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Investigation of stabilization and destabilization possibilities of water alumina suspension in polyelectrolyte presence

M. Wiśniewska [a,*], K. Terpiłowski [b,1], S. Chibowski [a], T. Urban [a], V.I. Zarko [c], V.M. Gun'ko [c]

[a] Department of Radiochemistry and Colloid Chemistry, Poland
[b] Department of Physical Chemistry-Interfacial Phenomena, Faculty of Chemistry, Maria Curie Skłodowska University, Maria Curie Skłodowka Sq. 3, 20-031 Lublin, Poland
[c] Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine

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ABSTRACT

Adsorbed polymers show stabilization–flocculation properties of colloidal suspension and they are widely used in technological applications (chemical and pharmaceutical industries, food processing, drinking water purification and wastewater treatment). Thus, the influence of polyacrylic acid (PAA) addition on the stability of synthesized alumina suspension as a function of solution pH was studied. The changes of the examined systems stability in time were monitored using the turbidimetry method. It was shown that the alumina suspension without the polymer is the most stable at pH 3 (electrostatic stabilization), whereas at the pH values 6 and 9 the systems are unstable (coagulation). The addition of PAA with the lowest molecular weight (i.e. 2000) at pH 3 causes large deterioration of the system stability (destabilization by charge neutralization), whereas at the pH values 6 and 9 significant improvement of analogous system stability is observed (electrosteric stabilization). PAAs with higher molecular weights (100 000 and 240 000) cause stabilization of the alumina suspension in the whole range of studied pH. At pH 3 it is rather steric stabilization. On the other hand, at the pH values 6 and 9 the steric mechanism of stabilization is combined with the electric one, leading to electrosteric interactions.

1. Introduction

The adsorption process of various substances (simple ions, organic compounds, natural and synthetic polymers) on the solid surface is very important due to both theoretical and practical aspects (Nosal-Wiercińska, 2010a, 2010b, 2012; Nosal-Wiercińska and Dalmata, 2010). Adsorbed polymers exhibit stabilization–flocculation properties, and hence they are widely used in many industries including chemical, pharmaceutical, automotive technologies, food processing and electrical engineering (Ross, 1995; Shahidi et al., 1999; Kadajji and Betageri, 2011; Jin et al., 2003; Moody, 1992; Duro et al., 1999; Farrokhpay, 2009). Determination of the colloidal system stability in the presence of macromolecular compounds is essential in the production of cosmetics, drugs and ceramics (Slivander, 2002; Tadros, 2008). On the other hand, destabilization properties of polymers leading to suspension flocculation are made use of in drinking water and wastewater treatment, as well as in mineral flotation (Tripathy and De, 2006; Wu et al., 2011; Hassan et al., 2009; Haydar and Aziz, 2009). Thus, it can be concluded that over the years polymers have gained huge practical application due to their specific interfacial properties. Opportunities offered by these materials are very important for both the processors and users of many products from various branches of industry.

The polymeric stabilization/destabilization of colloidal systems is distinguished by several significant advantages over the electrostatic mechanism due to adsorption of simple electrolyte ions (Napper, 1983). The most important of them are: lower sensitivity to the presence of supporting electrolyte ions, comparable effectiveness in aqueous and non-aqueous dispersion media, comparable effectiveness with both low and high contents of colloidal particles, as well as reversibility of flocculation.

The steric mechanism plays an essential role in stabilization of particles in the biological systems. This is caused by two reasons. Firstly, the ionic strength of biological dispersion is relatively high, and that is why electrostatic stabilization in this case would be less effective. Secondly, aqueous solutions of polymers (especially polyelectrolytes) are commonly found in the nature.

The practical use of the polymers as stabilizers or flocculants of colloidal suspensions requires basic investigations. The goal of these experiments is to define the adsorbed amounts of the polymer and conformation of its macromolecules on the surfaces of the solid particles. The structure and thickness of the polymeric adsorption layers determine the stability of such systems. The adsorption process of the macromolecular compounds on the solid surface is complex and depends on many factors, such as molecular weight and polydispersity

* Corresponding author at: Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland.
E-mail address: wisniewska@hektor.umcs.lublin.pl (K. Terpiłowski).
[1] Tel.: +48 81 5375622; fax: +48 81 5332811.

