

Influence of solution pH on stability of aluminum oxide suspension in presence of polyacrylic acid

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Abstract The effect of solution pH and molecular weight of polyacrylic acid (PAA) on its adsorption as well as on stabilization-flocculation properties of the colloidal Al_2O_3 and electrolyte solution systems was studied.

The measurements showed that at $\text{pH} = 6$, the presence of the polymer of molecular weight 2 000 and 240 000 does not change stability of Al_2O_3 suspension. However at $\text{pH} = 3$ and 9 the effect of polyacrylic acid is significant. At $\text{pH} = 3$ it creates destabilization of the suspension while at $\text{pH} = 9$ PAA it improves significantly the stability of Al_2O_3 .

It was shown that the increase in solution pH affects conformation of adsorbed macromolecules which causes the decrease in PAA adsorbed amount and thickness of polymer adsorption layer.

By comparing the values of diffusion layer and surface charges, main effects responsible for the decrease in surface charge and ζ potential of the solid in the presence of the polymer as well as suspension stability were determined.

Keywords Polymer adsorption · pH influence · Polyacrylic acid · Suspension stability · Alumina

1 Introduction

Studies of behavior of colloidal systems in high-molecular compound solutions are carried out in both theoretical and practical aspects (Fleer et al. 1993; Markovic 1996; Pan et

al. 2001; Fleer et al. 1993). Practical importance of adsorption of polymers on solid surfaces refers to their application in stabilization-flocculation processes. Stabilization of colloidal systems in the presence of polymer is due to electrostatic repulsion forces or repulsion originating from polymer layers so called steric stabilization (Pedersen and Bergström 1999).

If a polymer adsorbs flat on the solid surface, the stabilization mechanism mainly comes from electrostatic interactions. With the increase of polymer adsorption layer thickness, the contribution of steric interactions is greater. This effect becomes responsible for suspension stabilization. Generally polymers of small molecular weights are characterized by stabilization properties. However, polymers of large molecular weights while adsorbing on the surface of a few colloidal particles combine which results in flocculation. This process called bridging leads to the system destabilization (Napper 1983). By choosing a suitable polymer, it is possible to stabilize or flocculate.

The process of polymer adsorption on the solid surfaces is complex depending on many factors: polydispersity of the polymer, inorganic contamination in polymer samples and on the adsorbent surface, ionic strength and solution pH. Their total contribution decides about the polymer conformation at the interface (Napper 1983) which affects stability of largely dispersed system significantly.

The aim of the studies was determination of the effect of polyacrylic acid (PAA) molecular weight and solution pH on stabilization-flocculation properties of the aluminum oxide polyacrylic acid (PAA) system. The studies of system stability in the presence and absence of the polymer were carried out by monitoring the changes in intensity of infrared radiation which passes and is reflected backward from the suspension particles (Turbiscan Lab^{Expert}) and of suspension absorbance (Specord M42). In order to perform more accu-

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rate analysis of stabilization properties of a given system, there were determined adsorbed amounts of polymer, thickness of formed adsorption layers, density of surface charge and zeta potential of Al_2O_3 particles in the presence and absence of PAA.

The choice of the polymer PAA was made due to the fact that it is the main component of many industrial dispersing agents and flocculants. Besides this, its adsorption properties in metal oxide-polymer solution systems were well described in the literature (Gebhardt and Fuersternau 1983; Drzymała and Fuersternau 1987; Grządka and Chibowski 2009). Aluminum oxide used is characterized by the well defined Al_2O_3 /solution interface, insignificant solubility which enables studies in a large pH range.

2 Experimental

There was used Al_2O_3 produced by Merck. Before measurements the oxide was washed off with distilled water to achieve conductivity below $2 \mu\text{S}/\text{cm}$. The specific surface area of Al_2O_3 determined by means of the BET method was $155 \text{ m}^2/\text{g}$. The average grain size of the solid was 496 nm.

Polyacrylic acid (PAA) of the weight average molecular weights 2 000 and 240 000 produced by Aldrich was applied as the polyelectrolyte. In order to remove inorganic contaminants and diminish the range of polymer molecular weights, its solutions were subjected to filtration through cellulose membranes of the mesh sizes 1 000 and 100 000 respectively, produced by the Millipore firm.

All measurements of adsorption, stability, zeta potential and surface charge of the oxide in the presence and absence of the polymer were made in the NaCl medium of the concentration $1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$ at 25°C .

Adsorption of polyacrylic acid on the surface of Al_2O_3 in the range of polymer concentrations 10–200 ppm and solution pH 3–9 was carried out by means of the static method (Chibowski et al. 2000) using the measurement methods given below. A 0.04 g sample of Al_2O_3 were added into the Erlenmeyer flask containing 10 cm^3 of polymer solution of suitable concentration and pH as well as concentration of the basic electrolyte $C_{\text{NaCl}} = 1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$. The suspension was shaken at 25°C for 24 h. Then the sediment was centrifuged and 5 cm^3 of clear solution were taken up each time for further analysis. The amount of adsorbed polyelectrolyte was determined from the difference in polymer concentration from the reaction of polyacrylic acid with hyamine proposed by Crummett and Hummel (1963). Opacity after the addition of hyamine to the PAA solutions was measured nephelometrically. The nephelometric measurements were made using a spectrophotometer “Specord M42” with the software M 500 at the wavelength 500 nm. The obtained results were mean values of three independent measurements. The measurement error did not exceed 5%.

The measurements of Al_2O_3 suspension stability in the presence and absence of PAA were made at the three values of pH 3, 6 and 9. The Al_2O_3 suspension was prepared by the addition of a suitable amount of oxide to 20 cm^3 of NaCl solution of the concentration $1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$. The obtained suspension was subjected to the action of ultrasounds for one minute. After establishing pH, the suspension was moved to a measuring 7 cm high glass phial which was placed in a measuring thermostated chamber in the device Turbiscan Lab Expert with the cooling module TLAb Cooler. The Al_2O_3 samples with a polymer were prepared in an analogous way. A suitable volume of the starting solution PAA (of the concentration $1.25 \times 10^{-3} \text{ g}/\text{cm}^3$) ensuring the final concentration 100 ppm was added after suspension ultrasounding. The device is connected with the computer which stores and processes the data. The results are given in the form of diagrams of intensity of transmission and backscattering in the function of time. Each stability measurement was 15 hours long.

