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Influence of temperature on adsorption mechanism of anionic polyacrylamide in the Al_2O_3 –aqueous solution system

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A B S T R A C T

The influence of temperature on the adsorption mechanism of anionic polyacrylamide (PAM) on the alumina surface was studied in the temperature range 15–35 °C. The structure of polymer adsorption layer was determined from spectrophotometric, surface charge and zeta potential measurements. These methods enable determination of the following parameters: adsorbed amount of polymer, surface charge density and zeta potential of Al_2O_3 particles in the absence and presence of PAM. The influence of carboxyl groups content in the polyacrylamide macromolecules (varying from 5 to 50%) was also examined. The obtained results indicate that temperature influences the adsorption behaviour of anionic polyacrylamide on the Al_2O_3 surface. Slight increase of PAM adsorbed amounts with the temperature rise was obtained for the polymer samples characterized by the higher anionic group content (20, 30 and 50%). In the case of PAM with 5% content of these groups significantly larger adsorption was observed at 25 °C. The PAM presence causes also changes in electrokinetic properties (zeta potential and surface charge density values, as well as pH_{pzc} and pH_{iep} positions) of the examined system in the temperature range 15–35 °C.

1. Introduction

Polymers are a large group of substances currently used in many fields of industry, technology and science. Modern tools offered by the present technique allow production, modification and processing of the polymer, obtaining the synthetic macromolecular materials such as plastics, rubber or fibers. Polymers are also used for the manufacture of adhesives and paints. They can affect the properties of the interface and therefore can be used as emulsifiers. In addition, their ability to modify surface properties of solids promoted their use in stabilization or destabilization of colloidal particles. The latter process is particularly desirable in water purification. Emulsification, stabilization or flocculation of dispersed systems are closely related to the phenomenon of adsorption [1–8].

The process of polymer adsorption is used in many fields. Modern and recently intensively developed tendency in research is the adsorption of macromolecules on lipid layers. This finds application in designing of biosensors, implants and new pharmaceutical formulations [9–12]. However, the most popular and the closest to everyday life application of polymer adsorption is flocculation. This process involves the addition of a high-molecular weight polymer which reduces the repulsive interaction between the particles in the suspension. As a result, they form larger aggregates (flocks), so they can be easily separated from the solution. Polymers are widely used as flocculants. It has been shown that the number and size of flocks formed after the polymer addition increase more effective than in the presence of inorganic coagulants. Additionally, in such a case the collisions of particles in solution are more effective, which results in rapid destabilization of the system [13].

In such processes anionic, cationic and nonionic flocculants are widely used. One of them is polyacrylamide. Polyacrylamide (PAM) is a water-soluble polymer. It is obtained by the polymerization of acrylamide. Contrary to its monomer, it is non-toxic. It is used as a flocculant for wastewater treatment. There are also possible modifications to the PAM ionic form. The anionic polyacrylamide contains carboxyl groups which are obtained by hydrolysis of the amide groups or copolymerization process with acrylic acid monomers. On the other hand, the cationic form is obtained by copolymerization of acrylamide with cationic monomer (i.e. containing the quaternary amine group). The ionic polymers are used,

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among others, in recovery of metals after minerals processing [14]. Polyacrylamide has the tendency to form gel structures (i.e. cross-linked systems which have ability to absorb water). These structures should be distinguished from aggregates which are formed by the greater number of particles (being very close to each other). Polyacrylamide gels were mainly used in chromatography and electrophoresis of large molecules such as nucleic acids and proteins [15,16].

The main aim of this study was to investigate the adsorption of anionic polyacrylamide on the surface of aluminum(III) oxide and determination of surface properties of the system as a function of temperature. All measurements were carried out at three temperature values: 15, 25 and 35 °C. They enabled characterization of the structure of the polymer adsorption film which determines the Al_2O_3 suspension stability in the PAM presence. The polymeric probes differing with the content of carboxyl groups were used in the experiments. The pH changes in the 3–10 range lead to modification of both the ionization degree of macromolecules and the surface charge of metal oxide. Analysis of the obtained results allowed to propose the most probable mechanism of anionic polyacrylamide adsorption on the Al_2O_3 surface. In addition, there were specified conditions (temperature, pH, content of anionic groups of the polymer), under which polyacrylamide shows the greatest adsorption at the aluminum(III) oxide – polymer solution interface.

Temperature, the impact of which is the subject of the present research, is an important factor affecting the polymer adsorbed amount. Effect of temperature on the adsorption mechanism is different for various polymer/solvent/solid systems [17–29]. The temperature change influences the solubility of the polymer due to the modification of the interaction between the polymeric chains and the solvent molecules [20]. This determines the specific conformation of adsorbed macromolecules in the surface layer.

In addition, the temperature effect on the adsorption mechanism of macromolecular substances in the colloidal suspensions is challenging, because it is marginally described in the literature [21–23]. Ability to influence the polymer chain conformation by temperature change is closely related to the stability of colloidal systems. One can achieve a desired state of colloidal suspension stability only by temperature changing. Therefore, the presented studies can make a significant contribution to a better knowledge and understanding of the processes occurring at the solid – polymer solution interface at different temperature values.

