

Comparative studies of adsorption mechanism and conformation of nonionic polyethylene glycol (PEG) and anionic polyacrylic acid (PAA) macromolecules on the Al_2O_3 surface; the temperature influence

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The temperature influence on the structure of adsorption layers of nonionic polyethylene glycol (PEG 2 000) and ionic polyacrylic acid (PAA 2 000) on the Al_2O_3 surface in the 15-35 °C temperature range was studied. Adsorption and viscosity measurements allowed to determine parameters characterizing macromolecule conformation in the bulk solution (R_h – hydrodynamic radius of a polymer coil in the solution) and on the solid surface (Γ – adsorbed amount, δ – thickness of adsorption layer, d – mean density of adsorption layer). Moreover, potentiometric titrations and zeta potential measurements give additional information about differences in adsorption mechanisms of nonionic PEG and anionic PAA on the alumina surface.

1. INTRODUCTION

A great interest in the phenomenon of macromolecule adsorption on the dispersed solid surface [1-3] results from wide possibilities of application of such systems in industry, agriculture and environment protection. The conformation of polymer chains at the solid-liquid interface determines the stabilization and destabilization conditions in the colloidal systems. Macromolecule conformation on the solid surface depends on both the polymer (type – ionic, nonionic; its molecular weight; polydispersity index) and adsorbent (surface charge density (pH_{pzc}), potential zeta of the solid (pH_{iep}),

purity of solid surface). Moreover, pH and ionic strength of the solution as well as temperature have a great effect on adsorption mechanism of polymer chains at the solid/liquid interface.

Of all these factors only temperature and its influence on the structure of polymer adsorption layers have not been well examined and extensively discussed in the world literature so far [4,5].

Nevertheless, temperature is a very important factor, because its change causes the change of linear dimensions of polymer chains in the solution and on the solid surface. These conformational changes can lead to stabilization or destabilization of investigated systems. What is more, many industrial processes take place at different temperatures. These processes often produce a big volume of technological wastes, which contain highly dispersed solid and macromolecular substances. For this reason, better investigating and understanding of macromolecule adsorption mechanism on the dispersed solid surface as a function of temperature has a great contribution to elaboration of more effective and efficient separation methods.

Thus, the aim of presented studies was to determine the influence of temperature on the adsorbed amounts and the surface structures of polyethylene glycol (PEG) and polyacrylic acid (PAA) macromolecules with the same weight average molecular weights on the aluminum oxide surface. Moreover, comparative analysis of obtained data allowed to determine differences in adsorption mechanisms of nonionic PEG and anionic PAA on the alumina surface.

Both used adsorbent and polymers find great practical applications in many technological and ecological processes.

Polyethylene glycol and polyacrylic acid are used in industry as stabilizers and flocculants. Production of cosmetics, pharmaceuticals, paint and paper often requires addition of polymer with small molecular weight, which causes stabilization of such a system [6]. On the other hand, usage of polymer with high molecular weight leads to flocculation of colloidal suspension which finds application in recycling of environmentally hazardous wastes, decrease of plough-lands erosion and drinking water purification [7,8]. Moreover, polyethylene glycol is used as a plasticizer and a binder in ceramic processes [9].

The alumina was chosen for studies, because it is a very popular adsorbent and catalyst (ozonation and wet air oxidation processes [10]). Its thermal stability, mechanical strength, high surface area and minute solubility decided for its great practical applications. Moreover, its properties are made use of in the removal process of dissolved hazardous organic contaminants in water treatment technology [11].

2. EXPERIMENTAL

Crystalline γ - Al_2O_3 (Merck, purity 99%) was used in the studies. To achieve the supernatant conductivity below $2 \mu\text{S}/\text{cm}$, the alumina was washed by doubly distilled water. The specific surface area of solid obtained by the BET method was $155 \text{ m}^2/\text{g}$ (ASAP 2405, Micromeritics Instruments). The mean size of Al_2O_3 particles found by electrokinetic measurements was 496 nm (Zetasizer 3000, Malvern Instruments).

The nonionic polyethylene glycol – PEG (Aldrich) and anionic polyacrylic acid – PAA (Fluka) with the same average molecular weight equal 2000 were used as adsorbents. Before experiments, polymer solutions were filtered through the cellulose membrane (Millipore) to eliminate inorganic contamination and lower polymer fractions. The membrane was characterized by NMWL (nominal molecular weight limit) equal 1000. Such NMWL represents ability of membrane to retain macromolecules larger than those of the molecular weight 1 000. All molecules of lower or equal 1000 molecular weight pass through the membrane.

