

Temperature effect on adsorption properties of silica-polyacrylic acid interface

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IVMTT2009 Special Chapter
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Abstract The temperature influence on the adsorption mechanism of anionic polyacrylic acid (PAA) macromolecules on the silica surface was studied. For this purpose, the following techniques were applied: spectrophotometry, thermogravimetry, potentiometric titration and microelectrophoresis. This method allowed to determine the adsorbed amounts of polymer, changes in thermal characteristic of silica surface with adsorbed PAA, surface charge density of the solid as well as zeta potential of SiO₂ particles in the presence and absence of polyacrylic acid. All measurements were carried out in the temperature range 15–35 °C. The free energies of adsorption were calculated from the adsorption data fitted by the Langmuir model. The obtained results of increase of PAA adsorption and its adsorption free energies with the rising temperature suggest that adsorbed polymer conformation changes from the coiled structure to more stretched one. Moreover, the polymer adsorption on the silica surface at 25 °C leads to changes in the course of thermogravimetric curves as a result of surface properties modification of the solid by bonded macromolecules.

Keywords Polyacrylic acid · Silica · Macromolecule conformation · Thermogravimetry · Adsorption free energy

Introduction

Metal oxide–polymer solution systems exist in many industrial and ecological processes. The presence of macromolecular substances in the colloidal suspension of solid particles influences the stabilization–flocculation properties of such system. These conditions depend on conformation of polymer chains both adsorbed on the solid surface and in the bulk solution. On one hand, the adsorbed polymer may cause steric stabilization or bridging flocculation of suspension. In the case of polyelectrolytes, the stabilization process can be a result of electrosteric interactions. On the other hand, the unadsorbed polymer chains may be responsible for appearing of depletion forces in the solid particle suspension (depletion stabilization and depletion flocculation processes). In addition, the combination of steric or electrosteric stabilization with depletion mechanism occurs in many colloidal systems.

The ionic polymer–metal oxide particle systems are very complex and thus the type and strength of the forces governing the adsorption process depend on many parameters associated with polymer and solid characteristics as well as solution conditions. The most important are: polymer molecular weight, its polydispersity and degree of ionization of polymer chains; surface charge density, size, shape of adsorbent particles and its purity as well as pH and ionic strength of the solution and temperature. Of all these factors, only temperature effect on adsorption behaviour of polymer is scarcely and not extensively discussed in the world literature [1–3]. Nevertheless, my previous investigations [4–6] indicated that temperature rise causes noticeable changes in adsorbing macromolecules conformation and solid surface characteristics. Thus, the temperature conditions are very important for colloidal system stability in the presence of polymer [7] and stabilization or

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destabilization effect may be achieved by proper choice of temperature range.

The polymer adsorption process on the solid surfaces finds a great application in many fields of human activity, e.g. industry, environment protection, agriculture [8–10]. The flocculation properties of macromolecules have been used in water purification, separation of hazardous solids from chemical waste, removal process of deleterious components from paper pulp, flotation, oil recovery, decrease of plough-lands erosion and mineral technology which require separation of dispersed solid from liquid phase (purification of ceramic powders). On the other hand, the stabilization process is necessary in food processing, production of cosmetics, paints, coatings and pharmaceuticals.

Due to the fact that many industrial processes take place at different temperatures, better examining and understanding of macromolecule adsorption mechanism on the dispersed solid surface as a function of temperature is essential for such applications.

Thus, the aim of this study is the determination of the temperature influence on adsorption mechanism and conformation of anionic polyacrylic acid (PAA) on the silica surface. Silica was chosen for studies because it is a very popular adsorbent with well-defined solid–liquid interface [11]. Moreover, it is widely used in production of glass, water glass, cement, ceramics, enamel and casting moulds. Silica gel (xerogel of hydrated silica) is used as a stationary phase in chromatography, as a drying agent, catalyst and catalyst carrier. Various crystallographic forms of silica find a great application in jewellery (clear quartz-mountain crystal, amethyst, citrine, rose, smoky and milky quartzes).

Experimental

The samples of silica-SiO₂ (Merck) were used in the studies. The solid was washed with doubly distilled water to achieve the supernatant conductivity of less than 2 μS cm⁻¹. Silica was characterized by the BET surface area equal to 326 m² g⁻¹. This parameter was determined from the low temperature nitrogen adsorption–desorption method using the automatic adsorption analyzer ASAP 2405 (Accelerated Surface Area and Porosimetry) produced by Micromeritics Instruments.