2. Materials and methods

In the role of adsorbent γ – aluminum(III) oxide – Al_2O_3 was used. It was produced by Merck. Before starting the experiments metal oxide was washed with doubly distilled water to achieve the supernatant conductivity below 2 mS/cm. The specific surface area of the solid, determined using the BET method, was 155 m^2/g, whereas its mean particle diameter, measured with the Zetasaizer 3000 apparatus, was 469 nm.

Alumina was chosen for the studies because of its physicochemical properties: high surface area, minimal solubility, high thermal stability and high mechanical strength.

The anionic form of polyacrylamide (PAM), manufactured by Korona was used in experiments. Four polymer samples differing in the content of carboxyl groups were applied. The anionic groups come from the hydrolysis of a number of the amide groups during the polymer preparation. These groups are a source of negative charge of the polyacrylamide chains formed as a result of dissociation process [24,25]. The characteristics of the polymer samples are presented in Tables 1 and 2.

Before the experiments the stock polymer solutions were prepared. For this purpose 1 g of polymer dry weight was dissolved in doubly distilled water at approx. 45 °C. The determination of polymer solution concentrations included several stages. The first one was to weigh the each glass (three for each sample). Then onto each of them 1 cm^3 of polymer solution was dropped and the glasses were dried at 60 °C for 24 h. Next they were cooled and again weighed.

The obtained concentrations of the stock PAM solutions are given in Table 1. Stock solutions were used to prepare (by dilution with doubly distilled water) polymer solutions with the following concentrations: 3, 5, 10, 30, 50, 70, 100 and 120 ppm ($1.2\ 10^{-4}$ g/cm^3).

All measurements were carried out in the solution pH range 3–10 at three values of temperature: 15, 25 and 35 °C. NaCl (0.01 mol/dm^3) was used as the supporting electrolyte. This temperature range was chosen due to the measuring opportunities of applied apparatus, thermodynamically good quality of water as the polymer solvent, as well as the ability to compare obtained data with those determined for other polymer-solid systems.

Adsorption experiments were made by the static method in the polymer concentration range 5–120 ppm at the pH values: 3, 6 and 9 (±0,1) using 0.05 g of Al_2O_3. To adjust the appropriate pH of the samples the pH-meter (pH – Φ360 pH/temperature/mV Meter, Beckman) was applied. Such prepared suspensions were shaken in the water bath (OLS 200 Grant) for 24 h. After that the solids were centrifuged using a micro-centrifuge (type MPW – 223e, MPW MED INSTRUMENTS). The reaction of polyacrylamide with hyamine proposed by Crummet and Hummel [26] was applied. The solution turbidity was measured after 15 min using the UV-VIS spectrophotometer (Carry 1000, Varian) at 500 nm. To determine the amount of adsorbed polyacrylamide the calibration curve obtained earlier was used. It was calculated from the difference between the initial PAM concentration and that after the adsorption process.

The potentiometric titrations of Al_2O_3 with and without PAM (with the concentration 100 ppm) were performed in the thermostated Teflon vessel. The measuring set consisted of: thermostat RE 204 (Lauda), electrodes: calomel and glass (Beckman Instruments), pH-meter PHM 240 (Radiometer), laboratory stirrers and automatic microburette (765 Dosimat, Methrom). It was also connected with a computer equipped with a program Titr_v3 (author W. Janusz), which calculated the solid surface charge density (σ_0) [27]. 0.02 g of the alumina was added into the vessel with 50 cm^3 of the polymer solution in the supporting electrolyte (or only to the supporting electrolyte solution). Potentiometric titrations were carried out in the pH range 3–10 using the NaOH solution of the concentration 0.1 mol/dm^3.

The obtained results are presented as curves of the Al_2O_3 surface charge density (μC/cm^2) in the pH function. The pH_{pzc} (pzc-point of zero charge of the solid) values for all examined systems were obtained from the intersections of these dependencies with the x-axis.

To prepare the alumina suspension for the measurement of the zeta (ζ) potential, 0.03 g of Al_2O_3 was added to the NaCl solution of the concentration 0.01 mol/dm^3. The obtained suspension was subjected to ultrasonification for 3 min (ultrasonificator XL 2020, Labcaire System Limited). Then the appropriate temperature of the system was set. The suspension was divided into 6 equal portions and poured into flasks. In each flask the appropriate pH value: 3; 4.5; 5.5; 6.5; 8.5 and 10 was adjusted. During the pH determination the proper temperature of suspension was maintained by placing the sample in a thermostatic cell. Next, the zeta potential was measured using zetameter (Zetasizer Nano-ZS, Malvern Instruments). The suspensions containing the polymer (of the concentration 1 ppm) were prepared in the analogous way. The ζ potential was measured using the dip cell and the single result was