Polyethylene glycol ($[-\text{CH}_2-\text{CH}_2-\text{O}-]_n$) is a nonionic polymer and its chains do not contain functional groups.

Polyacrylic acid ($[-\text{CH}_2-\text{CH}(\text{COOH})-]_n$) is an anionic polymer and its macromolecules have carboxylic groups. These groups undergo dissociation with the increasing pH. At $\text{pH}=3$ the degree of carboxylic groups dissociation (α_d) equals 0.03. Due to the fact that $\text{pK}_{\text{PAA}}=4.5$ [12], at this value of pH 50% of carboxylic groups are dissociated ($\alpha_d=0.5$). Polyacrylic acid macromolecules are totally dissociated at $\text{pH}=7.5$ ($\alpha_d=1$) [13].

All experiments (adsorption, surface charge, zeta potential and viscosity measurements) were carried out in the $15\text{--}35 \text{ }^\circ\text{C}$ temperature range. The solution of NaCl ($1 \times 10^{-2} \text{ mole}/\text{dm}^3$) was used as the supporting electrolyte.

The adsorption measurements were performed by the static method at the polymer concentration 100 ppm, $\text{pH}=6$ and with 0.04 g of Al_2O_3 . The required pH value was adjusted by the use of 0.1 and 0.01M solutions of HCl and NaOH ($\phi 360 \text{ pH}/\text{Temp}/\text{mV}$ Meter, Beckman). The obtained suspension was shaken for 24 hours in water bath OLS 200 (Grant), meanwhile checking their pH. Then, the suspension was centrifuged and 5 ml clear solution was collected for further analysis.

The concentration of polymer before and after the adsorption process was determined based on the reaction of PEG with tannic acid [14] and polyacrylic acid with hyamine [15]. Both reactions cause the solution turbidity. In the case of polyethylene glycol its solutions were stored in the dark for 1 h and for polyacrylic acid for 15 min. Then, obtained turbidities were measured at 600 nm

(PEG) and 500 nm (PAA), respectively (UV-VIS Specord M42 spectrophotometer, Carl Zeiss Jena).

The surface charge density of the alumina in the absence and presence of polymer ($C_0=100$ ppm) was determined from the potentiometric titrations. Titrations were performed in a thermostated ($25\text{ }^\circ\text{C} \pm 0.2$) Teflon vessel in the following systems: NaCl- Al_2O_3 , NaCl- Al_2O_3 -PEG and NaCl- Al_2O_3 -PAA. For this purpose, 50 ml of polymer solution in the supporting electrolyte (or only supporting electrolyte solution) was introduced into this vessel. The added values of polymer and electrolyte solutions gave their required concentrations, for PEG and PAA 100 ppm and for the electrolyte 1×10^{-2} mole/dm³. The initial pH of the solution was 3-3.5. Then, 0.2 g of Al_2O_3 was added to the investigated system. The following appliances were used for measurements: burette Dosimat 665 (Methrom), pH-meter 71 pHmeter (Beckman) connected with the computer and the printer. The solid surface charge density was calculated with the special program *Miar_t* whose author is W. Janusz.

The zeta potentials of suspensions in the presence and the absence of polymer were measured with the Zetasizer 3000 laser zetameter (Malvern Instruments). For the zeta potential measurements the suspensions containing 0.02 g of Al_2O_3 in 100 ml of the polymer solution were prepared ($C_{\text{PEG}}=100$ ppm, $C_{\text{PAA}}=0.1$ ppm). Next, the appropriate pH value (ranging from 3 to 10.5) was adjusted. All probes were thermostated at the time of their preparation by the use of water bath OLS 200 (Grant).

The thicknesses of the polymer adsorption layers (δ), as well as the values of hydrodynamic radius of a polymer coil in the solution (R_h) were determined from the viscosity measurements [16] using a CVO 50 rheometer (Bohlin Instruments). The thickness of polymer adsorption layer was calculated from the following equation:

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

where: r - radius of solid particle, ϕ_p - volume fraction of the solid in the presence of the polymer, ϕ_o - volume fraction of the solid in the absence of the polymer.

The volume fraction of the solid is related to the suspension viscosity by the Einstein equation:

$$\frac{\eta}{\eta_o} = 1 + k\phi_o \quad (2)$$

where: η – viscosity of suspension, η_o – viscosity of the liquid phase, k – Einstein coefficient.

