Effect of acidity of the medium and polarization of the surface on albumin adsorption by carbon fibers

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Adsorption of bovine serum albumin (BSA) was studied at different acidities of the medium on the non-charged and titanium hydroxide-modified surfaces of the carbon fibers (ACF and ACF-B (Ti)). The fiber covered with titanium hydroxide was shown to have the highest adsorption capacity at pH = 4.7, which is close to the isoelectric point of BSA. The cathodic polarization has the greatest effect on the BSA desorption ability, which enabled the determination of conditions for recovering the adsorption capacity of the fibrous sorbent.

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

Electrochemical polarization of carbon materials with the developed surface, high electroconductivity, and relatively high adsorption capacity provides the means of controlling the equilibrium in the adsorbent—adsorbate system. Depending on the chosen potential, electrochemical polarization can affect the adsorption power of the material, accomplish desorption of various organic substances, and restore the adsorption capacity of adsorbents. The possibility of separation and concentration of proteins using polarized carbon materials is of great interest. Carbon materials modified by titanium and zirconium hydroxides can be promising for these purposes. Such coatings are biologically inert and stable in a wide pH range, which allows the broad variation of the electrochemical properties of the surface. Unfortunately, protein sorption on the electrochemically polarized carbon surface was insufficiently studied to the recent time despite its practical significance.

The purpose of this work was to study the influence of the pH of the solution and electrochemical polarization on the sorption of the model protein, *viz.*, bovine serum albumin (BSA), on the initial carbon fiber and the fiber modified by titanium hydroxide.

Experimental

Active carbon fibers (ACF) (Aktilen, multiple type) were used as adsorbents. The ACF covered with titanium hydroxide,[1] *viz.*, ACF-B (Ti), was used in addition to the initial fiber.

The specific surface, microporous volume, and effective pore radius of adsorbent samples were 1000 $m^2 g^{-1}$, 0.4 $cm^3 g^{-1}$, and 4 Å, respectively. The BSA samples (NIIEV, Minsk, Belarus) were used. The content of BSA in a solution was determined using the Lowry method.[2] Adsorption of BSA from a universal buffer solution (sodium phosphate—acetate—borate) was studied under static and dynamic conditions. All experiments were carried out at 20 °C.

Potentials, at which the protein adsorption values were measured, were chosen in the region where electrochemical transformations of BSA adsorbed by the electrode surface cannot occur. For this purpose, preliminary voltammetric measurements were performed in the protein—ACF system. It was also established that BSA adsorption was completely reversible (99.8%) already at a potential of −200 mV.

Procedures for ACF and ACF-B (Ti) potentiometric titration and experimental data processing were described in the previously published work.[3] Potentiometric titration curves were processed using the density functions method based on the assumption that the object of the study can contain an unlimited number of functional groups with similar ionization constants. Thus, the results of calculations represent the spectrum of pK (ρ function) for all surface functional groups.

To obtain elution curves for adsorption and desorption, the fiber was saturated with protein under dynamic conditions by pumping a solution containing the initial BSA (0.1 g L^{-1}) with a velocity of 1.2 cm min^{-1}. After the sorbent was saturated and the BSA concentration in a solution at the outlet of the column was equal to the concentration in the initial solution ($C = C_0$), the pumping of an adsorbate solution was terminated and the fiber surface polarized to $E = -0.300$ V. The cathodic Faraday process generated the OH^- ions and, hence, ionized the protein molecule, whose anions were desorbed upon repulsion from the cathode surface.

Results and Discussion

As known from the literature,[2] the pH variation results in the appearance or an alternation in the protein

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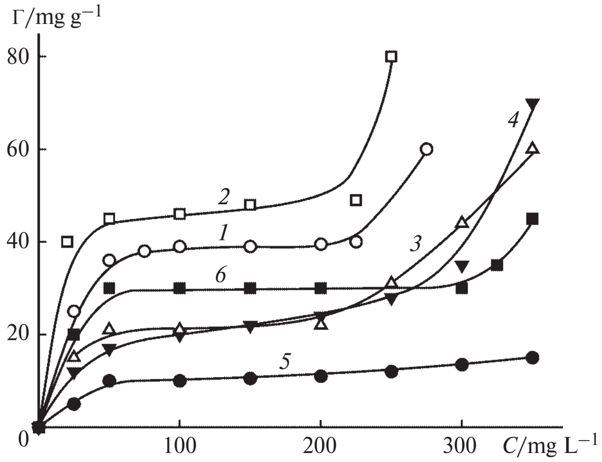

Fig. 1. Isotherms of BSA adsorption without polarization at pH = 4.7 (*1*, *2*), 6 (*3*, *4*), and 2.5 (*5*, *6*) for ACF (*1*, *3*, *5*) and ACF-B (Ti) (*2*, *4*, *6*).

