Nanostructured surfaces

Adsorption of cationic polyacrylamide in the mesoporous nanozirconia – polymer solution system

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The adsorption mechanism of cationic polyacrylamide samples (differing with molecular weight and cationic groups content) on the surface of mesoporous nanozirconia (pore size 31 nm, particle diameter 100 nm) was studied. The cationic PAM chains contains (besides the not ionizable amide groups) a certain number (i.e. 20, 35, 50 or 80%) of quaternary amine groups which are a source of positive charge of the polymer chains. Total dissociation of these groups (the degree of dissociation is 99.9%) are observed at pH 3 and 6. In turn, at pH 9 the degree of cationic groups dissociation is in the range 88.8-92.6%. The point of zero charge of ZrO_2 (pH_{pzc}) is equal to 5.93. At this pH value, the concentration of the positively ($-ZrOH_2^+$) and negatively ($-ZrO^-$) charged surface groups is the same, so the total charge of the solid surface is zero. Thus, ZrO_2 surface assumes the positive charge below pH 6, whereas above this value - negative.

The degree of dissociation of PAM cationic groups determines the conformation of the adsorbing polymeric chains. The total ionization of these groups at pH of 3 and 6 results in electrostatic repulsion of positive charges located along the polymer chain. This promotes the adoption of more stretched conformation by PAM macromolecules. The small reduction in the degree of dissociation at pH 9 causes that the conformation of the polymer chains is less developed. On the other hand, the penetration of mesopores occurring in the zirconium(IV) oxide structure by PAM macromolecules is possible. Adsorption on the pore surface is most likely at pH 9, at which PAM chains assume the least developed conformation and the electrostatic interactions between the metal oxide surface and polymer macromolecules are attractive. Under such conditions the greatest level of PAA adsorption on the nanozirconia surface was obtained. Moreover, the hydrogen bonds are formed between the adsorbate and adsorbent in the whole examined pH range. All types of polymer and surface groups (neutral and charged), may be involved in their formation. However, their presence is most evident at pH 3 (at which adsorbent-adsorbate electrostatic repulsion occurs).

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