSSION

The adsorption isotherms of NaDBS, SDS, and sodium alkyl sulfonates (S5–S13) on Diahope and XAD-7 at 25°C are shown in Figures 1 and 2, where the degree of adsorption is represented as the moles of adsorbed compounds per gram of adsorbent, 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 adsorbents increases as the carbon number of the sodium alkyl sulfonates increases, in the order S13 > S11 > S9 > S7 > S5. NaDBS and SDS show almost the same adsorbability for the carbon number of the adsorbates used. Diahope shows greater adsorbability than does XAD-7 for all the adsorbates used.

In the present experiments, the adsorption isotherms were approximated by the Langmuir-type equation [Eq. (1)], in which r represents the moles of compounds bound per gram adsorbent; C is the
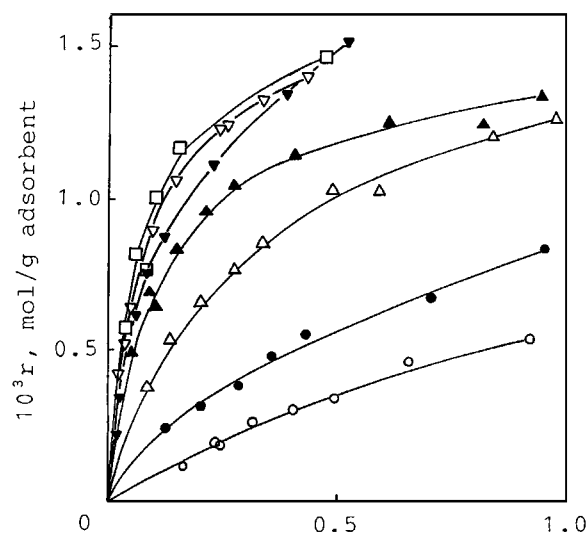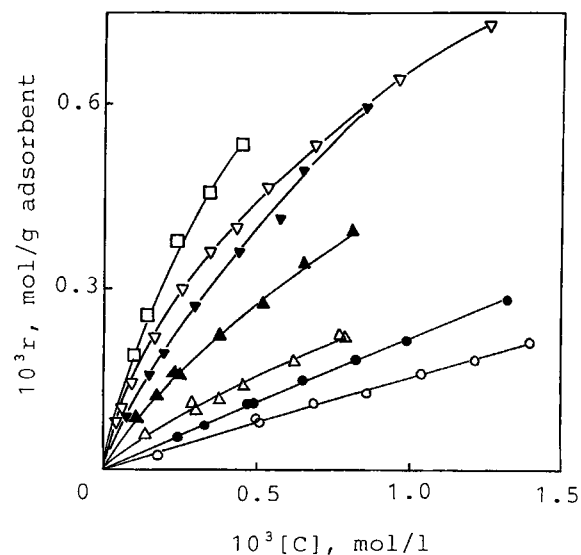

Figure 2 Adsorption isotherms of NaDBS, SDS, and sodium alkyl sulfonates on XAD-7 at 25°C: (∇) NaDBS; ($\blacktriangledown$) SDS; ($\bigcirc$) S5; ($\bullet$) S7; ($\triangle$) S9; ($\blacktriangle$) S11; ($\square$) S13.

concentration of free adsorbates; α and a are constants:

$$1/r = 1/\alpha[C] + 1/a \qquad (1)$$

or

$$[C]/r = 1/\alpha + [C]/a \qquad (2)$$

for the infinite dilution ($C = 0$), the equilibrium constant α, is equal to r/C in Eq. (2). If we use α as the degree of the adsorption, α is obtained from plots of $1/r$ vs. $1/C$ or nonlinear least squares fitting. The α values of NaDBS, SDS, and sodium alkyl

Table II Values of α of NaDBS, SDS, and Sodium Alkyl Sulfonates for Diahope and XAD-7 in Aqueous Solution at 25°C

	α (L/g adsorbent)	
Adsorbates	Diahope	XAD-7
NaDBS	21.9	1.66
SDS	13.4	0.982
S5	0.966	0.150
S7	2.01	0.236
S9	5.53	0.457
S11	12.6	0.745
S13	24.4	1.82

