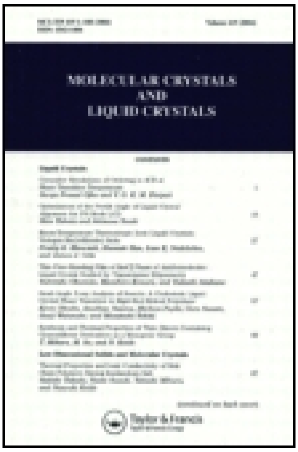

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Studies of the Alumina Suspension Stability in the Presence of Anionic Polymer—Influences of Polymer Molecular Weight, its Concentration and Solution pH

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Studies of the Alumina Suspension Stability in the Presence of Anionic Polymer—Influences of Polymer Molecular Weight, its Concentration and Solution pH

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The effect of an anionic polymer—polyacrylic acid (PAA) adsorption on the alumina (Al_2O_3) suspension stability was studied. The influence of the following parameters was examined: polymer molecular weight, its concentration and solution pH. Two methods were used to monitoring the suspension stability: turbidimetry and spectrophotometry. The conformational changes of macromolecules, both adsorbed and non-adsorbed, determine the stabilization—flocculation properties of the alumina suspension in the presence of the polymer.

Keywords Alumina; macromolecule conformation; polyacrylic acid; polymer concentration effect; suspension stability

Introduction

The great interest in the phenomenon of macromolecule adsorption on the dispersed solid surface is the result of wide application possibilities of stabilizing and flocculating properties of polymers [1–4]. They find practical industrial usage in the production of paints, paper coatings, printing inks, ceramics, cosmetics and pharmaceuticals. Moreover, polymers are compounds of agrochemicals and play a role as plough-lands erosion decreasing agents in agriculture. The important application of polymers in environmental protection is industrial and drinking water purification. For this reason, the studies of polymer adsorption on the solid-solution interface are carried out in both theoretical and practical aspects.

Two main mechanisms of colloidal suspension stabilization in the presence of polymer are steric stabilization and depletion stabilization. Steric stabilization [5,6] results from the repulsion of particles with completely covered by the adsorbed polymer surfaces (usually of low molecular weight). On the other hand, the depletion stabilization [7] takes place when macromolecules are not adsorbed on the surface of colloidal particles and prevent

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their bonding into aggregates. Polyelectrolytes, containing ionized functional groups show a combined mechanism of stabilization. It is described as electrosteric stabilization [8] and is a result of both electrostatic and steric interactions.

The destabilization of colloidal particles by adsorbed polymer chains results in flocculation. It is usually caused by polymers of large molecular weights and occurs at low concentrations of polymer in the solution (incomplete coverage of particle surface with the adsorbed polymer). The bridging flocculation and depletion flocculation are the most important types of flocculation. Bridging flocculation [9,10] takes place when adsorbed polymer macromolecules form bridges between colloidal particles. These polymer bridges can be created in two possible ways: a) one macromolecule is adsorbed on the surface of two or more colloidal particles, b) two macromolecules adsorbed on two different colloidal particles participate in bridge formation. The depletion flocculation [11,12] results in aggregation of solid particles in the presence of macromolecules non-adsorbed on their surfaces and occurs at high polymer concentrations.

The possibility of monitoring suspension stability is essential for practical reasons; therefore knowledge of system stability dependence on solution pH, molecular weight and concentration of polymer is of significant importance. It is possible to control the suspension stabilization properties by changes in these parameters.

The aim of the studies was the determination of the effect of polyacrylic acid (PAA) molecular weight and concentration as well as solution pH on stabilization-flocculation properties of the alumina system. The polyacrylic acid is the main component of many industrial dispersing and flocculating agents. The alumina finds widespread application in water treatment technology in the removal process of dissolved hazardous organic contaminants. This compound is also a catalyst for ozonation and in wet air oxidation processes.