The samples for measuring stability using the spectrophotometer “Specord M42” were prepared in a similar way. After establishing pH, the suspension was moved to a quartz developing dish which was placed in a spectrophotometer and the changes in suspension stability were monitored for 15 hours.

Density of surface charge of the oxide in the presence and absence of polyelectrolyte was determined by means of potentiometric titration of 0.2g Al_2O_3 samples in NaCl solution of the concentration $1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$. Titration was carried out in a thermostated cell. The set included: the automatic burette produced by the firm “Methron Dosimat 765”, the pH-meter by the Radiometer PHM 240 firm, both of which were connected with the computer and the printer. Density of Al_2O_3 surface charge was calculated using the program “Titr_v3”, whose author is W. Janusz.

The samples for measuring the ζ potential were prepared by ultrasonification of 0.01g of Al_2O_3 in 250 cm^3 of NaCl solution of the concentration $1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$. Then 50 cm^3 of the prepared suspension were put into each of five Erlenmeyer flasks and the required value of pH (3–10) was determined in each of them. Just before the measurement the measuring set was washed measured. The ζ potential of the particles of the solid with a polymer adsorbed on their surfaces in the NaCl $1.00 \times 10^{-2} \text{ mol}/\text{dm}^3$ medium was determined in a similar way.

The value of zeta potential was determined by means of the laser zetameter “Zetasizer 3000” produced by the Malvern Instruments firm.

Thickness of adsorption layers of PAA was determined using the viscosity method (Radeva et al. 2002) using a rotation remoter of CVO 50 type produced by Bohlin Instruments. In order to prepare a calibration curve there were prepared a few suspensions differing in volumetric fractions

of aluminum oxide (ϕ_0). The obtained suspensions were shaken for 24 h and then viscosities of suspension (η) and the viscosity of clean mother solution (η_0) were measured. Thus the relation (η/η_0) in the function ϕ_0 was obtained. Measurements of viscosity of the suspension with the adsorbed polymer were performed in an analogous way using a weighed amount of Al_2O_3 which ensured the solid volume fraction 12.6×10^{-3} . Knowing the radius of aluminum oxide particle and the value of solid volume fraction in the presence of polymer (ϕ_p) found on the calibration curve, there was determined adsorption layer thickness from the following relation:

$$\delta = r \left[\left(\frac{\phi_p}{\phi_0} \right)^{1/3} - 1 \right]$$

where:

r —the radius of solid particle,

ϕ_p —the volume fraction of the solid in the presence of the polymer,

ϕ_0 —the volume fraction of the solid in the absence of the polymer.

Thickness of adsorption layers was determined in the pH range 3–9 with the polymer concentration 100 ppm at 25 °C.

3 Results and discussion

Figures 1–3 present the dependence of transmission and backscattering of light after its transition through the aluminum oxide suspension in the presence and absence of PAA for various values of solution pH. These results were obtained using Turbiscan.

To estimate the total effect of polymer influence on stability of Al_2O_3 suspension, there was determined so called stability coefficient (TSI—Turbiscan Stability Index). This parameter takes into account all processes taking place in the sample (thickness of sediment and clear layer, process of particles settling) and the value TSI is obtained from their averaging. The way of calculating this coefficient is given in the following formula:

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

where:

x_i —the average backscattering for each minute of measurement,

x_{BS} —the average x_i ,

n —the number of scans.

The calculated values of TSI are given in Table 1. The larger value set the stability coefficient is, the less stable is a given system.

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 in the system (both 2 000 and 240 000) at pH = 6 insignificantly improves or practically does not change stability of Al_2O_3 suspension.

However, at pH = 3 and 9 the effect of PAA on suspension stability is significant, thereby at pH = 3 the presence of polymer evidently deteriorates stability of all systems under investigation and at pH = 9 polyacrylic acid significantly improves stability.

Stabilization-flocculation properties of the suspension in the presence of PAA depend on conformation assumed by macromolecules adsorbed on the solid surface. This conformation decides about the polymer adsorption and thickness of its adsorption layer. In the case of anionic polyacrylic acid it depends largely on solution pH.

As the effect of solution pH on PAA adsorption on the surface of Al_2O_3 was extensively discussed in our earlier papers (Wiśniewska 2007a, 2007b), here we only tabulate these data. Yet their knowledge is necessary to explain the obtained dependencies of stability of the systems under question in the function of solution pH. Thus Table 2 includes the adsorbed amounts of PAA on the surface of Al_2O_3 and thicknesses of its adsorption layers in the function of solution pH.

As follows from the analysis of the data in Table 2, with the increase of solution pH, the polymer adsorption on the surface of Al_2O_3 decreases but the thickness of adsorption layer increases. This is due to the increase of ionization of carboxylic groups in the PAA chain and changes in density of solid surface charge with the increasing pH of the solution (Wiśniewska 2008; Wiśniewska et al. 2009).

Figures 4–6 present the isotherms of Langmuir adsorption of polyacrylic acid on the surface of aluminum oxide. Their course is described by the linear form of the equation below.

$$\frac{c}{\Gamma} = \frac{1}{K(\Gamma)_{\text{max}}} + \frac{c}{(\Gamma)_{\text{max}}}$$

where:

C —the equilibrium concentration of the polymer in solution [mol/dm^3],

K —the Langmuir adsorption constant [dm^3/mol],

Γ —the adsorbed amount of polymer on the solid (real adsorption) [mol/m^2],

Γ_{max} —the adsorbed amount of polymer corresponding to the total filling of the monolayer with polymer segments (monolayer capacity) [mol/m^2].