In the case of the rigid spherical particles in infinitely dilute suspensions k is equal to 2.5. The value of the coefficient k depends on the shape and size of the colloidal particles and the suspension concentration [16]. For Al_2O_3 used in the study the value of the coefficient k was determined as 8.73.

The values of coefficient k and ϕ_p were obtained from a calibration curve. For this purpose a few suspensions of Al_2O_3 were prepared (0.5; 1; 1.5; 2; 2.5; 3; 3.5 and 4 g of the solid was added to 40 ml NaCl solutions). These suspensions corresponded to various volume fractions (ϕ_o) of alumina. Then, the required pH value was adjusted. The obtained suspensions were shaken for 24 h in water bath OLS 200 (Grant) and meanwhile their pH was checked. Then, their viscosities (η) and those of clear NaCl solution (η_o) were measured. In this way the $\eta/\eta_o=f(\phi_o)$ dependence (straight line) was obtained [16].

The η/η_o ratio in the presence of polymer was determined at the volume fraction of Al_2O_3 equal 1.26×10^{-2} . The increase of the solid particles radius in the presence of polymer (is equal to the adsorption layer thickness δ) resulted in the increase of volume fraction (ϕ_p) of the dispersed solid.

The values of the hydrodynamic radius of a polymer coil in the solution (R_h) were obtained from the dependencies:

$$R_h = f(\overline{s^2})^{1/2} \quad (3)$$

where: $(\overline{s^2})^{1/2}$ – root-mean-square radius of gyration, f – constant value irrespective of polymer molecular weight (for PEG $f=0.59$ and for PAA $f=0.66$ [17]).

$$(\overline{s^2})^{1/2} = \frac{(\overline{r^2})^{1/2}}{6^{1/2}} \quad (4)$$

where: $(\overline{r^2})^{1/2}$ – root-mean-square chain end-to-end distance.

$$(\overline{r^2})^{1/2} = \left(\frac{[\eta]M}{\phi} \right)^{1/3} \quad (5)$$

where: $[\eta]$ – intrinsic viscosity number [dm^3/g], ϕ – Flory-Fox constant approximately equal to 2.1×10^{21} , M – polymer molecular weight.

In order to determine the intrinsic viscosity number $[\eta]$, a few polymer solutions with the concentrations 50, 100, 150 and 200 ppm were prepared. The obtained solutions were shaken in the water bath and when they reached appropriate temperature, the required pH value was adjusted. Then their viscosities (η_i) and viscosities of the solvent (η_o) were measured. The reduced viscosity of each sample was calculated using the following equation:

$$\eta_r = \frac{\eta_i - \eta_o}{c} \quad (6)$$

On this basis the dependencies of reduced viscosity η_r versus the polymer concentration c were obtained. The values of intrinsic viscosity number $[\eta]$ were obtained by the extrapolation of a straight line to the concentration level equalling zero according to the equation:

$$[\eta] = \lim_{c \rightarrow 0} \eta_r \quad (7)$$

The mean densities of polymer adsorption layers (d) were calculated on the basis of the adsorbed amounts (Γ) and the adsorption layer thickness (δ) data.

3. RESULTS AND DISCUSSION

Table 1 shows the characteristics of PEG and PAA chain conformation in the solution and on the alumina surface at different temperatures. All data are calculated from the adsorption and viscosity measurements at pH=6. The same pH conditions are very important, especially in the case of anionic polyacrylic acid. Previous studies indicated that the adsorbed amount of PAA on the Al_2O_3 surface decreases with the increase of pH (from 1.25 mg/m^2 at pH=3 to 0.17 mg/m^2 at pH=9 (for 25 °C)) [18], while the PEG adsorption is practically independent of solution pH [19]. Such adsorption behaviour of polyethylene glycol is typical of nonionic polymers.

Due to the fact that PAA chains contain carboxylic groups undergoing dissociation, electrostatic interactions play an important role in the adsorption on the alumina surface.

The surface charge of alumina depends strongly also on pH of the solution. At $\text{pH} < \text{pH}_{\text{pzc}}$ ($\text{pH}_{\text{pzc}}=8$ at 25 °C) the electrostatic attractions between the partially dissociated carboxylic groups and the positively charged solid surface (adsorption increase). At $\text{pH} > \text{pH}_{\text{pzc}}$ the electrostatic repulsion between the

negatively charged totally dissociated PAA chains and the negatively charged solid surface produces lower adsorption.