Experimental

The aluminium oxide produced by Merck was used in experiments as an adsorbent. This oxide was washed off with doubly distilled water to achieve a supernatant conductivity lower than 2 μS/cm. The Al_2O_3 has the following physicochemical properties: specific surface area – 155 m^2/g, mean pore size – 6.1 nm (both obtained from BET method, automatic adsorption analyser ASAP 2405, Micromeritics Instruments) and average grain size – 496 nm (Zetasizer 3 000, Malvern Instruments).

An anionic polymer - polyacrylic acid (PAA) of weight average molecular weights 2 000 and 240 000 produced by Aldrich were applied as the polyelectrolyte. The polymer solutions were filtrated through cellulose membranes of with mesh sizes of 1 000 and 100 000 respectively, produced by Millipore. Next, the polymer solutions with initial concentration 1.25×10^{-3} g/cm^3 were prepared.

The stability measurements in the presence and absence of the polymer were made in the NaCl solution which was the supporting electrolyte. The NaCl concentration was 1×10^{-2} mol/dm^3. The experiments were carried out at three pH values: 3, 6, and 9 and at polymer concentrations: 100 and 500 ppm.

The Al_2O_3 suspension was prepared by the addition of a 1 g of oxide to 20 cm^3 of NaCl solution of the concentration 1×10^{-2} mol/dm^3. The obtained suspension was ultrasonified for one minute. After this time, the formed sediment (0.9 g) was removed by decantation. Thus, the solid content in the stable suspension was 0.1 g. Next, the required solution pH was adjusted. The suspension was moved to a 7 cm high glass phial. This phial was placed in a measuring thermostated chamber in the turbidimeter Turbiscan Lab$^{\mathrm{Expert}}$ with the cooling module TLab Cooler. Alumina samples with a polymer were prepared in an analogous way. A suitable volume of the PAA initial solution of concentration 1.25×10^{-3} g/cm^3, ensuring the final concentration 100 or 500 ppm was added after ultrasonification process. The device was connected to a computer which stored and processed the data. The results are given in the form of curves of transmission and backscattering intensity as a function of time. Each stability measurement was 15 hours long and the single scans were collected every 15 min.

To estimate the total effect of polymer influence on suspension stability, the stability coefficient (TSI – Turbiscan Stability Index) calculated. This parameter takes into account all single measurements during experiments and the TSI value is obtained from their averaging. All processes taking place in the sample including thickness of sediment and clear layer as well as particles settling were added up. This coefficient was calculated with the special computer program from the following formula:

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

where:
x_i – the average backscattering for each minute of measurement,
x_{BS} – the average x_1,
n – the number of scans.

The samples for stability measurements by the use of the spectrophotometer Specord M42 (Carl Zeiss Jena) were prepared in a similar way. After establishing pH, the suspension was moved to a quartz cuvette which was placed in a spectrophotometer. The changes in suspension absorbance were monitored for 15 hours.

Results and Discussion

The transmission and backscattering curves for the aluminium oxide suspension in the presence and absence of polyacrylic acid for various values of solution pH are presented in Figs. 1–3. These results were obtained using Turbiscan. The existence of peaks in the backscattering curves indicated, that the sediment layers formed on the vial bottom. Its width corresponds to the thickness of the sediment layer. On the other hand, the width of transmission peak informs about thickness of the clear layer at the top of the investigated suspensions. When backscattering gradually drops during the time of experiment (15 hours) it means that the suspension is relatively stable and the rate of particles migration is not large. Contrary to this, if backscattering changes rapidly (the single scans are distinctly separated from each other) the suspension is unstable and the dynamics of particle migration is high.

The polymer concentration was 500 ppm. The data obtained for analogous systems at polymer concentration 100 ppm was extensively discussed in our earlier paper [13] and here we only tabulate them in the form of TSI indexes. The calculated values of TSI are given in Table 1. The larger the TSI value is, the less stable a given system is.