The values of Γ_{max} and K were determined for all studied systems from the above lines. Knowing the value of constant K , the free adsorption energy of the polymer on the

Fig. 1 Transmission and backscattering at pH = 3 for the systems: **(a)** $\text{Al}_2\text{O}_3\text{--NaCl}$, **(b)** $\text{Al}_2\text{O}_3\text{--NaCl-PAA 2 000}$, **(c)** $\text{Al}_2\text{O}_3\text{--NaCl-PAA 240 000}$

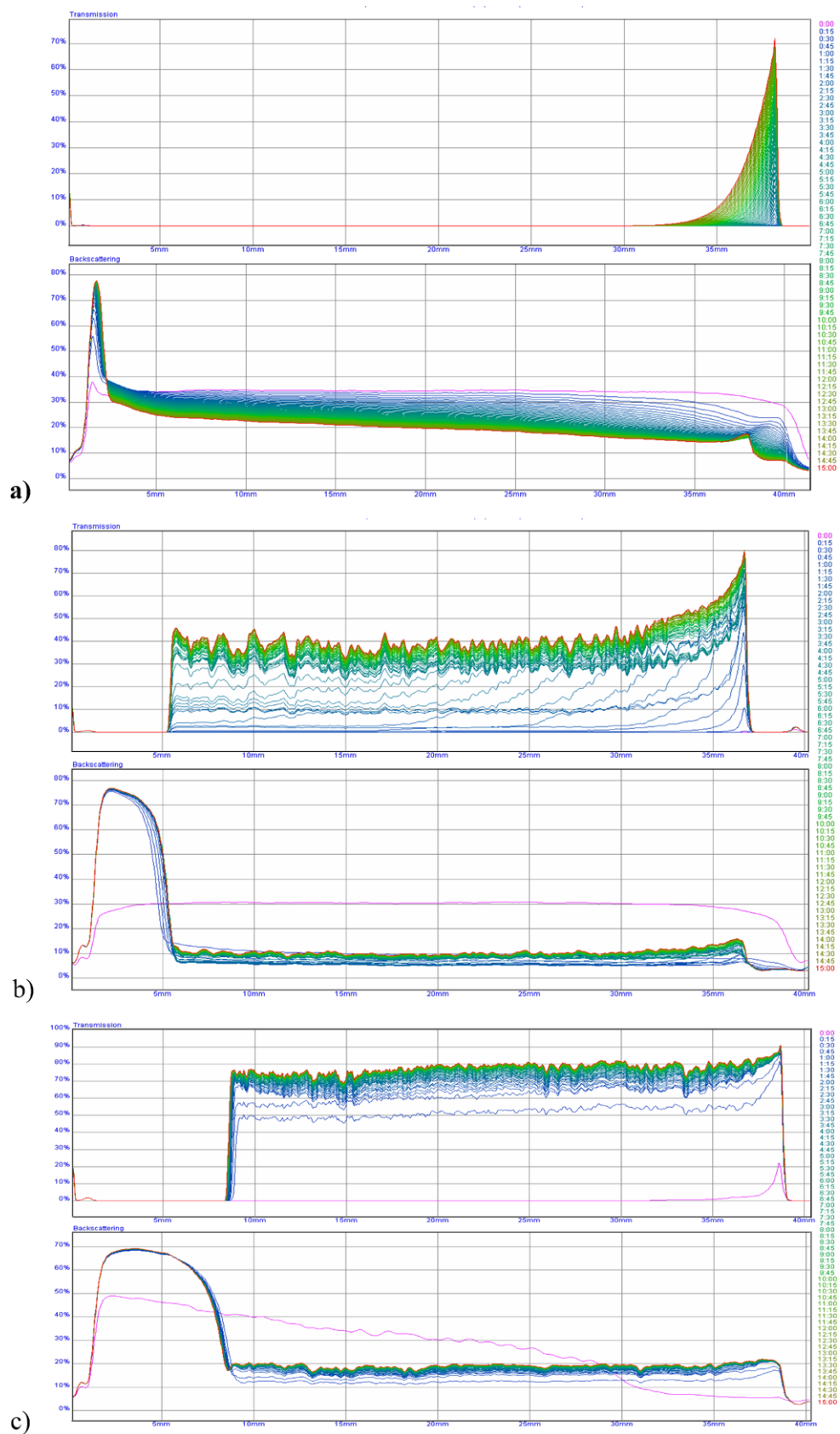


Fig. 2 Transmission and backscattering at pH = 6 for the systems: **(a)** $\text{Al}_2\text{O}_3\text{--NaCl}$, **(b)** $\text{Al}_2\text{O}_3\text{--NaCl-PAA 2 000}$, **(c)** $\text{Al}_2\text{O}_3\text{--NaCl-PAA 240 000}$

