The influence of polarization of the sorbent on sorption of albumin by carbon fibers

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The sorption of bovine serum albumin (BSA) on non-charged and polarized surfaces of carbon fibers (ACF) and carbon fibers modified with titanium hydroxide (ACF-Ti) was studied. It was shown that cathodic polarization considerably influences the reversibility of the BSA sorption and decreases the BSA sorption by ACF and ACF-Ti to a larger extent than anodic polarization. A change in the surface charge mainly influences sorption of albumin by ACF-Ti, which is due to different surface properties of the initial and titanium-containing adsorbents.

Key words: adsorption, electrosorption, polarization, surface charge, carbon fibers, protein, titanium hydroxide, modified sorbents.

Electrochemical polarization of carbon sorbents, possessing highly extensive surface areas, good electrical conductivities, and relatively high adsorption capacities,[1] provides the possibility of affecting the equilibria in adsorbent—adsorbate systems in a specified way. Modification of the surface of carbon materials by, for instance, titanium hydroxide, which forms strong coatings and is stable over a broad pH range, makes it possible to change the electrochemical properties of polarizable adsorbents over wide limits. Electrochemical polarization of a sorbent at an appropriately chosen potential can be used to control the adsorption properties, to desorb various organic compounds, and to restore the adsorption capacity of the adsorbent.[1] However, sorption of proteins on an electrochemically polarized carbon surface, in particular, on the surface of activated fibers, has scarcely been studied, although the use of surface polarization (electrosorption) for protein—surface systems could substantially extend the potential of methods for protein separation based on sorption phenomena.

Adsorption in the system comprising a model protein (bovine serum albumin (BSA)) and activated fibers has been studied previously.[2]

The purpose of the present work is to study the influence of electrochemical polarization on the sorption properties of this system.

Experimental

Activated carbon fibers (ACF) Actylen of the braid type were used as sorbents. In addition to the initial ACF, fibers coated[3] with titanium hydroxide (ACF-Ti) were used.

The specific surface area of the adsorbents found by the BET method using adsorption of nitrogen, the micropore volume, and the effective pore radius for the adsorbents studied were 1000 $m^2 g^{-1}$; 0.4 $cm^3 g^{-1}$; and 4 Å, respectively. The BSA preparation was produced at the NIIEV research institute (Minsk). The content of BSA in solutions was determined by the Lowry method.[4] Adsorption of BSA was studied under static conditions in a standard three-electrode cell. All measurements were carried out in the universal sodium phosphate—acetate—borate buffer solution. The reversibility of the adsorption on a noncharged surface was studied using BSA labeled with the ^{125}I isotope. For this purpose, the sorbent containing ^{125}I-BSA, preadsorbed under the conditions studied, was placed in a solution of native BSA and the decrease in the γ-activity of the sorbent was determined. The degree of reversibility S was found from the equation

$$S = N_s A_0/(N_1 A_e 100),$$

where N_s is the number of moles of ^{125}I-BSA adsorbed on the material; N_1 is the number of moles of native BSA brought in the contact with the sorbent; A_0 and A_e are the activities of the sample before and after the exchange, respectively.

The potentials at which the protein adsorption was measured were chosen in the range in which no electrochemical transformations of the protein adsorbed by the electrode surface occur. Therefore, voltammetric measurements in the protein—activated carbon surface were preliminarily carried out.