Analysis of the transmission and backscattering data (Figs. 1–3) as well as the TSI values (Table 1) lead to the conclusion that the presence of polyacrylic acid (PAA concentration 500 ppm) in the system at $\mathrm{pH} = 6$ insignificantly improves stability of Al_2O_3 suspension. On the other hand, at $\mathrm{pH} = 3$ the PAA adsorption causes a distinct decrease in the alumina suspension stability, whereas at $\mathrm{pH} = 9$ the presence of polyacrylic acid significantly improves the stability of investigated systems.

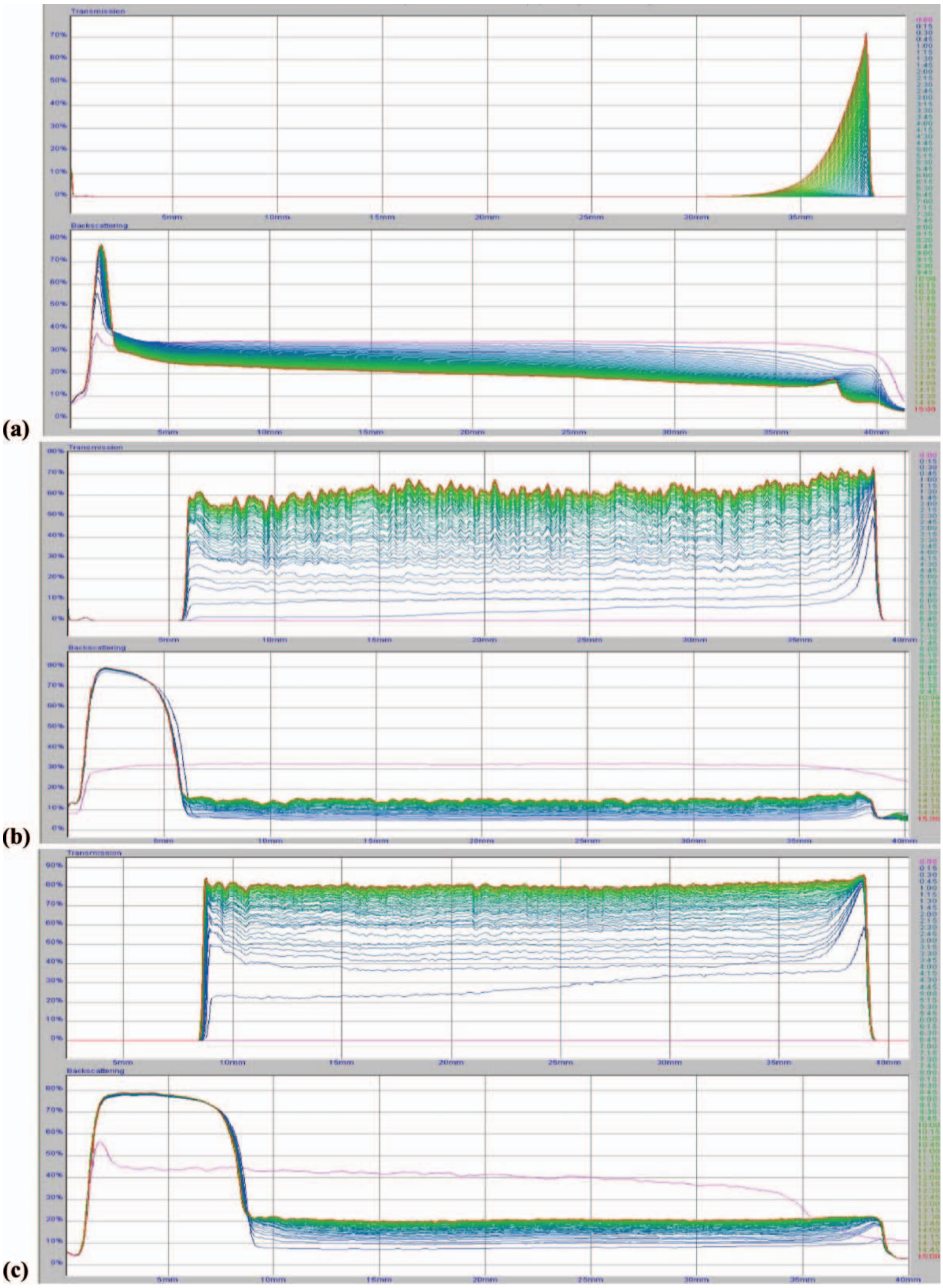

Figure 1. Transmission and backscattering at pH = 3 for the systems: a) Al_2O_3–NaCl, b) Al_2O_3–NaCl-PAA 2 000, c) Al_2O_3-NaCl-PAA 240 000; $C_{PAA} = 500$ ppm.

Stabilization-flocculation properties of the alumina suspension in the presence of PAA results from changes in conformation of macromolecules both adsorbed on the solid surface and non-adsorbed in the bulk solution with the increasing pH. This conformation determines the polymer adsorbed amount and thickness of its adsorption layer. Previous investigations