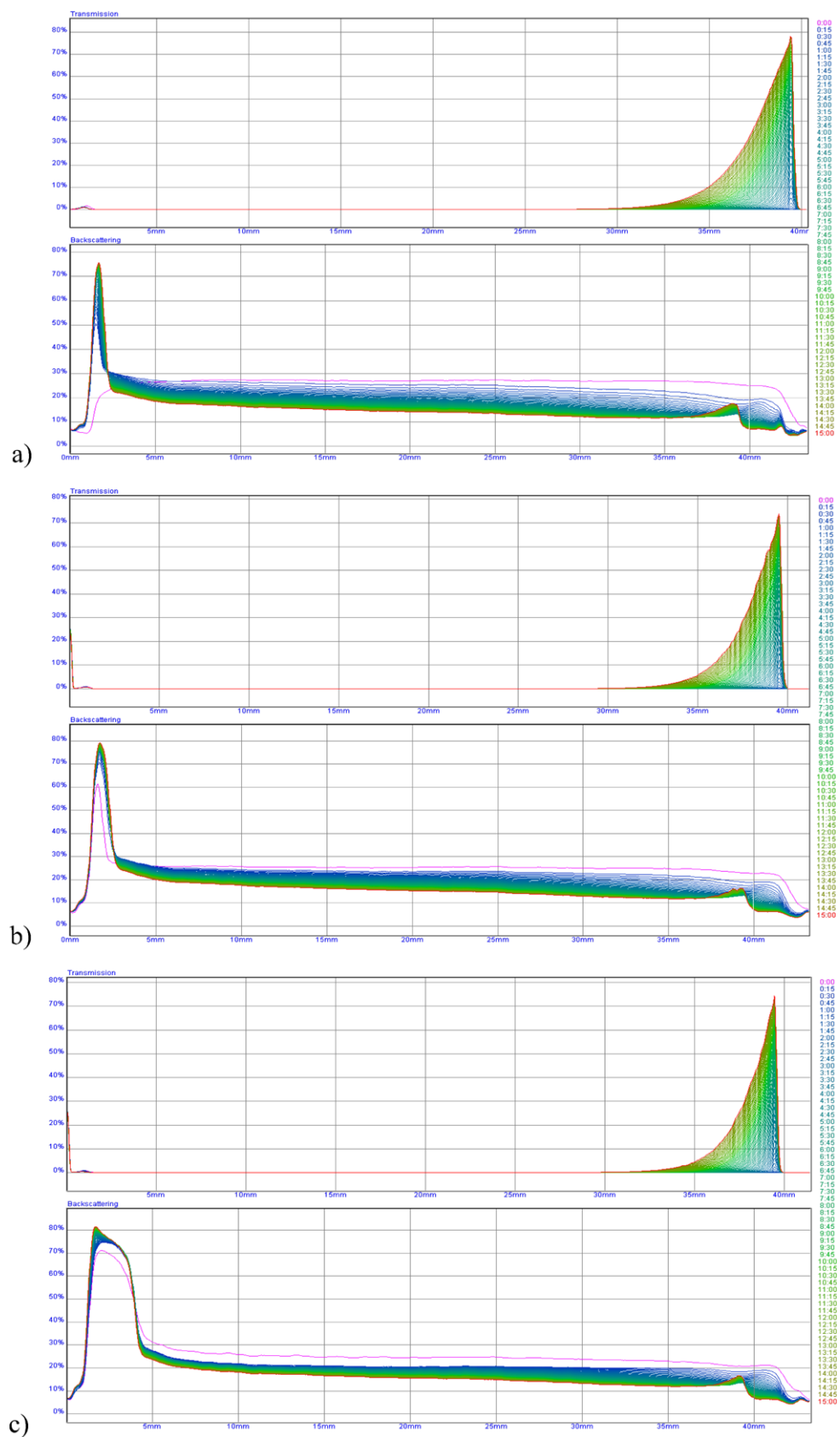
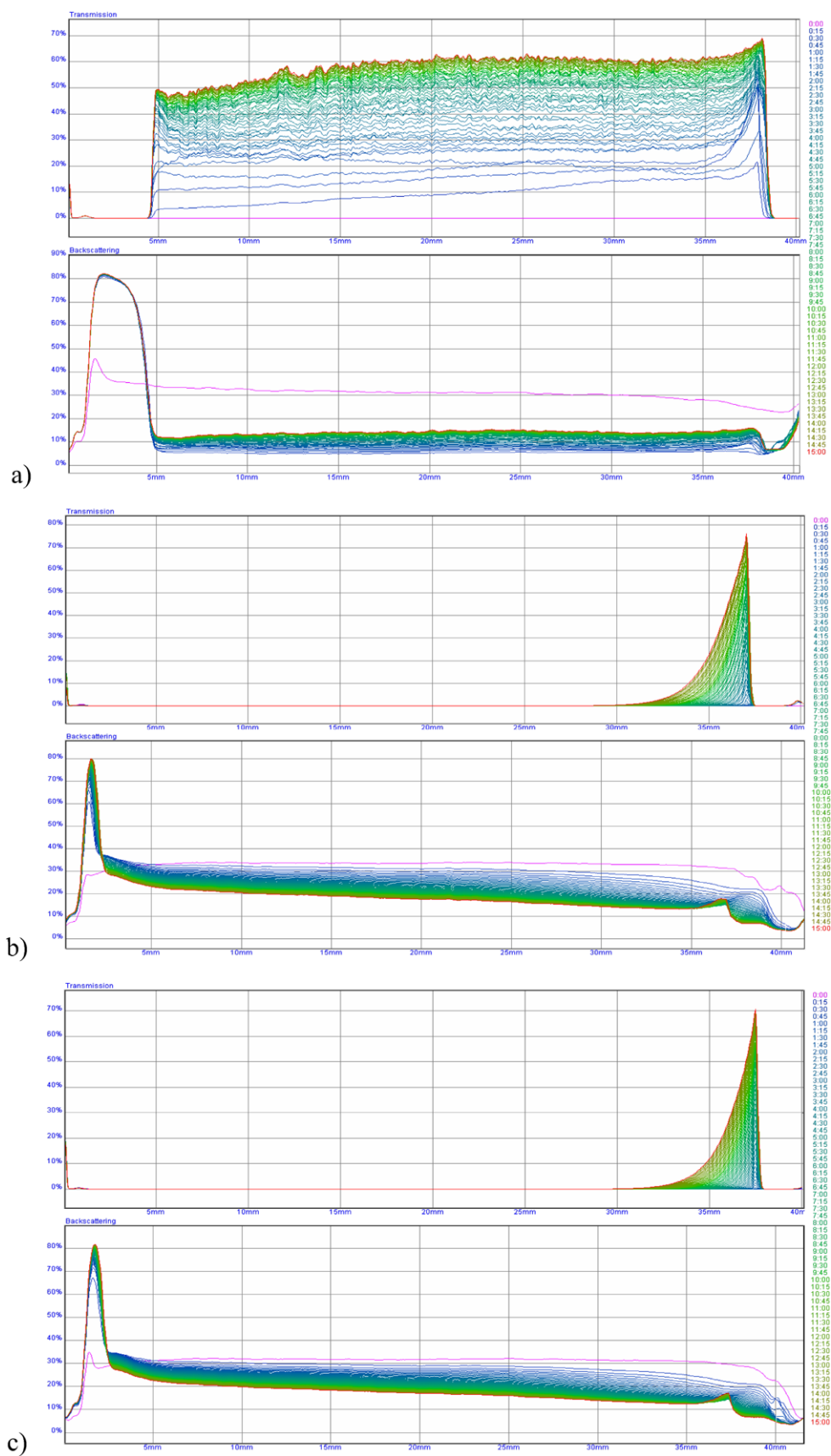


Fig. 3 Transmission and backscattering at pH = 9 for the systems: **(a)** Al_2O_3 –NaCl, **(b)** Al_2O_3 –NaCl–PAA 2 000, **(c)** Al_2O_3 –NaCl–PAA 240 000



solid surface (ΔG_{ads}) was calculated from the formula:

$$\Delta G_{\text{ads}} = -RT \ln K$$

where:

R —the gas constant [8.314 J/(Kmol)],

T —the temperature [K].