Besides the electrostatic interaction, the hydrogen bridges type interactions have to be presented in the studied systems (especially at $\text{pH} > \text{pH}_{\text{pzc}}$), because adsorption of PAA takes place in the whole studied pH range. Otherwise, adsorption at $\text{pH} > \text{pH}_{\text{pzc}}$ should not occur due to strong electrostatic repulsion between the PAA chains and the alumina surface.

The comparative analysis of the adsorbed amounts of PEG 2000 and PAA 2000 indicated that for all studied temperatures PAA macromolecules have greater affinity for alumina surface (higher adsorption) than that of PEG chains. In the case of PAA macromolecules two types of forces are responsible for their adsorption on the solid surface: electrostatic interactions and hydrogen bridges type interactions, whereas PEG chains are connected with the Al_2O_3 surface only through hydrogen bonds.

The analysis of the data in Table 1 confirms that the amounts of adsorbed PEG and PAA on the Al_2O_3 surface increase with the rise of temperature. It is caused by conformational changes of polymer chains from polymer the coils (at 15°C) to the more stretched structures with long tails and loops (at 35°C). Such behavior is confirmed by thickness of the polymer adsorption layer. The polymer adsorption layers get thicker with the increasing temperature.

Tab. 1. Parameters characterizing the PEG and PAA macromolecule conformations in the bulk solution and on the Al_2O_3 surface, $C_{\text{NaCl}} = 1 \times 10^{-2} \text{ mole/dm}^3$, $C_{\text{PAA}} = 100 \text{ ppm}$, $\text{pH} = 6$.

Polymer	T [°C]	R_h [nm]	Γ [mg/m ²]	δ [nm]	$d \times 10^5$ [g/m ³]
PEG 2 000	15	1.8	0.27	1.7	1.59
	25	2.1	0.39	2.4	1.62
	35	2.4	0.46	3.3	1.39
PAA 2 000	15	2.2	0.34	1.7	2.0
	25	2.7	0.41	2.7	1.5
	35	3.1	0.66	5.1	1.29

The analysis of the parameters concerning chains in the bulk solution (R_h) and in the adsorbed polymer layer (δ) suggests that with the rise of temperature the values of these parameters increase, which means that conformations of polymer chains become more and more stretched. Moreover, the values of R_h parameter are higher than those of δ . It is due to the polymer segments interactions with the solid surface leading to flatter conformation of the adsorbed chains.

Besides, the mean density of the polymer layer (d) decreases with the rise of temperature for PAA. It confirms the assumed adsorption mechanism. The temperature increase causes more stretched conformation of the adsorbed macromolecules and decreases the mean density of the polymer layer. In the case of PEG the mean densities of the polymer layer change insignificantly. It results from the nonionic character of polyethylene glycol. The lack of electrostatic interactions in the system causes that thickness and structure of the PEG adsorption layer are not so sensitive to temperature changes compared to PAA.

Moreover, practically all parameters describing PAA chain conformation are higher than those of PEG. It is caused by the fact that the PAA chains contain carboxylic groups undergoing dissociation. At pH=6 the degree of dissociation of polyacrylic acid equals 0.97 [13]. These dissociated groups repel negatively charged groups at the solid surface and each other causing more stretched conformation of PAA chains in the bulk solution as well as at the alumina surface.

Figures 1–6 present the surface charge density and the zeta potential of the alumina without and with polymer at different temperatures.

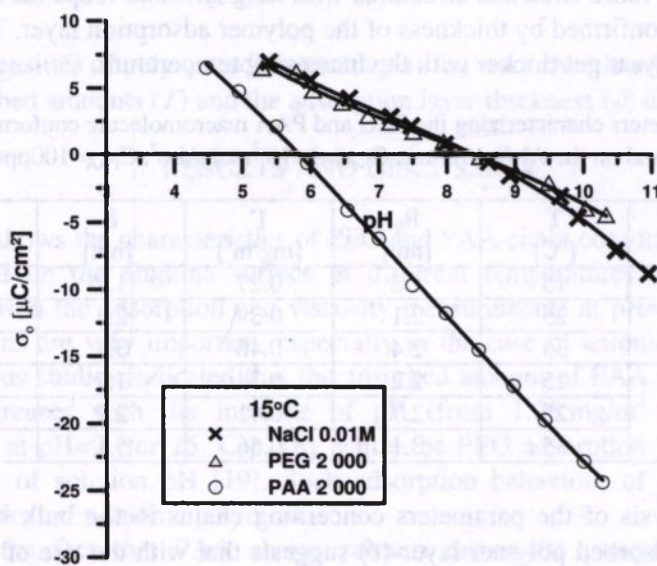


Fig. 1. The surface charge of Al_2O_3 without and with polymer at 15 °C.