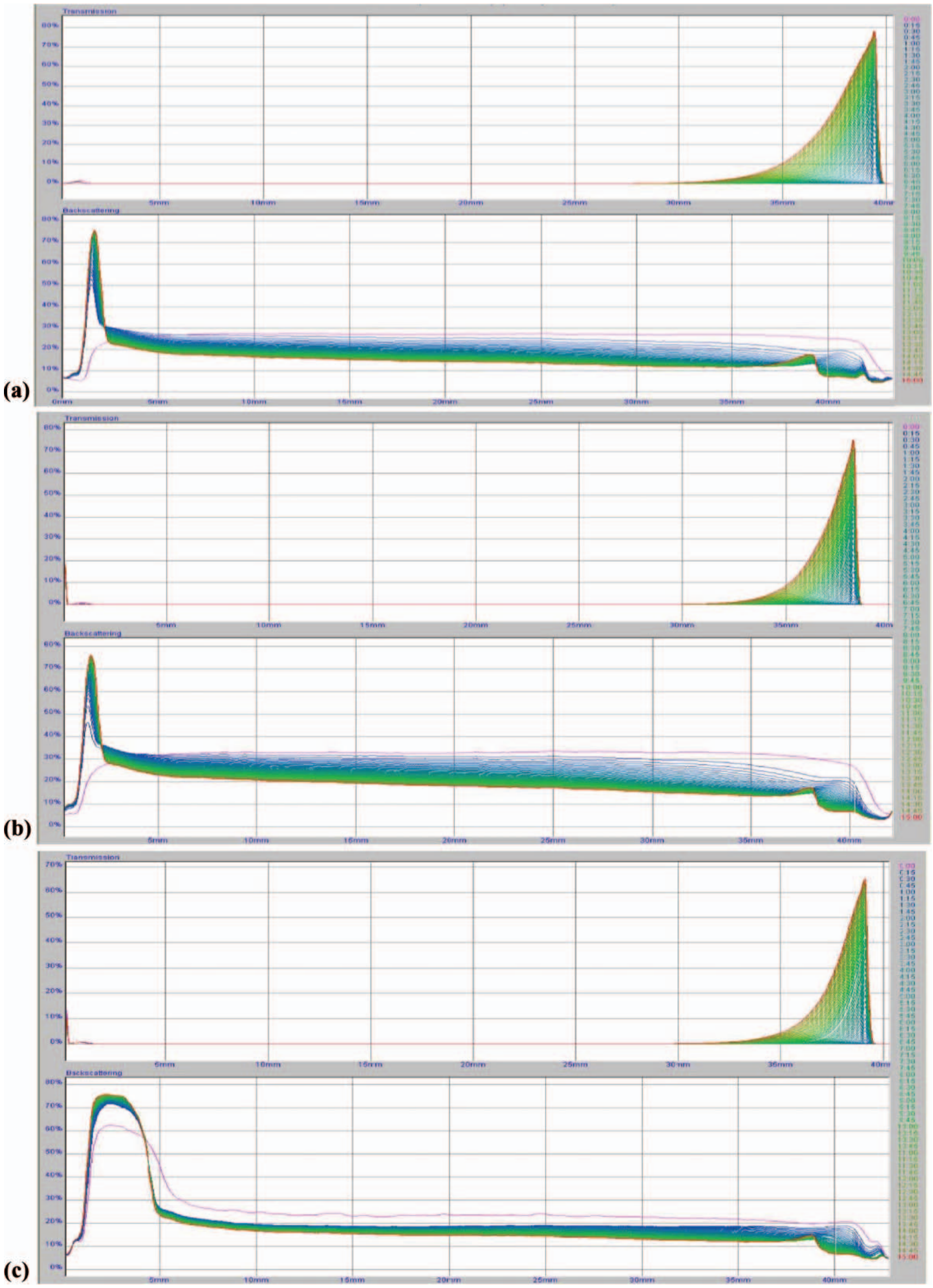

Figure 2. Transmission and backscattering at pH = 6 for the systems: a) Al_2O_3–NaCl, b) Al_2O_3–NaCl-PAA 2 000, c) Al_2O_3-NaCl-PAA 240 000; C_{PAA} = 500 ppm.

[13] indicated that the increasing pH causes a decrease in PAA adsorption on the Al_2O_3 surface and increases the thickness of polymer adsorption layer. Such behaviour results from changes in the degree of dissociation of the carboxylic groups in the PAA chain and changes in density of solid surface charge with the increasing pH [14,15].

