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Sorption of sodium dodecylsulfate and cetyltrimethylammonium bromide on polyurethane foams

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The appearance of sorption isotherms and a maximum sorption value for sodium dodecylsulfate and cetyltrimethylammonium bromide on polyurethane foams depend upon the nature of electrolyte and the type of sorbent.

Polyurethane foams (PUF) are porous sorbents whose hydrophobic polymeric matrix possesses various polar functional groups (polyether, polyester, urethane, urea, isocyan, *etc*.). Due to such a combination of properties these sorbents are successfully used for effective sorption of both nonpolar and polar molecules.[1]

Ionogenic surfactants may serve as apt objects for investigating the sorption properties of PUF. In solution ionogenic surfactants may exist either in the ionic state or form micelles because of the diphilic structure of their molecules. In addition, separation of ionogenic surfactants is an important task as they are wide spread water pollutants.[2]

In spite of the fact that the sorption of sodium dodecylsulfate on PUF is mentioned in the literature,[3] physico-chemical sorption processes have not been fully studied. The aim of the present paper is to investigate the sorption of anionic surfactants by sodium dodecylsulfate (SDS) and cationic surfactants by cetyltrimethylammonium bromide (CTMA).

The sorption was conducted in a static system described earlier.[4] Polyurethane foams were used as pellets (10 mm high, 16 mm in diameter, weight varied from 0.03 to 0.05 g of polymer grade). The equilibrium concentrations of surfactants were determined *via* the sorption–photometric method worked out in our laboratory: CTMA by Bromophenol Blue, SDS by tris(1,10-phenanthroline)iron(II) chloride or using ion-selective electrodes.[5] Equilibrium was established in less than 60 min.

The sorption of SDS and CTMA on polyether-based PUF (140, 5–30 and M-40), on polyester-based PUF (2200) and their copolymer (VP) was studied. (In brackets are shown trade marks).

Table 1 shows partition coefficients (cm^3 g^{-1}) for ionogenic surfactants and pyrene calculated at pH ~ 5 and surfactant concentrations below critical micelle concentration (cmc). The sorption of ionogenic surfactants by ether-based PUF depends on the structure of the polymer unit: PUF 140 based on ethylene oxide is more efficient than PUF M-40 based on propylene oxide; PUF 5-30 containing both ethylene oxide and propylene oxide is intermediate as regards its sorption ability. Polyester-based PUF (2200) and copolymer of polyether- and polyester-based PUF (VP) sorb the more hydrophobic cation of cetyltrimethylammonium better than the less hydrophobic anion of dodecylsulfate. This difference, depending on the PUF type, makes it possible to assume that ionogenic surfactants sorb both *via* hydrophobic interactions and *via* specific ones. Moreover, the polyurethane foams studied do not differ in hydrophobity, as our investigations into evaluating sorbent surface hydrophobity carried out by standard methods[6] with pyrene as a test substance show. Partition coefficients of pyrene on all sorbents are approximately equal (see Table 1).

It is known that polyether fragments such as crown- and noncyclic polyethers are able to bind cations of alkali, alkaline earth and some transition metals, ammonium and hydroxonium ions[7] with formation of positively-charged units of the polymer matrix and hence with an increase in the sorption of negatively charged solutes. In fact, partition coefficients for SDS ($C_{\mathrm{SDS}} = 6\times10^{-5}$ M, pH ~ 5) increase from 370 (in the

Table 1 Partition coefficient (lg *D*) for sorption of cetyltrimetylammonium bromide **1**, sodium dodecylsulfate **2** and pyrene **3** on different types of polyurethane foam.

Polyurethane foam	**1**	**2**	**3**
140	3.40	2.57	4.02
5–30	3.00	2.32	4.06
M-40	2.56	1.85	3.99
2200	2.85	1.70	4.03
VP	2.90	1.70	4.12

[a] Solution volume 25 ml; sorbent 0.03–0.04 g; pH ~ 5, ion strength ~ 0; $C_{\mathrm{surfactants}} = 6\times10^{-5}$ M; $C_{\mathrm{pyrene}} = 1\times10^{-6}$ M.

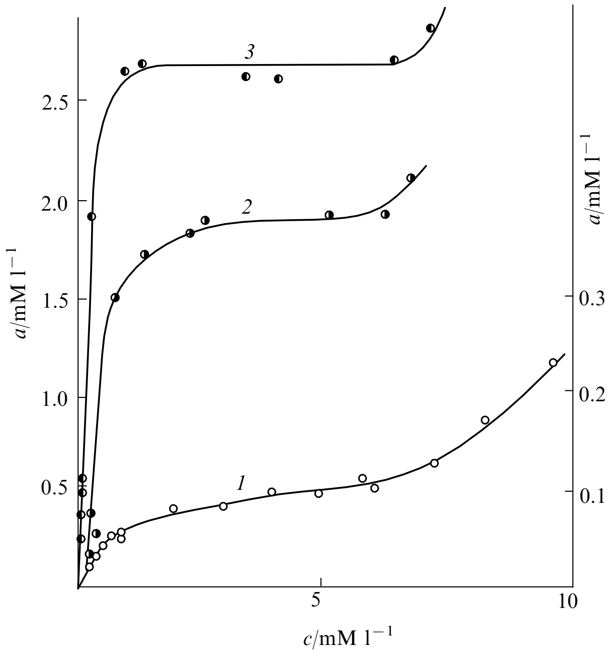

Figure 1 Sorption isotherms of sodium dodecylsulfate on polyurethane 5–30 solution volume 25 ml; sorbent 0.03–0.04 g; pH ~5, ion strength ~0 (*1*); in the presence of 0.4 M Na_2CO_3 (*2*) and 0.4 M H_2SO_4 (*3*).

absence of nitrates of metals) to 1050, 1380, 2950 and 2140 cm^3 g^{-1} in the presence of 0.1 M nitrates of Li, Na, K and NH_4^+, respectively on PUF 140 and from 210 to 680, 790, 1240, 720 cm^3 g^{-1} on PUF 5–30. Comparing partition coefficients one can see that PUF display increased selectivity in sorbing SDS from KNO_3 solution and the sequence of changes in partition coefficients is the same as for anion complexes of metals described in ref. 7.