The obtained results are given in Table 3.

The obtained values of Gibbs free energy of PAA segments on the surface of Al_2O_3 confirm the fact that bonding of polymer macromolecules with the active sites of the adsorbent takes place through hydrogen bridges because hydrogen interaction energy ranges from 12 to 33 kJ/mol (Pigoń and Ruziewicz 1980).

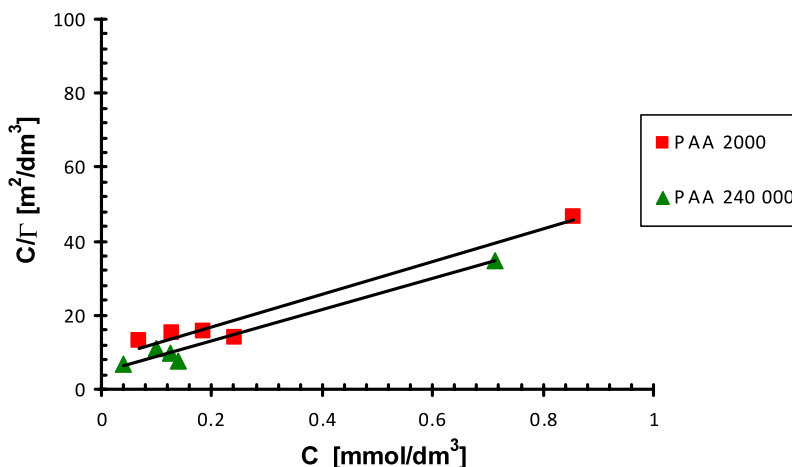
Table 1 Stability coefficient TSI for the Al_2O_3 suspension in the presence and absence of PAA, 25 °C, $C_{\text{PAA}} = 100$ ppm

System	TSI		
	pH = 3	pH = 6	pH = 9
Al_2O_3	13.64	13.77	68.03
Al_2O_3 -PAA 2000	52.81	10.65	15.41
Al_2O_3 -PAA 240 000	74.96	10.01	14.17

Table 2 Adsorbed amounts and thickness of PAA adsorption layers on the surface of Al_2O_3 in the function of solution pH; $C_p = 100$ ppm, 25 °C

Polymer	pH = 3		pH = 6		pH = 9	
	Γ	δ	Γ	δ	Γ	δ
	[mg/m ²]	[nm]	[mg/m ²]	[nm]	[mg/m ²]	[nm]
PAA 2000	1.23	1.5	0.39	2.7	0.14	5.3
PAA 240 000	1.44	6.5	0.57	9.6	0.27	12.1

Fig. 4 Langmuir adsorption isotherms of PAA on the surface of Al_2O_3 at pH = 3



Langmuir Isotherms, pH=3

The comprehensive analysis of the obtained data i.e. adsorbed amount of PAA adsorption, thickness of its adsorption layer as well as the value of calculated free adsorption energy indicates that at pH = 3 conformation of adsorbed macromolecules is flatter.

It results from the fact that in this range of pH, electrostatic attraction occurs between the positively charged solid surface ($\text{pH}_{\text{pzc}} \text{Al}_2\text{O}_3 = 8$) and the single dissociated carboxylic groups of PAA ($\alpha_{\text{dis}} = 0.03$ at pH = 3) (Das and Somasundaran 2001). Moreover, this relatively small number of dissociated functional groups causes that the adsorbed macromolecules have a more coiled structure which enables their greater packing on the adsorbent surface. As a result, great adsorption and large values of free adsorption energy are obtained with small thickness of polymer adsorption layer.

Conformation of the adsorbed polymer in the range of low pH values is presented schematically in Fig. 7.

Further increase of pH results in larger and larger dissociation of carboxylic groups in the polymer chain and at pH = 6 α_{dis} reaches the value 0.969 (Chibowski et al. 2004). This causes development of coiled macromolecules, whereby their conformation on still positively charged surface of Al_2O_3 is more stretched (Fig. 7). Such conformation favors formation of a thicker polymer layer and smaller adsorption compared to those at pH = 3. At the same time calculated ΔG_{ads} assume intermediate values between those obtained for pH = 3 and 9.

At pH above pH_{pzc} macromolecules are fully dissociated and the adsorbent surface is negatively charged. Strong electrostatic repulsion between individual segments of PAA macromolecule and also between the PAA macromolecules and the surface cause significant straightening of adsorbing chains. On the oxide surface there is formed an adsorption layer mainly consisting of loose structures of loops and tails type which ensures the largest thickness of adsorption layer