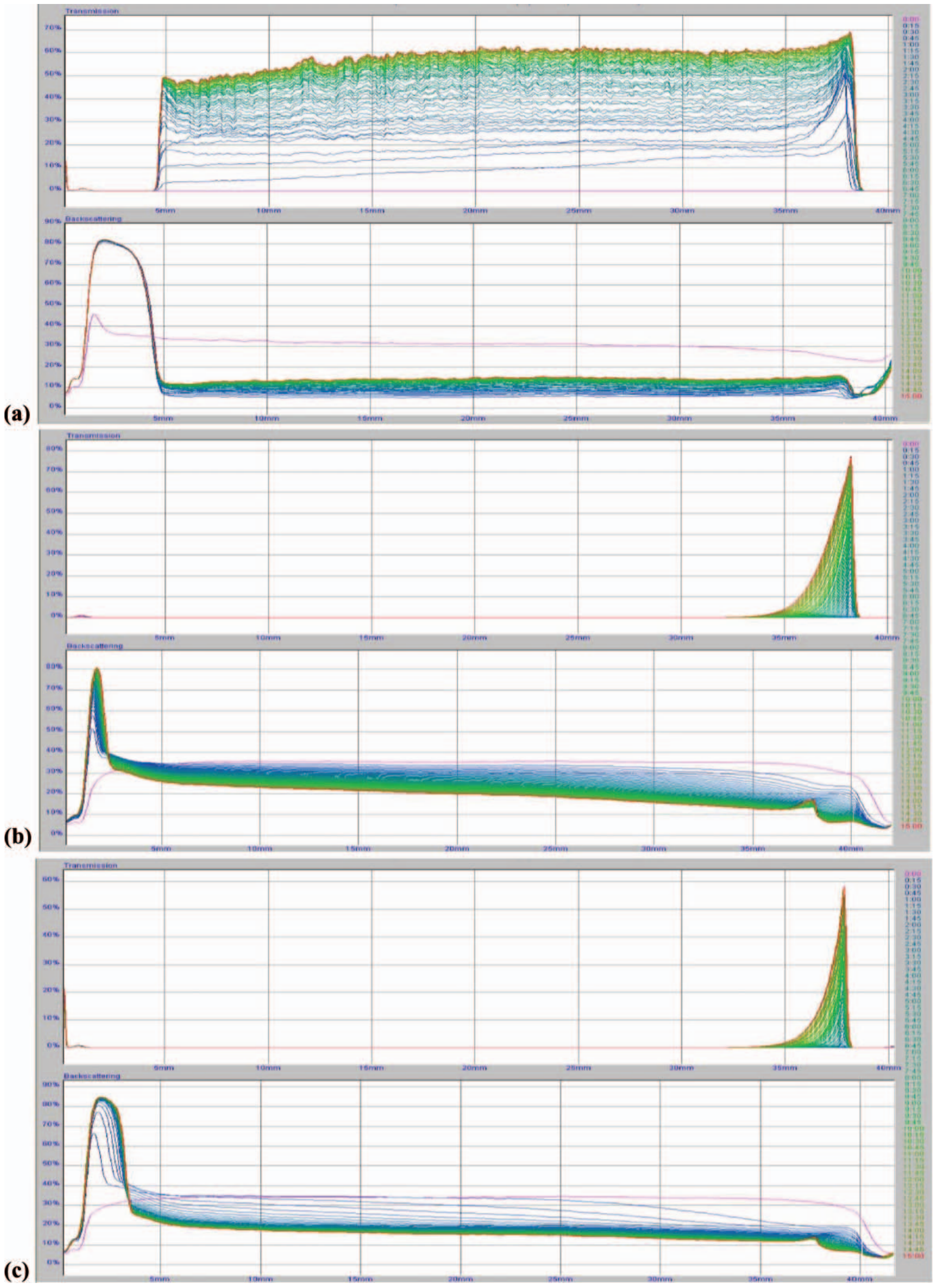

Figure 3. Transmission and backscattering at pH = 9 for the systems: a) Al_2O_3–NaCl, b) Al_2O_3–NaCl-PAA 2 000, c) Al_2O_3-NaCl-PAA 240 000; $C_{PAA} = 500$ ppm.

At pH = 3 the electrostatic attraction between the positively charged solid surface ($pH_{pzc} \approx 8$) and the single dissociated carboxylic groups of PAA ($\alpha_{dis} = 0.03$) occurs. Moreover, a very small number of dissociated functional groups results in a more coiled structure of adsorbed macromolecules. Such coiled conformation of PAA chains enables

Table 1. The TSI indexes for Al_2O_3 suspension in the presence and absence of polyacrylic acid at 25°C.

		TSI		
System	C_{PAA} (ppm)	pH = 3	pH = 6	pH = 9
Al_2O_3	-	13.64	13.77	68.03
Al_2O_3 – PAA 2 000	100	52.81	10.65	15.41
	500	72.07	14.39	14.15
Al_2O_3 – PAA 240 000	100	74.96	10.01	14.17
	500	82.94	9.83	18.20

more efficient packing on the adsorbent surface. As a result, greater adsorptions with small thickness of polymer adsorption layer were obtained.

At pH = 6 α_{dis} reaches the value 0.969 [14] and the electrostatic repulsion between dissociated carboxylic groups causes the development of coiled macromolecules. Their conformation on still positively charged surface of Al_2O_3 is more stretched, which favours smaller adsorption and formation of a thicker polymer layer.

At pH = 9 PAA macromolecules are fully dissociated and the adsorbent surface is negatively charged. Strong electrostatic repulsion between carboxylic groups of PAA macromolecules and also between the PAA macromolecules and the surface causes significant straightening of adsorbing chains. The polymer adsorption layer mainly consists of loop and tail structures which ensure the thickest adsorption layer and the lowest adsorption of polymer. The occurrence of PAA adsorption on the alumina surface under condition of strong electrostatic repulsion proved that hydrogen bridges are formed between polymer chains and adsorbent surface.

The analysis of transmission and backscattering curves at pH 3 and 6 (Figs. 1a and 2a) suggests that Al_2O_3 suspension without the polymer is quite stable (TSI = 13.64 and 13.77, respectively). The contrary behaviour is observed at pH = 9 (Fig. 3a), when the aluminium oxide suspension with the absence of polymer is unstable (TSI = 68.03). This is caused by the fact that at pH = 9 both surface and diffusion layer charges have the smallest absolute values [12]. Thus the repulsive interactions between solid particles are weak and coagulation takes place.