Results and Discussion

Adsorption of proteins is known[4] to depend on the pH of the solution, which causes generation or change in the charges of the protein molecules and the sorbent surface. Figure 1 shows the dependences of the adsorption of BSA at a constant initial concentration in the solution (1 mg mL^{-1}) on the pH of the solution for the sorbents studied. The maximum adsorption of albumin coincides with its isoelectric point (pI 4.7). To explain this finding, a hypothesis has been stated[5] according to

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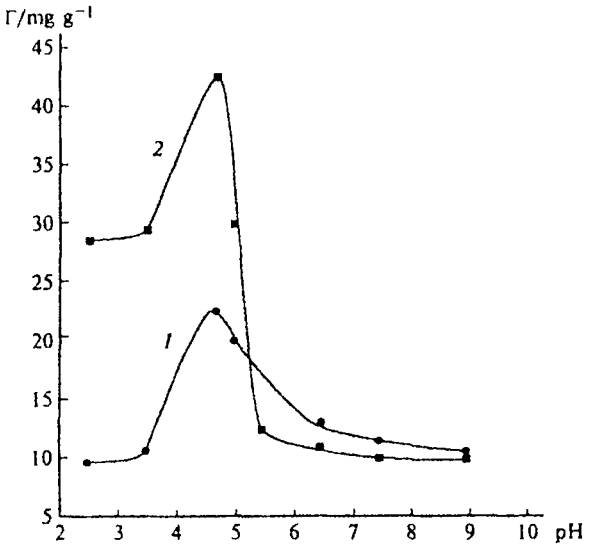

Fig. 1. Dependence of the adsorption of BSA on the pH of the solution: (*1*) ACF; (*2*) ACF-Ti.

which the enhancement of the adsorption at pH = pI is due to the rigid structure of the protein molecule at this pH. Therefore, the molecule occupies the minimum area on the surface, because its conformation is least prone to flattening out under the action of surface forces.

Examination of the plots shown in Fig. 1 indicates that the nature of the adsorbent surface has an appreciable influence on the adsorbability of BSA. Thus the amount of BSA adsorbed (for identical initial concentrations of BSA) on ACF-Ti is much larger than that in the case of the nonmodified fiber. This is apparently due to the fact that the number of adsorption sites on the surface coated with titanium hydroxide is much greater.

Displacement of the pH from the isoelectric point to the acidic or alkaline region sharply decreases the amount adsorbed. The amount of albumin adsorbed on ACF-Ti at low pH values is 3 times larger than that in the alkaline pH region, whereas for the initial fiber, these values are roughly the same. This is apparently due to the fact that the mechanisms of interaction of protein molecules with the surfaces of the initial and titanium-hydroxide-modified fibers are different. The possibility of coordination of electron-donating groups of proteins in acidic solutions to titanium hydroxide has been shown previously.[6] Evidently, this accounts for the fact that at low pH values, the carbon surface modified by titanium hydroxide contains more sites for the adsorption of BSA molecules than the initial ACF surface.[7]

Figures 2 and 3 illustrate the dependences of the adsorption of BSA on its equilibrium concentration in the solution at pH 2.5 for noncharged and polarized fiber surfaces. Almost all isotherms measured in the 250—300 mg L^{-1} concentration range contain an inflection, which is usually explained in the literature by rearrangement and closer packing of molecules on the

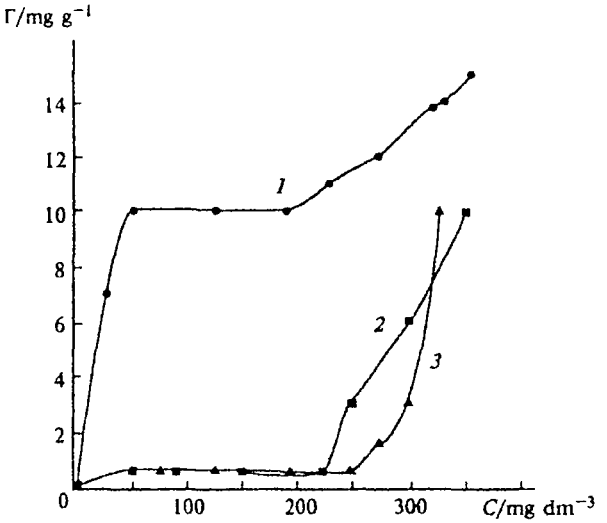

Fig. 2. Isotherms of sorption of BSA on ACF at various surface polarizations: ΔE = 0 (*1*); −200 (*2*); 200 (*3*) mV.

