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Effect of polyvinyl alcohol adsorption on the mixed alumina–silica–titania suspension stability

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ABSTRACT

The adsorption and electrokinetic properties as well as the stability of the AST71 suspension in the absence and presence of polyvinyl alcohol (PVA) were examined. AST71 is a mixed oxide of alumina, silica and titania. All measurements were carried out as a function of solution pH and the polymer molecular weight. The pooled result analysis showed that the PVA adsorption amount strongly depends on the solution pH. The higher solution pH value is, the more polymer macromolecules are adsorbed on the solid surface. This dependence is mainly associated with the PVA chain conformation. The adsorption of polyvinyl alcohol changes the stability of the AST71 suspension, but only in the solution of pH 9. Under these conditions the system without PVA is unstable, which is connected with the isoelectric point of the solid particles. In the presence of the polymer the electrosteric stabilization occurs.

Introduction

Solid surface modification is a very important research issue. It enables the synthesis of the solid of the surface properties which are highly desirable in many industrial processes. Thus, suitable surface modification of solid particles increases the range of their possible practical applications. There are numerous methods of surface modification, which may lead to changes in various characteristics of solid surface (e.g. charge, roughness, reactivity, surface energy [1,2]). Furthermore, these methods can make the solid biocompatible with a specific component of the system or the environment [3,4]. The literature describes many ways of the surface modification, such as modification by attaching specific functional groups and plasma modification [5–7]. Surface engineering is a widely developed scientific discipline aimed at production of surface layers and coatings [8].

Synthesis of mixed oxides is a very innovative way to change the surface properties. These substances are prepared by sol–gel, high-temperature hydrolysis, chemical vapour deposition (CVD) and other techniques [9]. They consist of some mineral oxides, such as alumina, titania and silica. The percentage of each oxide is often a key factor determining the properties of the solid particles. For example, mixed oxides of different titania content have various electrokinetic and adsorption properties in the presence of a macromolecular compound. Thus, the synthesis of mixed oxide of a certain percentage of each mineral oxide is a controlled way to obtain appropriate surface properties relative to polymers, metal ions, microorganisms etc. [10].

Mixed oxides have the specific surface in the range of 30–500 m^2/g. It mainly depends on the primary particle size and true material density. Mixed oxides are hydrophilic due to the bridging of hydroxyl groups and other polar sites. Dissociation of the above hydroxyls, proton attachment to them or the adsorption of solvated ions contribute to the change of Gibbs free energy of inter-particle interactions as well as the particle interactions with the liquid. It affects many properties of the dispersions, e.g. stability, depending on pH, temperature and other physicochemical factors [11–13].

Owing to specific surface properties, mixed oxides have many applications, i.e. they are used as catalysts, adsorbents, fillers and dyes [14,15]. Evaluation of the use possibility requires the knowledge of adsorption, electrokinetic and stability properties

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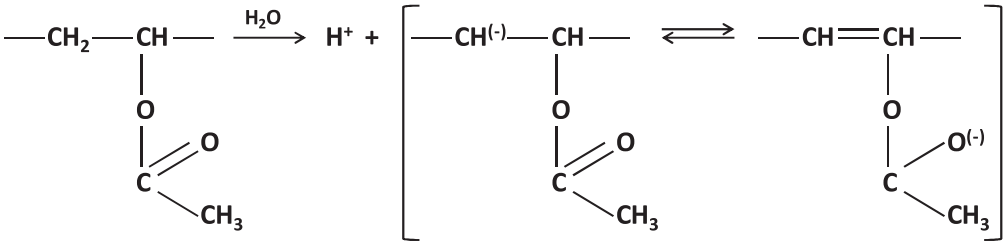
of the solid particles in the specified system. This paper describes a probable stability mechanism of the ternary oxide (AST71) suspension in the absence and presence of polyvinyl alcohol (PVA). Moreover, it characterizes the adsorption process of the above oxide as well as the electrokinetic properties of the AST71–PVA system. All requests were done based on the results of numerous experiments, including turbidimetric stability measurements, spectrophotometic measurements of the PVA adsorption amount as well as measurements of electrokinetic potential. The synthetic polymer adsorption on the AST71 surface and the AST71 suspension stability in the absence and presence of PVA are a novel issues, not described in the literature. Additionally, the turbidimetric method, used for the stability measurements, is a highly innovative element of the experiments. The main aim of this article is to provide information that will increase the possibility of the AST71 practical use. In contrast to ternary oxides, the stability of the binary mixed oxides, including alumina and silica, in the presence of selected polymers has been described in the literature [16,17]. Moreover, many papers described the properties of natural solids were published [18–20].

The choice of the polymer used in the experiments was imposed by its wide application in industry. PVA is a component in adhesives, paints, medicines, water-based paint. In addition, it is used in medicine and to produce films, protective gloves, oil and fibre [21].

Materials

Mixed oxide called AST71, consisting of titania (71%), silica (8%) and alumina (21%), was used as the adsorbent in the experiments. This oxide was prepared in the Institute of Surface Chemistry of National Academy of Sciences of Ukraine in Kiev by chemical vapour deposition—CVD. The average particle size of AST71 was 24 nm [9]. Its specific surface area, determined by the BET method, is equal to 74 m^2/g.

In turn, polyvinyl alcohol–PVA, of two molecular weights (72 000, 100 000) was used as the adsorbate. The main method for PVA preparation is the hydrolysis of polyvinyl acetate, which is shown below.



The PVA 72 000 degree of hydrolysis is 97.5%, while the PVA 100 000 degree of hydrolysis is 86%. This means that 2.5% (PVA 72 000) or 14% (PVA 100 000) of acetate groups in the PVA macromolecules do not undergo hydrolysis to hydroxyl groups. C–H bonds located at α position relative to the acetate groups are of acidic properties. The proton from the $–CH_2–$ group adjacent to the segment containing the acetate groups can dissociate. Negative electric charge can be located on the carbonyl oxygen of the acetate group. Thus there is formed a resonant structure, in which the negative charge moves between the specific parts of the macromolecule, as shown below. In this way, the acetate groups in the PVA chains adopt a negative charge.

Methods

All measurements were performed at 25 °C, as a function of solution pH (3, 6 or 9 ± 0.1). NaCl with the concentration of 0.01 mol/dm^3 was used as a supporting electrolyte.

Stability measurements

Stability measurements of the AST71 suspension in the absence and presence of PVA were made using a turbidimeter *Turbiscan Lab*^{Expert} with a cooling module *TLab Cooling*. The suspensions without polymer were prepared by the addition 0.02 g of solid to the 0.01 mol/dm^3 NaCl solution (15 cm^3). The samples containing PVA were made by the addition of the same amount of AST71 to the 0.01 mol/dm^3 NaCl solution (15 cm^3). Each system was subjected to sonification for 3 min. The polymer was added just before the measurement started. The single measurement lasted 15 h during which the relevant data was recorded every 15 min. The results were obtained as the curves of transmission and backscattering of light passing through the sample during the measurement. Moreover, the system stability was determined on the basis of TSI (Turbiscan Stability Index) values. The TSI factor was calculated by the computer software working with the turbidimeter from the following formula:

$$\mathrm{TSI} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{BS})^2}{n-1}} \quad (1)$$