Fig. 5 Langmuir adsorption isotherms of PAA on the surface of Al_2O_3 at pH = 6

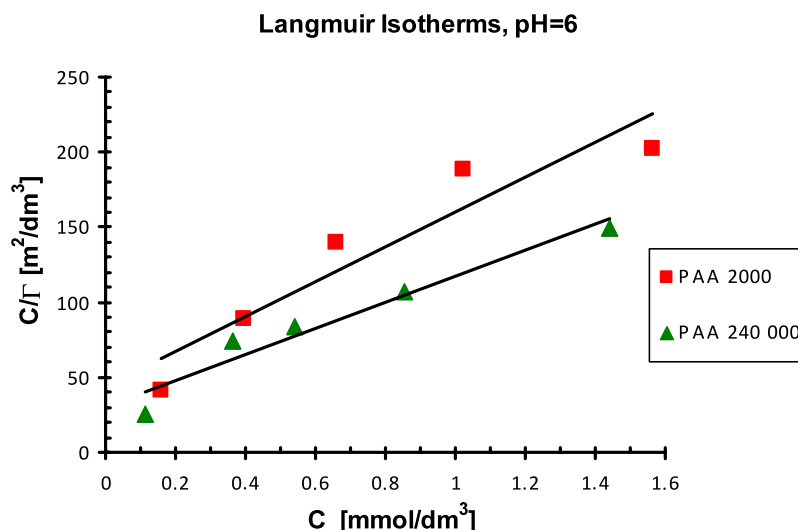


Fig. 6 Langmuir adsorption isotherms of PAA on the surface of Al_2O_3 at pH = 9

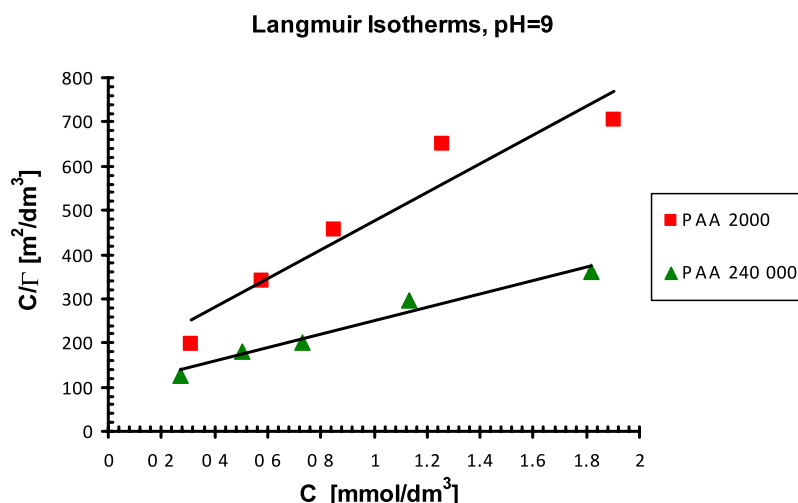


Table 3 Parameters characterizing the adsorption process of PAA on the surface of Al_2O_3 in the function of solution pH

Polymer	pH	Γ_{\max} [mol/m ²]	K [dm ³ /mol]	ΔG_{ads} [kJ/mol]
PAA 2 000	3	8.132×10^{-7}	1.559×10^5	−29.64
	6	3.115×10^{-7}	7.263×10^4	−27.75
	9	1.112×10^{-7}	5.904×10^4	−27.24
PAA 240 000	3	7.130×10^{-9}	3.009×10^7	−42.69
	6	3.461×10^{-9}	9.447×10^6	−39.82
	9	1.960×10^{-9}	5.296×10^6	−38.38

under these pH conditions with simultaneously the lowest adsorption of polymer (Fig. 7). Such stretched conformation of adsorbed chains, which interact with the solid surface through single segments, causes that the calculated values ΔG_{ads} are the lowest under these conditions.

Some information about the influence of polymer on stabilization—floculation behavior of aluminum oxide suspension in the presence and absence of PAA can be obtained analyzing the changes of surface and Al_2O_3 diffusion layer charges with and without polyacrylic acid adsorbed on its surface.

Figures 8 and 9 present the dependences of surface charge density and zeta potential of aluminum oxide in the absence and presence of PAA. Their course was discussed in detail in our earlier paper (Wiśniewska 2007a, 2007b). In this paper we only determine the effect of electrokinetic properties of the Al_2O_3 -PAA interface on the system stability.

As follows from the analysis of transmission and backscattering curves at pH = 3 (Fig. 1), Al_2O_3 suspension without the polymer is quite stable ($\text{TSI} = 13.64$). This is due to the largest relative values of the charge of surface and diffusion layers (Figs. 8 and 9) under these pH conditions which ensure electrostatic stability of Al_2O_3 suspension.

Fig. 7 Schematic presentation of solution pH effect on the structure of PAA adsorption layer on the surface of Al_2O_3

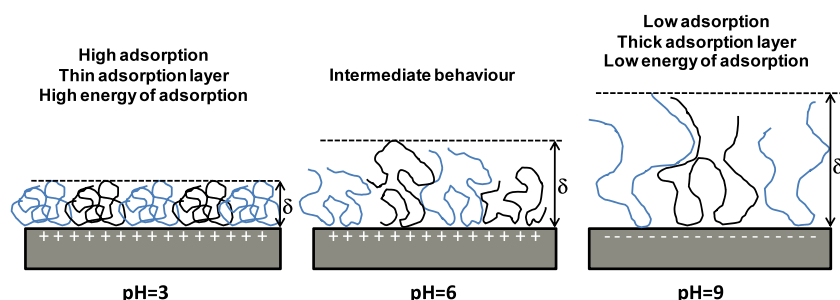


Fig. 8 Surface charge of Al_2O_3 in the presence and absence of PAA in the function of solution pH, $C_{\text{PAA}} = 100 \text{ ppm}$, 25°C

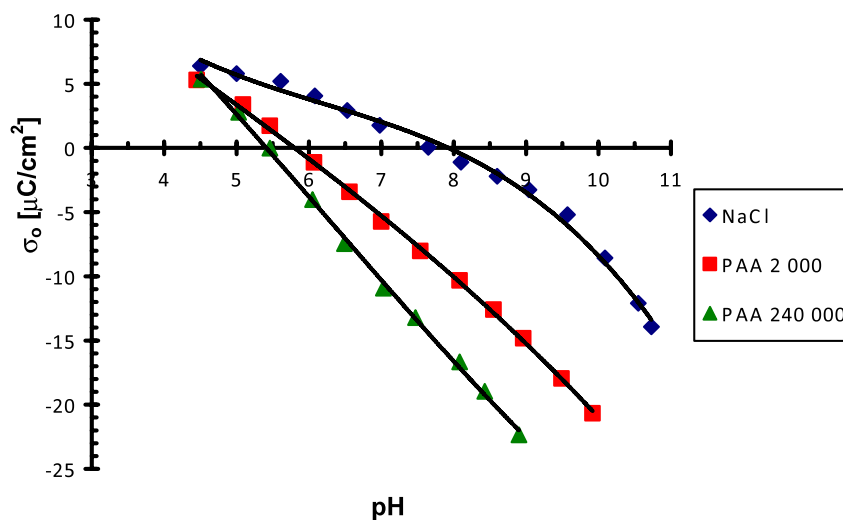
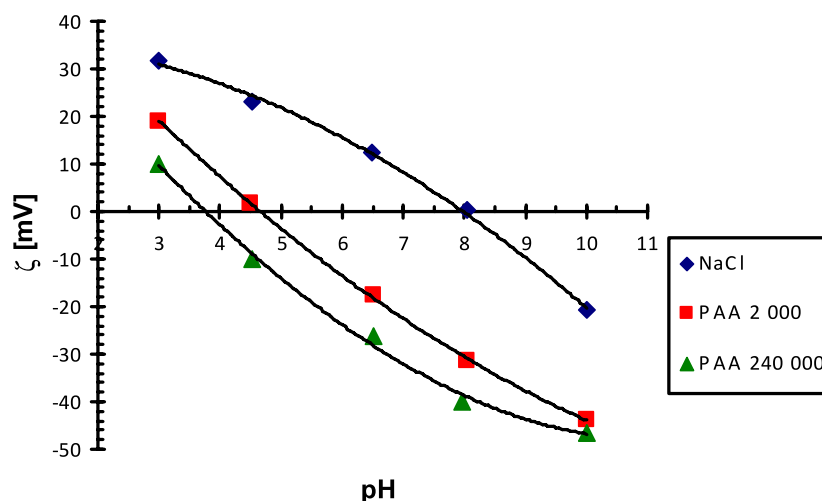