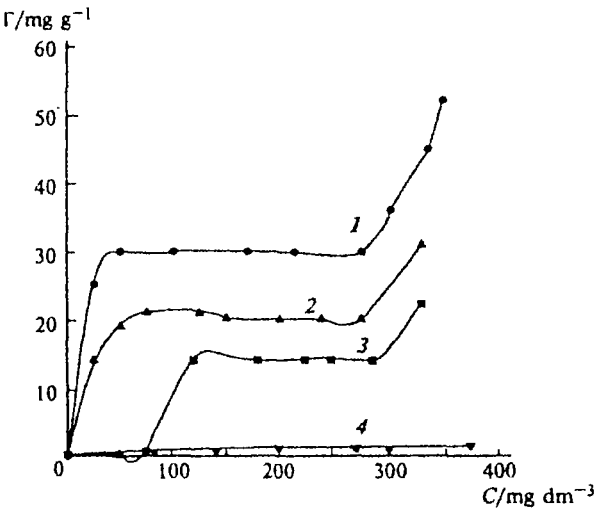

Fig. 3. Isotherms of sorption of BSA on ACF-Ti at various surface polarizations: ΔE = 0 (*1*); −200 (*2*); 200 (*3*); −300 (*4*) mV.

solid surface.[8] This change in the amount adsorbed might also be due to multilayer adsorption at which protein molecules interact with a layer of molecules already attached to the solid surface.

Comparison of the isotherms obtained for the adsorption of BSA on carbon fibers with the data on the adsorption of albumin on active carbons available from the literature[1,8,9] indicates that the fiber surface can adsorb much more protein. This can be due to the difference between the structures of fibrous and granulated materials. The labile fibrous structure of carbon fibers, unlike the structure of active carbons, facilitates the adsorption of protein macromolecules.

Polarization of carbon fibers results in a decrease in the BSA amount adsorbed. In fact, upon cathodic polar-

Table 1. Degree of reversibility of the adsorption of BSA (α) on the initial (ACF) and titanium-containing (ACF-Ti) fibers at various pH values

Adsorbent	ΔE/mV	α (%)		
		pH 2.5	pH 4.7	pH 6
ACF	0	3.6	1.5	1.3
	−200	91.4	23.7	33.6
	−300	—	97.7	100
ACF-Ti	0	46.7	7.4	13.8
	−200	100	38.9	95.8

ization, OH^- ions appear on the negatively charged surface of the sorbent and the pH value in the near-electrode region increases.[10] Apparently, this process occurs in a thin near-electrode layer, because the pH of the bulk of the solution (buffer) remains virtually constant. The BSA molecules in the near-electrode layer acquire a negative charge due to the acid-base equilibrium of the ionogenic groups of the proteins. In the case of anodic polarization, protons appear on the positively charged surface, and the protein molecules at low pH become positively charged. In the case of the initial ACF, the cathodic and anodic polarizations cause virtually identical decrease in the amount of albumin adsorbed, whereas in the case of titanium-containing fiber, the increase in the negative charge of the surface diminishes adsorption more appreciably. These regularities agree with the results presented in Fig. 1, which displays the substantial decrease in the amount of BSA adsorbed on ACF-Ti upon an increase in the pH of the solution and much less pronounced dependence of the adsorption on the pH in the acid region compared to that for the initial sample.

The results of the study of the reversibility of the adsorption of BSA on nonpolarized and cathode-polarized carbon fiber surfaces are presented in Table 1.

It can be seen that irrespective of the acidity of the medium, the ACF-Ti surface adsorbs reversibly a larger amount of the protein. This may be due to the difference between the natures of the surfaces of ACF and ACF-Ti. Cathodic polarization has a substantial effect on the reversibility of the protein adsorption and in all cases (irrespective of the pH of the medium and the type of the adsorbent), it results in more reversible adsorption.

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