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of the polymer, pH and ionic strength of the solution, temperature, as well as purity of the polymeric and adsorbent samples. Even a small change in any of these parameters can have a large effect on the suspension stability in the polymer presence.

Thus, the main aim of this work is to determine the changes in stability of the aluminum oxide (alumina) suspension in the presence of anionic polyacrylic acid (PAA). Due to the fact that conformation of PAA macromolecules depends on the solution pH and the polymer molecular weight, their influence was investigated. The alumina was synthesized in the Chuiko Institute of Surface Chemistry (Kalush, Ukraine).

The similar studies were performed using commercial available powder alumina delivered by Merck. Their results have been published (Wiśniewska et al., 2012). These aluminum oxides (synthesized and commercial) have different physicochemical characteristics and as indicated turbidimetry measurements show quite different stability behaviors in the absence and presence of the polymer. Moreover, the stability results of the synthesized alumina have been enriched with the additional parameters calculated from the obtained turbidity results: the rate of particle (aggregates, flocks) migration, the particle (aggregates, flocks) diameters and the thickness of formed sediment.

Polyacrylic acid belongs to the group of ionic polymers and is used as an effective stabilizer and flocculent of colloidal suspensions. It is applied in the production of cements, dispersants, auxiliaries for the fiber preparation, thickeners, as well as stabilizers of the latex rubber and various types of emulsions and suspensions (Coen et al., 1996; Abdelaal et al., 2012; Toshima et al., 2001; Hierrezuelo et al., 2010). On the other hand, alumina has found practical usage as a catalyst and a catalyst carrier of many chemical reactions. Moreover, it is a very popular packing for chromatography columns and it is a base material for pigments (Ni and Chen, 2001; Müller, 2004).

2. Experimental

The samples of aluminum oxide (alumina) were used in the study (pilot plant in the Chuiko Institute of Surface Chemistry, Kalush, Ukraine). The adsorbent was characterized by the BET surface area of 87 m^2/g and the mean pore diameter of 7.2 nm. Both parameters were determined by the low-temperature nitrogen adsorption–desorption isotherm method (Micromeritics ASAP 2405 analyzer). The point of zero charge (pH_{pzc}) of alumina was 6.2 (obtained from the potentiometric titration) and its isoelectric point (pH_{iep}) was 7.9 (zeta potential measurements — Zetasizer 3000, Malvern Instruments).

Polyacrylic acid (PAA, Fluka) with the weight average molecular weights of 2000, 100 000 and 240 000 was used in the experiments.

All measurements were carried out in the presence of NaCl solution (1×10^{-2} mol/dm^3) which was used as the supporting electrolyte. Moreover, the stability experiments were performed at the solution pH values 3, 6 and 9 at 25 °C. The polymer concentration was approximately equal to 770 ppm, which provided the surface coverage $\theta = 1$. The solid content in the suspensions under investigation was 0.1%.

The stability measurements of alumina suspensions without and with PAA were carried out using Turbiscan Lab^{Expert} with the cooling module TLab Cooler. This apparatus possesses the electroluminescence diode which emits the collimated light beam ($\lambda = 880$ nm) passing through the investigated suspension. The apparatus has two synchronized detectors. The transmission detector recorded light passing through the probe at the angle 0° in relation to the incident light direction. The other one is the backscattering detector registering the light scattered at the angle 135°. The obtained data are stored and converted by the computer program. The results are presented in the form of curves, which show the intensities of transmission and backscattering as a function of time.