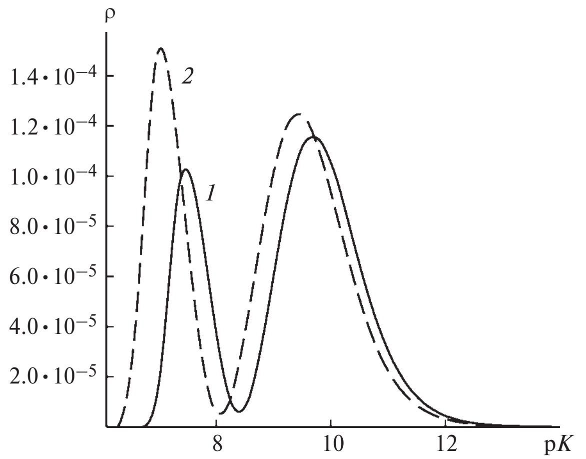

Fig. 2. Spectra of the ionization constants of the surface functional groups for ACF (*1*) and ACF-B (Ti) (*2*); ρ is the distribution function of ionization constants of surface groups (analytical concentrations of the group with p*K* in the interval from p*K* to (p*K* + dp*K*)).

charge and in changes in the adsorbent surface. The variation of the pH of the medium changes the degree of dissociation of functional groups of the solid surface**4** and protein molecules**5** resulting in the appearance of additional electrostatic interactions, which affect the adsorption. The adsorption isotherms of BSA on the non-polarized fiber surface at different pH values of a solution are presented in Fig. 1. The comparison of these curves shows that the highest sorption ability of BSA is achieved at pH 4.7, which corresponds to the isoelectric point of the protein (pH = pI). At this pH the protein molecule is most "compactly" **5** arranged on the sorbent surface. The adsorption of BSA on ACF-B (Ti) is higher than that on the non-modified fiber. This is probably related to a much greater number of adsorption sites on the surface covered with titanium hydroxide. The calculation by the density functions method**3** showed that the modification increases the number of surface functional groups on the surface of the fiber. Since the fiber surface is characterized by a pronounced chemical and energetic heterogeneity, *i.e.*, it contains many functional groups with close but still different ionization constants, the concept of discrete constants for surface groups becomes meaningless. The real pattern of the acid-base properties of the surface can be reflected only by the p*K* spectrum representing the group distribution over the p*K* scale. Two peaks corresponding to two types of the surface functional groups can be seen in each p*K* spectrum (Fig. 2). The surface areas of the peaks correspond to the concentrations of groups of each type. The comparison of the p*K* spectra for the initial and modified fibers shows that the modification increases the concentration of functional groups with a lower p*K*.

The isotherms of BSA adsorption from a solution with pH 4.7 on the non-charged and polarized fiber surfaces (Fig. 3) show that an increase in the surface charge decreases the sorption of BSA on the fibrous materials. It is known**6** that the Faraday processes occurred on the carbon electrode surface change the pH of a solution. This, in turn, ionizes the organic component, whose ionic form (unlike the molecular form) is absorbed to a lower extent by the carbon surface.**7** This process likely occurs in a thin near-electrode layer because the pH of a bulk solution (buffer) remains almost unchanged. For the modified carbon material, the decrease in the sorption of BSA is higher than that for the non-modified adsorbent. The lowest adsorption is observed during the cathodic polarization of ACF-B (Ti). This is due to the fact that an increase in the negative charge of the surface favors the generation of OH^- ions, ionization of BSA,

