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Albumin adsorption influence on the stability of the mesoporous zirconia suspension

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A B S T R A C T

In this paper, the stability mechanism of the mesoporous zirconia suspension in the albumin presence was described. The albumin adsorption on the zirconia surface depends on pH and ionic strength. The highest adsorption was observed at the albumin p*I* value (for HSA 3.1 mg/m^2). The protein adsorption affects the suspension stability. It causes mainly its increase related to electrosteric stabilization phenomenon (pH 3, 6 and 9). At pH 4.6 there is the system destabilization due to the adsorption of the macromolecules with zero net charge. Under these conditions the greatest stability change was also observed (TSI from 8.38 to 23.97).

Introduction

In recent years the interest in mesoporous materials has increased significantly. These compounds have a pore diameter in the range 2–50 nm and relatively high surface area [1]. The above solids can be characterized by an ordered [2,3] or disordered [4] structure. Mesoporous silica and mesoporous alumina are the most frequently reported representatives of this group. The first procedure of mesoporous silica synthesis was patented in 1970 [5]. However, the interest in these materials began to rise sharply after 1990 [6–8]. Mesoporous materials have many applications, which are widely described in the literature [9–16]. Currently, many works on the synthesis of new materials with improved properties are carried out [17,18].

This study focused on the mesoporous zirconia nanoparticle usage. The main aim was to determine the zirconia stability mechanism as well as the electrical double layer structure formed on the ZrO_2 nanoparticles in the absence and presence of albumins (bovine serum albumin—BSA, human serum albumin—HSA, ovalbumin—OVA). This has been performed based on the stability, adsorption and electrokinetic measurements. Counterions can behave in two ways within the mesopores. In analogy to the Helmholtz model they can form compact cylindrical layer or in analogy to the Guy–Chapman model they may diffuse into the pore center driven by thermal motions [19]. The albumin adsorption can change appropriately this structure. All measurements were carried out as the function of pH value due to the zirconia industrial applications. The metal oxide suspension stability usually depends on the solution pH and therefore the appropriate pH change allows the process modeling. The high system stability is highly desirable in cosmetic, pharmaceutical and paint industry. On the other hand, low suspension stability is essential in separation procedures, including water and sewage purification.

Zirconia is a crystalline solid with high chemical and mechanical resistance [20]. In turn, albumins are the most numerous proteins in serum involved, inter alia, in maintaining a constant blood osmotic pressure [21]. The presented results, especially concerning the properties of the system without proteins, can be very helpful in the development of new industrial zirconia applications. This material can be used as catalyst thanks to it specific structure. A large pore size in the mesoporous body allows the reaction of large active complexes and bulky molecules [9]. Solids with mesopores can be also used as a stationary phase in High Performance Liquid Chromatography (HPLC) [12]. Moreover, they can be important in membrane separation [13].

On the other hand, the results on the zirconia suspension properties in the albumin presence have medical significance. Zirconia can be used as scaffold for tissue regeneration, like SBA-15

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or MCM-48 [14], or play a major role in drug-delivery systems [15]. Mineral oxides are frequently used as implant coatings. This is due to their biocompatibility with the organism, corrosion resistance and low chemical activity [22]. The protein adsorption on the solid surface is a key process in implantation. It occurs shortly after the implant insertion and determines the implant acceptance or rejection. In other words, the protein adsorption mediates body cell interactions with the implant surface. For this reason, the probable albumin adsorption mechanism on the zirconium(IV) oxide surface was described in this paper.

It is also worth mentioning that substances with mesopores can play a significant role in environmental sciences. They allow heavy ion removal from the aqueous media that is highly desirable in environmental remediation [16]. Zirconia can be useful in the polymer removal from water and wastewater. The presented stability results will be certainly helpful in the proper procedure development [23].

Experimental

Materials

Zirconium(IV) oxide (ZrO_2, zirconia), delivered by *Sigma-Aldrich* company, was used as an adsorbent. It was a mesoporous material of the average pore diameter equal to 31 nm, specific surface area—21.7 m^2/g and the particle average size—smaller than 100 nm (nanoparticles). The adsorbent pore diameter and surface area were determined by BET method, whereas the size distribution was established using a mastersizer 2000 (*Malvern Instruments*). The zirconia parameters are summarized in Table 1. Its size distribution is shown in Fig. 1.