The analyzed suspension in a glass vial (7 cm long) was placed in the thermostated measurement chamber. The suspension with 0.02 g of oxide in 20 cm^3 of NaCl solution was sonicated for 1 min. Then the required pH value of the solution was adjusted. The suspension was shaken in a water bath for 30 min and during this time its pH was checked. The changes in the suspension stability were monitored for 15 h (single scans were collected every 15 min). The probes of the alumina suspension with polyacrylic acid were prepared in a similar way. An appropriate volume of the PAA solution, the desired surface coverage $\theta = 1$ ($C_{PAA} \approx 770$ ppm), was added to the suspension after sonication.

Based on the transmission and backscattering data the stability parameters were calculated. The stability parameters are: the rate of particle (aggregates, flocks) migration [μm/min], the particle (aggregates, flocks) diameters [μm], the thickness of formed sediment [mm] and the turbiscan stability index (TSI). These data were calculated using the programs TLab EXPERT 1.13 and Turbiscan Easy Soft. The migration rate was calculated using the multiple light scattering theory. The particle diameter calculation was based on the general law of sedimentation, that is Stokes' law extended to the concentrated dispersions (Snabre and Mills, 1994):

$$V(\varphi, d) = \frac{\left|\rho_p - \rho_c\right| \cdot g \cdot d^2}{18 \cdot \nu \cdot \rho_c} \cdot \frac{[1-\varphi]}{\left[1 + \frac{4.6\varphi}{(1-\varphi)^3}\right]} \quad (1)$$

where: V — particle migration velocity (μm/min), ρ_c — continuous phase density (kg/m^3), ρ_p — particle density (kg/m^3), d — particle mean diameter (μm), ν — continuous phase dynamic viscosity (cP), and φ — volume of dispersed solid fraction (%).

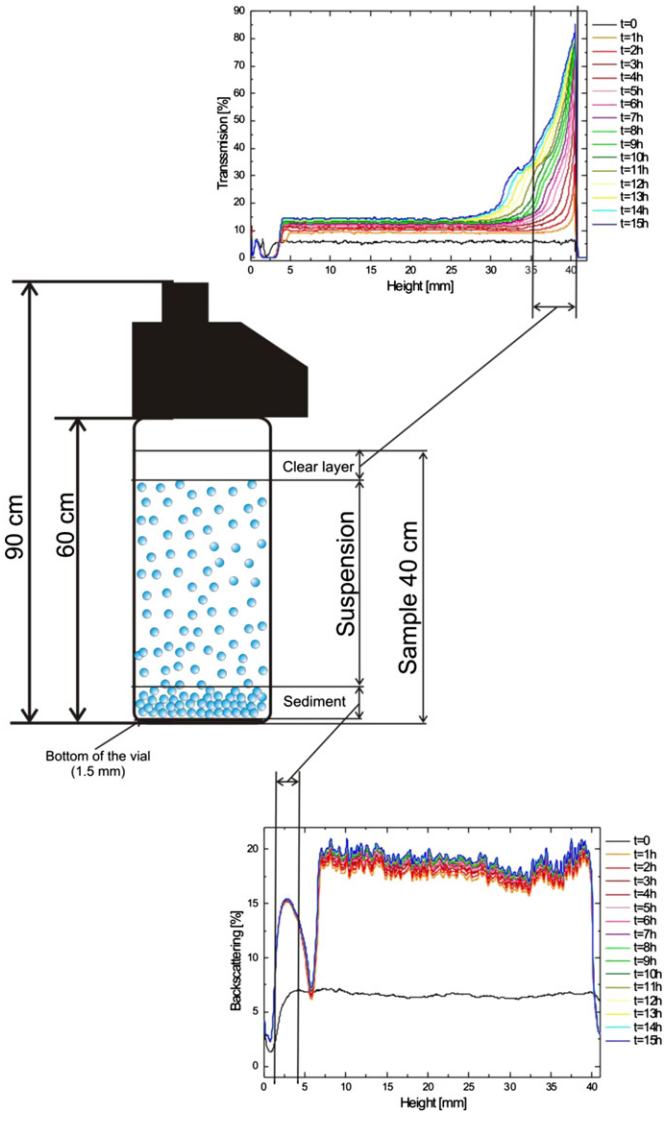

Fig. 1. Schematic picture of measuring vial containing suspension.