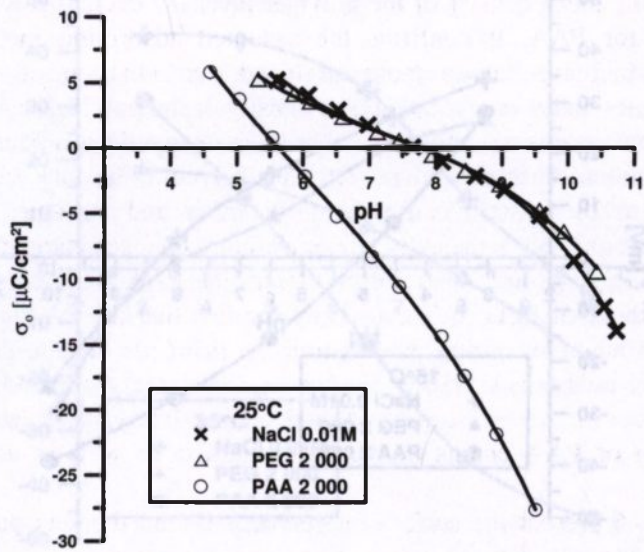


Fig. 2. The surface charge of Al_2O_3 without and with polymer at 25 °C.

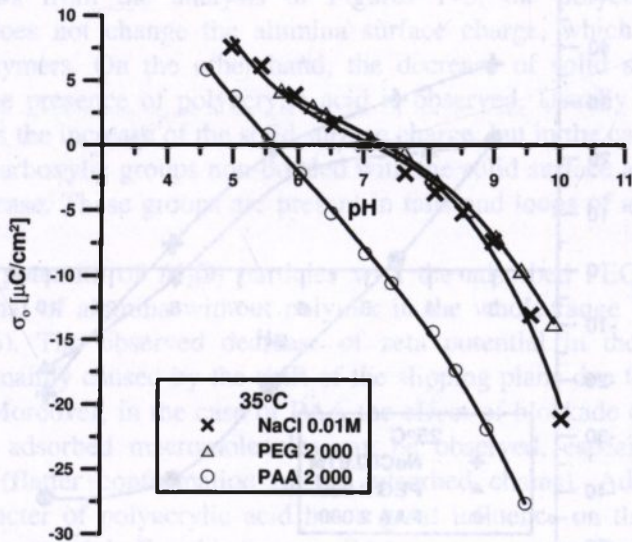


Fig. 3. The surface charge of Al_2O_3 without and with polymer at 35 °C.

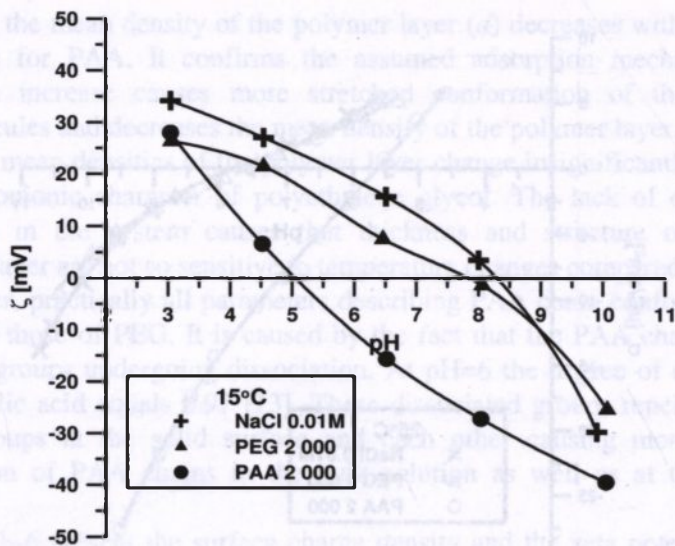


Fig. 4. The zeta potential of Al_2O_3 particles without and with polymer at 15 °C.