Figure 1 Adsorption isotherms of NaDBS, SDS, and sodium alkyl sulfonates on Diahope at 25°C: (∇) NaDBS; ($\blacktriangledown$) SDS; ($\bigcirc$) S5; ($\bullet$) S7; ($\triangle$) S9; ($\blacktriangle$) S11; ($\square$) S13.
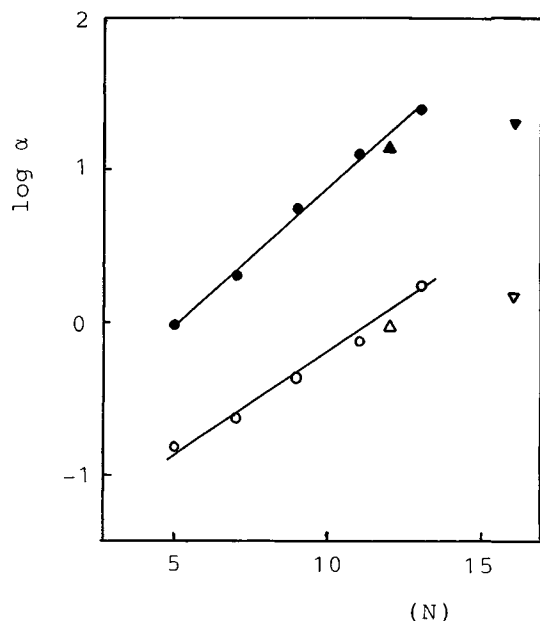
Figure 3 Relationship between log α and N at 25°C. Adsorption systems on Diahope: (●) sodium alkyl sulfonates; (▼) NaDBS; (▲) SDS, on XAD-7, (○); sodium alkyl sulfonates: (▽) NaDBS; (△) SDS.

sulfonates for both adsorbents are listed in Table II. As shown in Table II, the α values of sodium alkyl sulfonates for each adsorbent increase with an
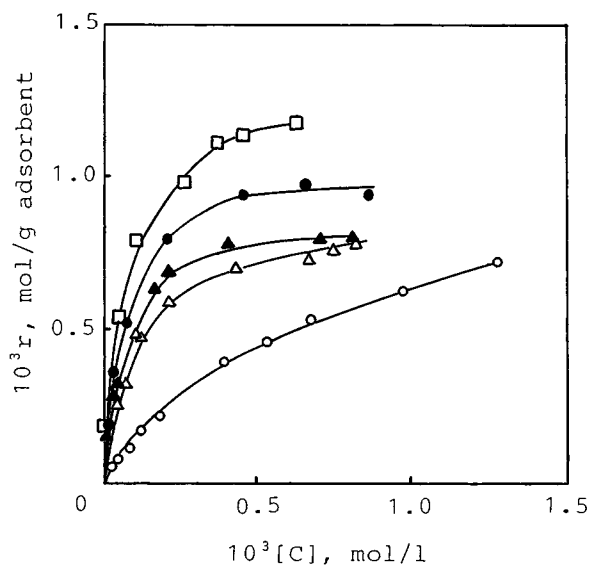

Figure 4 Adsorption isotherms of NaDBS on XAD-7 at 25°C in the presence of various concentrations of NaCl. Concentrations of NaCl: (○) without NaCl; (△) 0.05 mol/ L; (▲) 0.1 mol/L; (●) 0.2 mol/L; (□) 0.3 mol/L.

Table III Values of α for Adsorption of NaDBS with Diahope and XAD-7 in Various Concentration of NaCl at 25°C

Conc of NaCl (mol/L)	α (L/g adsorbent)	
	Diahope	XAD-7
0	21.9	1.66
0.05	89.8	9.35
0.1	98.1	15.9
0.2	138	18.2
0.3	153	18.6

increasing carbon number of the adsorbates. Diahope exhibits larger adsorption affinities than does XAD-7. Moreover, α is found to be related to the carbon number (N) of sodium alkyl sulfonates. Figure 3 shows a linear relation of log α and N for both adsorbents. SDS shows almost the same relation as obtained from its carbon number, but NaDBS is not related because of its different structure. Similar relations have been found in the adsorption of fatty acid sodium salts on activated carbons.[7] These results suggest that the effect of hydrophobic interaction seems to play an important role on adsorption. Thus, the principal contribution to the affinity of the adsorbates for both adsorbents arises from the nonpolar van der Waals force exerted between the hydrophobic parts of the adsorbate and the adsorbent surface. The above results show that the adsorption mechanism of XAD-7 is not different from that of activated carbon, although the pore size of both adsorbents are different.

To gain further insight into the adsorption behavior, a study is undertaken in the presence of sodium chloride. Figure 4 shows adsorption isotherms of NaDBS on XAD-7 in various concentrations of NaCl. Calculated α values for the adsorption of NaDBS on both adsorbents are listed in Table III. It is found that α increases with an increase in the salt concentration for both adsorbents. This effect is due to the shielding of the electric field around the adsorbates on addition of the salt, resulting in an increased surfactant adsorption.

Finally, in the present study, it was found that the adsorption affinities remarkably increased with an increase in the length of alkyl group in the adsorbates for both adsorbents. Furthermore, the amount of adsorption increased with addition of sodium chloride into the solutions. These behaviors suggested that the effect of hydrophobic interactions between apolar side groups of the adsorbates and

adsorbent surface seems to play an important role on adsorption.

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