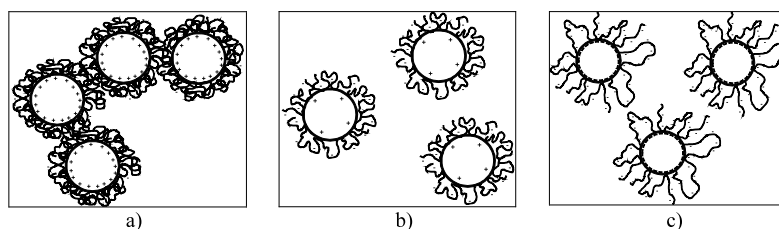
Fig. 9 Zeta potential of Al_2O_3 particles in the presence and absence of PAA in the function of solution pH, $C_{\text{PAA}} = 0.1 \text{ ppm}$, 25°C



The addition of polyacrylic acid causes rapid decrease in its stability whereby the polymer of larger molecular weight gives a better effect. The values of TSI coefficients for PAA 2000 and 240 000 are 52.81 and 74.96 respectively (Table 1). The evidence for it is appearance of a thick layer of sediment after 15 min from the beginning of measurement for PAA 2000 as well as at $t = 0$ for PAA 240 000. Moreover, along the whole length of the measuring phial there is observed clarification of solution during the experiment

(there is increase in % transmission in time) and in the case of PAA 240 000 the solution over the sediment is practically clear after 15 h (transmission along the whole length of the phial is 80%). This means that the polymer of the molecular weight 240 000 causes more effective destabilization of the suspension compared to PAA 2000. In the case of PAA of smaller molecular weight, part of aluminum oxide molecules remains in the suspension (not all undergo destabiliza-

Fig. 10 Schematic presentation of the effects largely responsible for changes in stability of Al_2O_3 suspension in the presence of PAA at different solution pH



tion) as indicated by 40% transmission at a larger height of the phial maintained for 15 h.

Destabilization of solid suspension in the presence of PAA at pH = 3 probably results from large affinity of adsorbing PAA chains for solid surface (the largest adsorption). Under these conditions attractive electrostatic interactions between the surface and the polymer occur which causes creation of compact polymer layer on the solid surface. Practically nondissociated PAA chains in adsorbed layer of one particle can interact with polymer macromolecules adsorbed on another one. As a result, there are formed large structures composed of interrelated solid particles covered with a densely packed polymer layer (Fig. 10a). Therefore under such pH conditions significant contribution to decrease in aluminum oxide suspension stability in the presence of PAA is made by bridging interactions leading to flocculation of the system. This effect is more significant in the case of PAA of larger molecular weight

From the analysis of transmission and backscattering curves at pH = 6 (Fig. 2), it can be seen that in all studied systems (without and with the polymer), sediment is formed on the bottom of the measuring phial as evidenced by the obtained backscattering peaks. The peak width is determined by the thickness of the formed sediment. In the case of Al_2O_3 suspension without the polymer, the first scan at $t = 0$ does not exhibit maximum which indicates that the suspension at the very beginning was stable. The maximum appears only after 15 minutes. However, in the presence of the polymer (both PAA 2 000 and PAA 240 000), the sediment already formed at $t = 0$. The smallest thickness of sediment was in the case of Al_2O_3 without the polymer and the largest for the suspension of aluminum oxide with adsorbed PAA 240 000.

Moreover, suspension clarification at the top of the measuring phial (transmission peak occurs) is observed in all systems. The peak width is equivalent to the thickness of clear layer. The thickest clear layer is found for the solid suspension without the polymer.

In the intermediate range of studied pH values, backscattering drops gradually during the time of experiment (i.e. 15 hours) for all systems which means that the suspension is relatively stable in this range and the rate of particles migration is not large. However, it should be stressed that changes in backscattering though slow, are of the largest importance

for the Al_2O_3 suspension without the polymer. This fact indicates that molecules sedimentation in this suspension was slower compared to that in the other systems. As follows from the data in Table 1, relatively most stable systems were obtained at pH = 6. The parameter TSI assumes the value 13.77 for the Al_2O_3 suspension without the polymer and the addition of PAA improves the system stability insignificantly. TSI assumes the values 10.65 and 10.01 in the presence of PAA 2 000 and 240 000 respectively. Steric interactions can contribute to improvement of stabilization properties of solid suspension in the presence of the polymer. The average thickness of adsorption layer and the average amount of the high-molecular compound adsorbed on the aluminum oxide surface (Table 2) probably ensure effective repulsion between Al_2O_3 molecules. The spatial obstacle in the form of loosely tangled polymer chains between them makes their direct contact impossible thus slightly improving the system stability (Fig. 10b).

However, it is quite contrary at pH = 9 (Fig. 3), when the aluminum oxide suspension with the absence of polymer is characterized by much smaller stability (TSI = 68.03) compared to pH = 3 and 6 (TSI = 13.64 and 13.77 respectively). This is caused by the fact that at these pH values absolute value of both surface and diffusion layer charges is much smaller than e.g. at pH = 3 (Figs. 8 and 9). Then the repulsive interactions between solid molecules are much weaker and not able to assure the system stability and its coagulation takes place. The addition of polymer improves significantly stability of Al_2O_3 suspension at pH = 9 (TSI = 15.41 and 14.77 for PAA 2 000 and 240 000).