The addition of polyacrylic acid (PAA concentration 500 ppm) at pH = 3 causes a rapid decrease in the alumina stability (Figs. 1b and 1c). This destabilization of the solid suspension in the presence of polymer results from its largest adsorption. The single carboxylic groups ($-COO^-$) adsorb on the positively charged alumina surface causing its charge neutralization. On the other hand, the creation of compact polymer layer consisting of weak dissociated PAA chains results in absence of electrostatic repulsion between solid particles totally covered by polymer. Thus in the investigated systems the aggregation takes place. This effect is more significant in the case of PAA with greater molecular weight. The values of TSI coefficients for PAA 2 000 and 240 000 are 74.96 and 82.94 respectively (Table 1). It is confirmed by appearance of a thicker layer of sediment after 15 min from the beginning of measurement for PAA 240 000 in comparison to PAA 2 000. Moreover, along the whole length of the measuring vial the clarification of solution during the experiment is observed. It is proved by increase in% transmission in time.

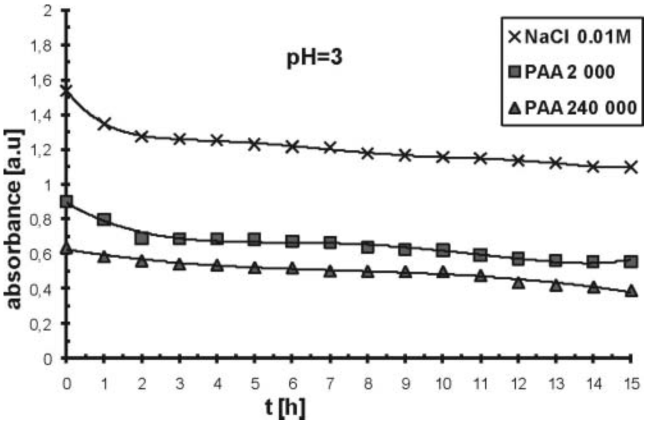

Figure 4. Absorbance of Al_2O_3 suspension in the presence and absence of PAA, $C_{PAA} = 500$ ppm, pH = 3.

Addition of polyacrylic acid, at a concentration of 100 ppm caused an insignificant effect on suspension destabilization. It results from the fact that in such situations the polymer does not neutralize the charge of solid particles effectively in comparison to the case of high polymer concentration.

Similar analysis of transmission and backscattering curves at pH = 6 (Figs. 2b and 2c) indicated that adsorption of PAA insignificantly improves the stability properties of the alumina suspension. The backscattering drops gradually during the time of experiment for all systems. Thus the suspensions are relatively stable and the particle migration rates are not large. At such pH conditions the average adsorption of the polymer and average thickness of its adsorption layer were obtained. Such a structure of the adsorption layer assures steric stabilization of the solid particles. Loosely tangled polymer chains adsorbed on the surfaces of colloidal particles make their direct contact impossible. Thus slight improvement of the system stability is observed. Moreover, polyacrylic acid at a concentration of 500 ppm is a more effective stabilization agent than PAA at a concentration is 100 ppm (Table 1). This

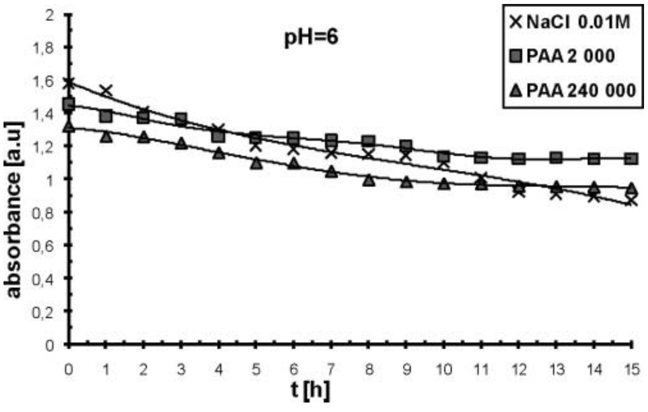

Figure 5. Absorbance of Al_2O_3 suspension in the presence and absence of PAA, $C_{PAA} = 500$ ppm, pH = 6.