From our point of view, specific interactions between surfactant cations and ethylene oxide polymer units are also possible for CTMA and are similar to interactions between cationic surfactants and crown ethers.[8] In this case CTMA cation sorbed on PUF becomes a surface ion, unlike SDS anion which is present as a counter-ion in the double electric layer.

One of the main factors influencing ionogenic surfactant sorption is surface charge, the value and sign of which are governed by the electrolyte ions present in solution. When PUF interact with salts of alkali metals or mineral acid solutions sorbent modification takes place owing to both the binding of alkali metal ions and hydroxonium ions with polyether fragments and to a proton joining to urethane groups.[4] In fact, PUF are ion exchangers with positive charges localized on the surface. In this paper the sorption of SDS from 0.4 M solutions of Na_2CO_3 and H_2SO_4 on PUF 5–30 was studied (Figure 1). The greater sorption of SDS from 0.4 M solutions of H_2SO_4 beings about more effective binding hydroxonium ions under these concentration conditions. The sorption isotherms of SDS are of Langmuir type. The calculated values of the maximum sorption a_m, mol g^{-1} and the sorption constant K are given below:

Medium	pH 5, $\mu = 0$	0.4 M Na_2CO_3	0.4 M H_2SO_4
a_m, mol g^{-1}	1.0×10^{-4}	1.8×10^{-3}	2.7×10^{-3}
lg K	6.12±0.11	6.36±0.09	6.71±0.07

Comparing the data obtained one can see that increasing the positive charge on the PUF surface leads to an increase in the sorption equilibrium constant and, in the maximum sorption value, the equilibrium SDS concentration in solution not reaching the value of the CMC.

Other trends are observed on the isotherms for sorption of cationic surfactants. As shown in Figure 2 the sorption of CTMA on PUF 5–30, M-40 and 2200 (curves 1, 4, 5) from neutral solution (pH ~5–6) increases sharply after reacting a plateau. As a rule, this kind of sorption is connected with the formation of surfactant associates on the solid surface.[9] It is important to stress that such a sharp increase in CTMA sorption is observed on reaching a certain surfactant equilibrium concentration not exceeding the CMC for each particular system. The increase in the positive charge on the PUF surface in sorbing CTMA from 0.4 M Na_2CO_3 and 0.4 M H_2SO_4 (Figure 2, curves 2, 3) does not decrease the maximum sorption value for surfactant cation as compared with sorption from aqueous solution. This fact confirms once again the supposition concerning the specific interaction between CTMA cation and PUF surface.

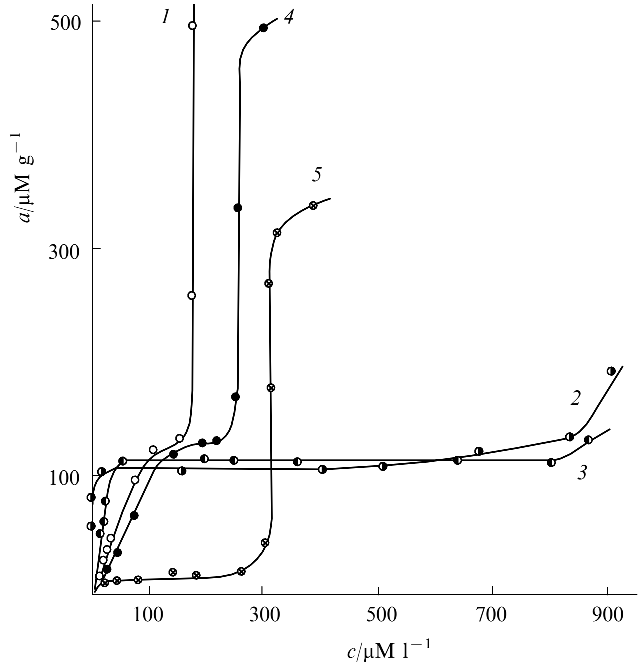

Figure 2 Sorption isotherms of cetyltrimetylammonium bromide on polyurethane 5–30 (*1*)–(*3*), 2200 (*4*), M-40 (*5*) solution volume 25 ml; sorbent 0.03–0.04 g; pH ~5, ion strength ~0 (*1, 4, 5*); in the presence of 0.4 M Na_2CO_3 (*2*) and 0.4 M H_2SO_4 (*3*).

Unlike the case of an aqueous solution, the instant when the isotherms corresponding to sorption from the solution of electrolytes reach the plateau is shifted to lower equilibrium CTMA concentrations, while the instant corresponding to the beginning of the formation of polymolecular layers is shiffed to higher CTMA concentrations. Evidently this is connected with the fact that in the presence of strong electrolytes both the charge on the sorbent surface and the state of ionogenic surfactants in solution change. In particular CMC is decreased; the latter fact is mentioned in ref. 10.

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[‡] $KHSO_5$ was prepared by neutralization of Caro's acid or the Oxone reagent ($2KHSO_5 + KHSO_4 + K_2SO_4$) was used as its source.

[§] Mp (from 1,2-dichloroethane): **1a**, 107 °C; **2a**, 108 °C; **3a**, 84 °C; **4a**, 153 °C; **5a**, oil; **6a** was not isolated in the pure state; **7a**, 105 °C.