Bovine serum albumin (BSA), human serum albumin (HSA) and ovalbumin (OVA) were used as adsorbates. All proteins were delivered by *Sigma-Aldrich* company. BSA is a globular protein of 66 kDa [24]. Its isoelectric point (p*I*) is in the range of 4.7–5 [25,26]. In turn, HSA has a mass of 66 kDa and p*I* equal to 4.7 [27]. Due to high amino acid sequence similarity (76%), BSA and HSA are considered as homologues. Their molecules are approximately heart-shaped in the pH range 4–8 [28]. OVA is a glycoprotein of 45 kDa [29] and the p*I* value in the range 4.43–4.9 [30,31]. Due to amino acid sequence and structure, it was classified as serpin [32]. All albumins used in the experiments are characterized by low internal stability, i.e. they are 'soft' proteins [33].

Methods

All measurements were performed at 25 °C using 0.01 M NaCl as a supporting electrolyte. The adsorption and stability measurements were carried out as a function of solution pH value (3, 4.6, 6 or 9).

Potentiometric titration

The potentiometric titration was carried out to determine the adsorbent surface charge in the absence and presence of albumins. In this method the surface charge density (σ^0) is determined based on the difference in base volume added to the suspension

Table 1
Adsorbent characteristics.

Adsorbent	Chemical formula	S_{BET} [m^2/g]	D [nm]	D_p [nm]
Zirconium(IV) oxide	O=Zr=O	21.7	<100	31

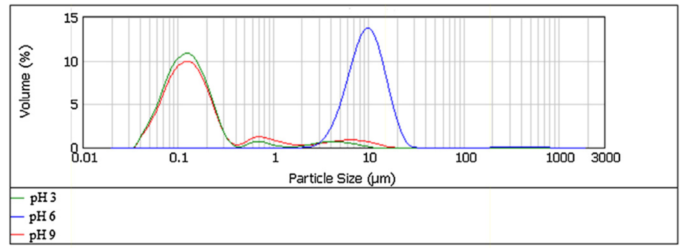

Fig. 1. Zirconia size distribution at various pH values.

containing polymer and supporting electrolyte solution in order to achieve a specific pH value using the formula [34]:

$$\sigma^0 = \frac{\Delta V \cdot c \cdot F}{m \cdot S_w} \quad (1)$$

where: ΔV—the difference in the base volume added to a suspension and a supporting electrolyte solution that leads to the specific pH value ($\Delta V = V_s - V_e$), c—the base concentration, F—the Faraday constant, m—the metal oxide mass in a suspension, S_w—the metal oxide surface area.

The measurements were conducted using the computer program 'titr_v3' developed by W. Janusz and the apparatus consisting of: teflon thermostated vessel, water thermostat RE 204 (*Lauda*), glass and calomel electrodes (*Beckman Instruments*), pHmeter PHM 240 (*Radiometer*), automatic microburette Dosimat 765 (*Metrohm*), PC and printer.

At first, the potentiometric titration of the supporting electrolyte was performed. Then the zirconia suspension in the absence and presence of albumins was titrated. The albumin concentration was 10, 50 or 100 ppm, whereas the solid weight was equal to 0.8 g. All systems were titrated using 0.1 M NaOH. The measurement started at the pH value approximately 3.5.

Electrokinetic potential measurements

The microelectrophoresis phenomenon was used for the zeta potential determination (Zetasizer Nano ZS, *Malvern Instruments*). In this method colloidal particles move in the electric field of the electrophoretic cell. The potential reading is made automatically when the particle movement is compensated for by the applied voltage. According to Hückel, the speed (u) of the colloids moving in the electric field is associated with the zeta potential (ζ) by the equation:

$$u = \frac{2}{3}\frac{\zeta\epsilon}{\eta} \quad (2)$$

where ε—the dielectric constant, η—the viscosity.

At the beginning, the zirconia zeta potential was measured. In the next step, the suspensions containing the albumin (10, 100 or 500 ppm) were examined. The samples were prepared by adding 0.0075 g ZrO_2 to the appropriate solution. Each system was sonicated for 3 min. During the measurement, the solution pH value was changed automatically using a titrator. The examined pH range was 3–9. One result was the average of three measurements. The error did not exceed 5%.

Adsorption amount measurements

The albumin adsorption amount was determined based on the protein concentration difference before and after the adsorption process. The albumin concentration was established spectrophotometrically (spectrophotometer UV–Vis *Cary 100, Agilent Technology*)