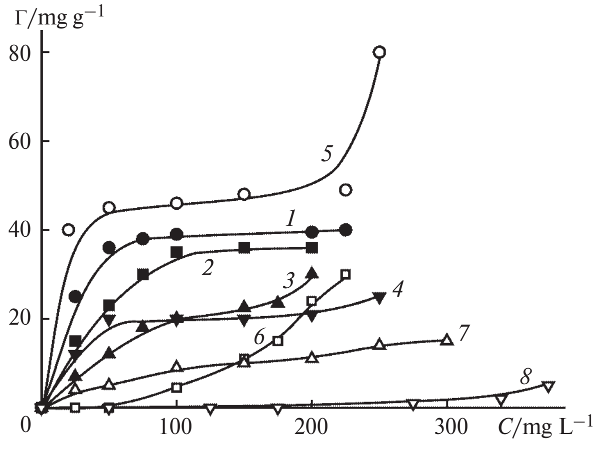

Fig. 3. Isotherms of BSA adsorption on the polarized ACF (*1—4*) and ACF-B (Ti) (*5—8*) surfaces at ΔE = 0 (*1*, *5*), –200 (*2*, *6*), +200 (*3*, *7*), and –300 mV (*4*, *8*), pH = 4.7.

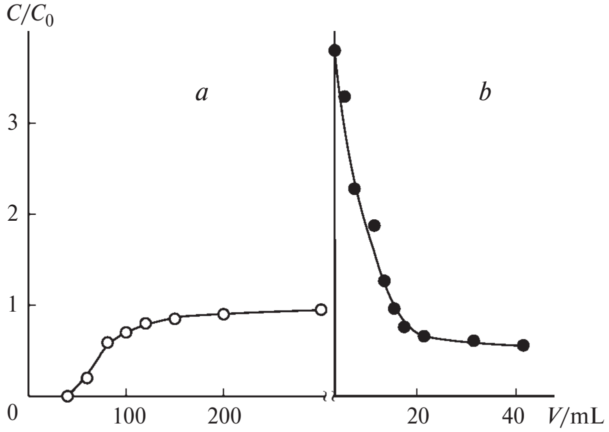

Fig. 4. Elution curves of adsorption (*a*) and desorption (*b*) of BSA on ACF-B (Ti) at $\Delta E = 0$ (*a*) and −300 mV (*b*).

and repulsion of likely charged ions from the carbon sorbent surface. It has previously been shown[8] that in an alkaline medium the adsorption of albumin on the ACF-B (Ti) surface is much lower than on the non-modified fiber. Thus, conditions for protein removal from the solid surface can be selected involving sorbents with different properties and varying regimes of sorbent polarization.

The elution curves of BSA adsorption (*a*) and desorption (*b*) on ACF-B (Ti) are presented in Fig. 4. The adsorption elution curve (at the open circuit potential) has no specific features characteristic of microporous sorbents.[7] The sharp increase in the elution desorption curve is a result of elution of the organic component (accumulated in the near-electrode space) upon passing an eluent solution (0.1 M K_2SO_4). It is seen that already 30 mL of the eluate contains the main amount of the previously adsorbed BSA. This can be used for isolating and concentrating protein molecules from a solution.

References

1. RF Pat. No. 2026732; *RZhKhim.*, 1995, **14**, 1402004P (in Russian).
2. A. Darbre, *Practical Protein Chemistry*, Wiley and Sons, New York, 1986.
3. S. Yu. Bratskaya and A. P. Golikov, *Zh. Anal. Khim.*, 1998, 265 [*Russ. J. Anal. Chem.*, 1998 (Engl. Transl.)].
4. N. Kallay, D. Babic, and E. Matwevic, *Colloids Surfaces*, 1989, **19**, 375.
5. W. Norde, *Adv. Colloid Interface Sci.*, 1989, **25**, 257.
6. A. Soffer and M. Folman, *J. Electroanal. Chem.*, 1972, **38**, 25.
7. A. M. Koganovskii, *Adsorbtsiya i ionnyi obmen v protsessakh vodopodgotovki* [*Adsorption and Ion Exchange in Water Preparation Processes*], Naukova Dumka, Kiev, 1983, 238 (in Russian).
8. I. V. Sheveleva, V. A. Avramenko, and V. Yu. Glushchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1998, 1496 [*Russ. Chem. Bull.*, 1998, **47**, 1451 (Engl. Transl.)].

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