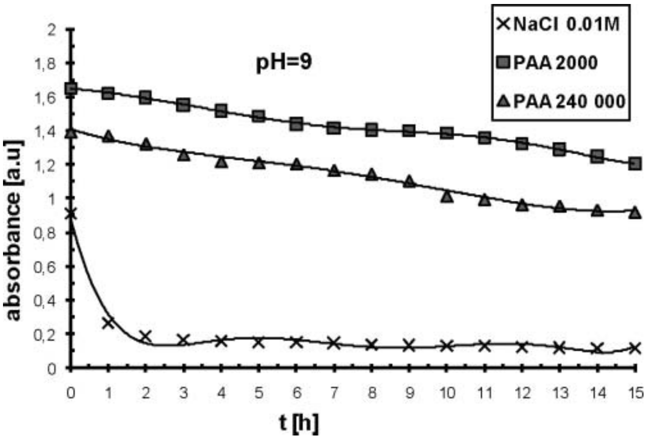

Figure 6. Absorbance of Al_2O_3 suspension in the presence and absence of PAA, $C_{PAA} = 500$ ppm, pH = 9.

results from the thicker and densely packed adsorption layer in the case of polymer with higher concentration. As a result, the steric interactions are stronger.

A completely different situation occurs at pH = 9 (Fig. 3), at which the aluminium oxide suspension in the absence of polymer is unstable (TSI = 68.03) and addition of polymer meaningfully improves its stability (TSI = 14.17 and 18.20 for PAA 2 000 and 240 000, respectively). Under these pH conditions polymer chains are completely dissociated and alumina surface is negatively charged. It results in strong electrostatic repulsion between the solid particles covered with the polymer. These repulsive interactions are intensified by non-adsorbed macromolecules containing dissociated carboxylic groups. As a consequence, both steric and electric effects are responsible for system stability improvement. This electrosteric stabilization is practically independent of polymer concentration.

To verify the results obtained on Turbiscan, the changes in alumina suspension stability in the absence and presence of PAA were monitored by means of the spectrophotometer UV-VIS. Figures 4–6 present the changes of Al_2O_3 suspension absorbance as a function of time at pH = 3, 6 and 9. The larger the absorbance is, the more stable the system is. As follows from these figures, at pH = 3 the presence of polymer in the system deteriorates stability of Al_2O_3 suspension. On the other hand, at pH = 6 the addition of polyacrylic acid slightly influences suspension stability and at pH = 9 the addition of polymer improves it. The results obtained by both methods are in good agreement.

Conclusions

Two methods namely spectrophotometry and turbidimetry were used to monitor Al_2O_3 suspension stability in the presence and absence of polyacrylic acid (PAA concentration 500 ppm). The results obtained by both techniques are in good agreement. The most stable systems occur at pH = 6, at which the addition of polymer insignificantly improves system stability. At pH = 3 the presence of polymer considerably decreases the stability of Al_2O_3 suspension. However, at pH = 9 the addition of polymer meaningfully improves the system stability. It was proved that stabilization-flocculation properties of Al_2O_3 suspension in the presence of PAA depend on conformation of adsorbed and non-adsorbed macromolecules. This conformation changes with the increasing solution pH and polymer concentration.

The most probable mechanism of system destabilization in the presence of PAA at pH = 3 is neutralization of solid surface charge by adsorbed polymer chains. The insignificant increase in stability of Al_2O_3 suspension with adsorbed PAA at pH = 6 may be due to steric interactions. On the other hand, electrosteric forces are mainly responsible for the increase in stability of the alumina suspension in the presence of polymer at pH = 9.

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