Under these conditions polymer chains are completely dissociated which results in strong electrostatic repulsion between the solid particles covered with the polymer. These intermolecular repulsive interactions are still enhanced by dissociated functional groups in unadsorbed polymer chains in the solution. As a result, system stability is significantly improved both in steric and above all electric aspects (large negative charge of adsorbed PAA layer). Electrosteric interactions between Al_2O_3 particles with the adsorbed polymer are presented schematically in Fig. 10c. Measurements of stability changes carried out by means of the spectrophotometer UV Vis M42 confirm the studies of Al_2O_3 suspension stability on Turbiscan.

Figures 11–13 present the changes of Al_2O_3 suspension absorbance in the presence and absence of PAA at pH = 3,

Fig. 11 Absorbance of Al_2O_3 suspension in the presence and absence of the polymer, $C_{\text{PAA}} = 100$ ppm, $\text{pH} = 3$, 25°C

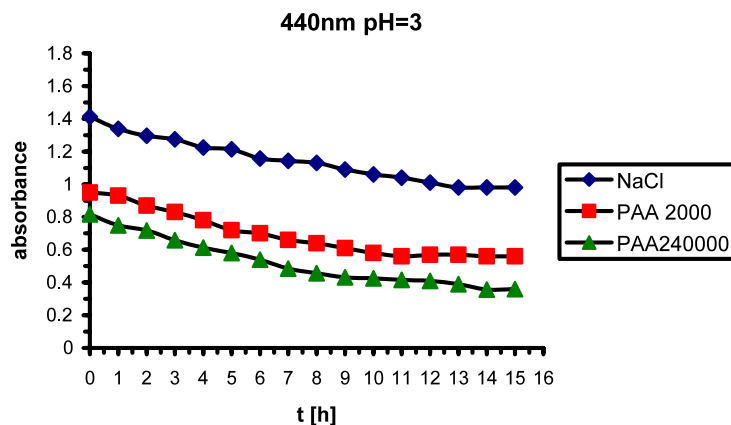


Fig. 12 Absorbance of Al_2O_3 suspension in the presence and absence of the polymer, $C_{\text{PAA}} = 100$ ppm, $\text{pH} = 6$, 25°C

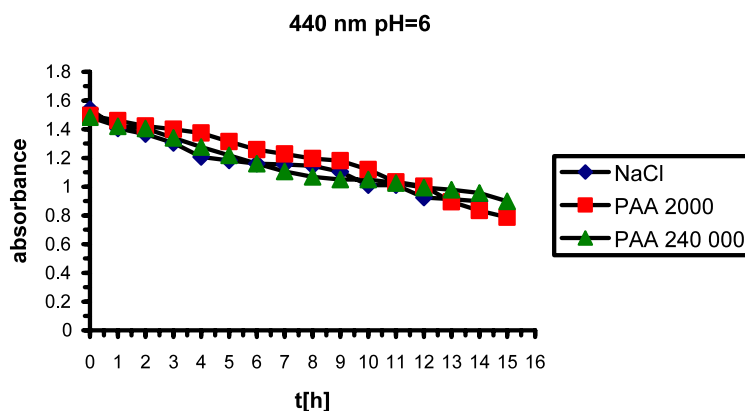
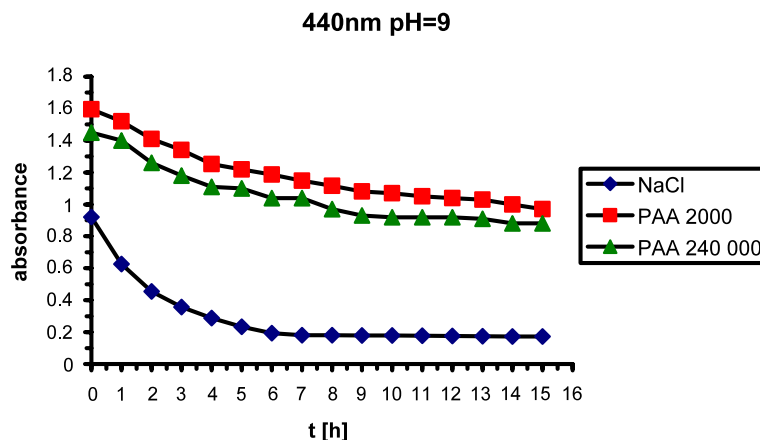


Fig. 13 Absorbance of Al_2O_3 suspension in the presence and absence of the polymer, $C_{\text{PAA}} = 100$ ppm, $\text{pH} = 9$, 25°C



6 and 9. The larger the absorbance is, the more stable system is. As follows from the figures, at $\text{pH} = 3$ the presence of polymer in the system deteriorates stability of Al_2O_3 suspension. However, at $\text{pH} = 6$ the addition of polyacrylic acid does not change suspension stability and at $\text{pH} = 9$ the addition of polymer improves it.

The results concerning the effect of PAA adsorption on stabilization-flocculation properties of Al_2O_3 suspension obtained by both methods are in good agreement.

4 Conclusions

Measurements of Al_2O_3 suspension stability in the presence and absence of polyacrylic acid made using the two methods (spectrophotometric and on Turbiscan) showed that the most stable systems occur at $\text{pH} = 6$. However, at $\text{pH} = 9$ the addition of polymer improves the system stability and at $\text{pH} = 3$ the presence of polymer significantly decreases stability of Al_2O_3 suspension. The results obtained by these methods are in good agreement.

It was shown that stabilization-flocculation properties of Al_2O_3 suspension in the presence of studied polymers depend on conformation of adsorbed macromolecules. The conformation changes with the increasing solution pH. In turn, the increase of solution pH causes drop in the PAA adsorption on the surface of Al_2O_3 and promotes formation of thicker adsorption polymer layers.

The calculated values of free adsorption energy also decrease with the increasing solution pH. The complete analysis of all obtained dependencies indicates that bridging flocculation may be responsible for destabilization of the system in the presence of PAA at pH = 3. However, insignificant increase in stability of Al_2O_3 suspension with adsorbed PAA at pH = 6 may be due to steric interactions. In turn, electrosteric forces are probably responsible for the increase in stability of aluminum oxide suspension in the presence of polymer at pH = 9.

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