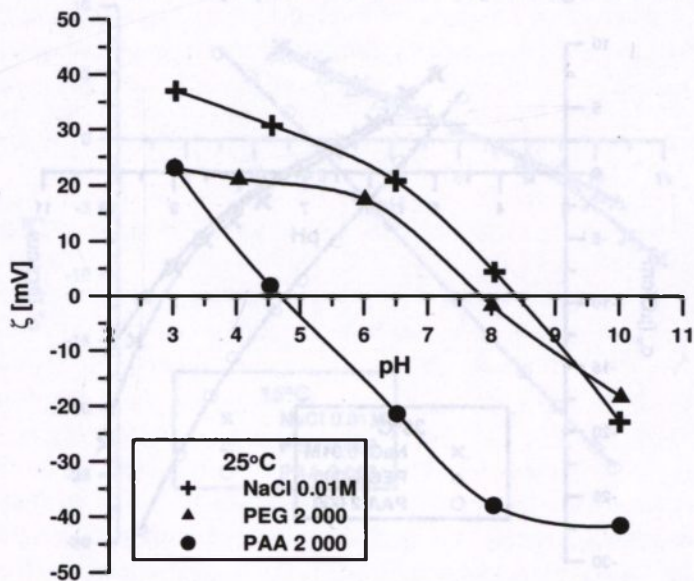


Fig. 5. The zeta potential of Al_2O_3 particles without and with polymer at 25 °C.

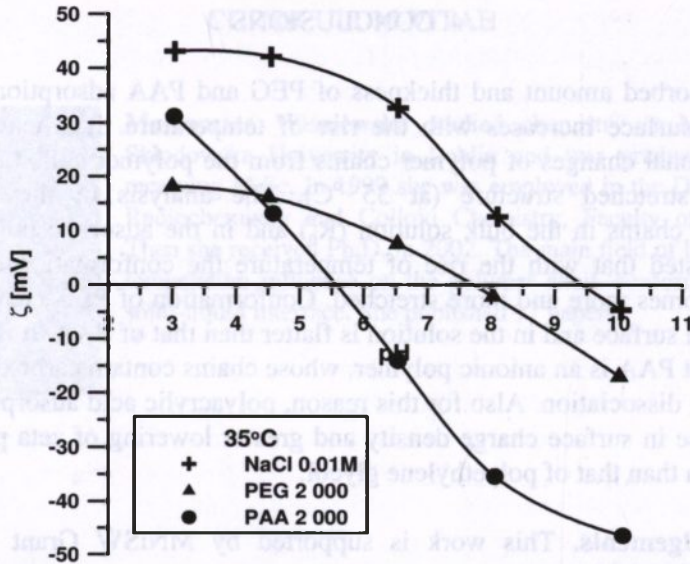


Fig. 6. The zeta potential of Al_2O_3 particles without and with polymer at 35 °C.

As follows from the analysis of Figures 1–3, the polyethylene glycol adsorption does not change the alumina surface charge, which is typical of nonionic polymers. On the other hand, the decrease of solid surface charge density in the presence of polyacrylic acid is observed. Usually adsorption of anions causes the increase of the solid surface charge, but in the case of PAA the dissociated carboxylic groups non-bonded with the solid surface are responsible for this decrease. These groups are present in tails and loops of adsorbed chain structures.

The zeta potential of Al_2O_3 particles with the adsorbed PEG and PAA is lower than that of alumina without polymer in the whole range of studied pH (Figures 4–6). The observed decrease of zeta potential in the presence of polymers is mainly caused by the shift of the slipping plane due to the polymer adsorption. Moreover, in the case of PAA the effect of blockade of solid active sites by the adsorbed macromolecules can be observed, especially at lower temperature (flatter conformation of the adsorbed chains). Additionally the anionic character of polyacrylic acid has a great influence on the decrease of diffuse layer potential. For this reason, PAA causes greater decrease of zeta potential of the solid particles than PEG.

4. CONCLUSIONS

The adsorbed amount and thickness of PEG and PAA adsorption layers on the Al_2O_3 surface increases with the rise of temperature. It is caused by the conformational changes of polymer chains from the polymer coils (at 15 °C) to the more stretched structure (at 35 °C). The analysis of the parameters concerning chains in the bulk solution (R_h) and in the adsorbed polymer layer (R_s) suggested that with the rise of temperature the conformation of polymer chains becomes more and more stretched. Conformation of PEG chains both on the alumina surface and in the solution is flatter than that of PAA. It is caused by the fact that PAA is an anionic polymer, whose chains contain carboxylic groups undergoing dissociation. Also for this reason, polyacrylic acid adsorption causes the decrease in surface charge density and greater lowering of zeta potential of the alumina than that of polyethylene glycol.

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5. REFERENCES

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