The samples of polyacrylic acid (PAA; Fluka) with the following weight average molecular weights: 2000, 60000 and 240000 were used in the study. All polymer solutions were filtered through the cellulose membranes (Millipore) to eliminate inorganic contamination and lower polymer fractions.

All measurements were carried out in the temperature range 15–35 °C chosen due to the fact that the θ

temperature for the aqueous polyacrylic acid solutions equals 14 °C [12]. NaCl solution (1 × 10⁻² mol dm⁻³) was used as the supporting electrolyte.

The adsorption measurements at pH = 6 were taken with the static method in the polymer concentration range 10–200 ppm and with 0.03 g of SiO₂. The pH of solutions was set by the use of pH-meter ϕ 360 (Beckman) as well as of HCl and NaOH solutions. The prepared suspensions were shaken in water bath (OLS 2000, Grant) for 24 h and meanwhile the pH of solutions was checked. Then, the suspensions were centrifuged, and 5 mL of the clear polymer solutions were collected for further analysis. The amount of the polymer adsorbed was determined from the difference between the PAA concentration in the solution before and after the adsorption process. The concentration of polymer was determined from the reaction of polyacrylic acid with hyamine proposed by Crummet and Hummel [13]. The obtained turbidity was measured with the UV–VIS Specord M42 spectrophotometer (Carl Zeiss Jena) at the wavelength 500 nm.

The experimental adsorption isotherms were fitted by the Langmuir adsorption model according to the equation:

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

where c equilibrium concentration of the polymer in the solution/mol dm⁻³, K the Langmuir adsorption constant/dm³ mol⁻¹, Γ adsorbed amount of the polymer on the solid surface/mol m⁻², Γ_{\max} maximum adsorbed amount corresponding to the totally filled monolayer (monolayer capacity)/mol m⁻².

The linear relationships were obtained (Γ/c vs. c) for each molecular weight of PAA. The values of K and Γ_{\max} were determined from the intercept and gradient of these plots, respectively.

The free energies of adsorption (ΔG_{ads}) were calculated from the following equation:

$$\Delta G_{\text{ads}} = -RT \ln K \quad (2)$$

where R gas constant –8.314 J K⁻¹ mol⁻¹, T temperature/K.

The obtained results are placed in Table 1.

The thermogravimetric analysis of the samples was performed on a derivathograph Q-1500D (MOM Hungary). The TG and DTG curves were measured in the temperature range 20–1000 °C with a furnace-heating rate of 10 °C min⁻¹. The probes for these measurements were prepared by adding 0.45 g of SiO₂ to 150 mL of NaCl or NaCl with PAA ($C_{\text{PAA}} = 100$ ppm) solutions. Then, these suspensions were shaken in water bath for 24 h at 25 °C and at pH = 6. Next, these probes were centrifuged. The solid with or without polymer was dried and collected for further thermogravimetric analysis.

Table 1 Parameters characterizing adsorption process of PAA on the SiO₂ surface as a function of temperature, C_{NaCl} = 1 × 10⁻² mol dm⁻³, pH = 6

Polymer	N _{segm}	T/°C	Γ _{max} /mol m ⁻²	K/dm ³ mol ⁻¹	ΔG _{ads} /kJ mol ⁻¹
PAA 2000	28	15	7.469 × 10 ⁻⁷	1.926 × 10 ³	-18.12
		25	2.516 × 10 ⁻⁷	1.069 × 10 ⁴	-23.00
		35	2.096 × 10 ⁻⁷	2.151 × 10 ⁴	-25.56
PAA 60000	833	15	8.655 × 10 ⁻⁹	2.971 × 10 ⁵	-30.19
		25	7.747 × 10 ⁻⁹	5.329 × 10 ⁵	-32.65
		35	7.096 × 10 ⁻⁹	8.896 × 10 ⁵	-35.10
PAA 240000	3333	15	2.636 × 10 ⁻⁹	1.544 × 10 ⁶	-34.14
		25	2.607 × 10 ⁻⁹	2.001 × 10 ⁶	-35.97
		35	2.400 × 10 ⁻⁹	3.084 × 10 ⁶	-38.28

N_{segm} number of segments in single polymer chain

The surface charge density of silica in the absence and presence of polymer was determined from the potentiometric titrations. For this purpose, 50 mL of polymer solution in supporting electrolyte (or only the supporting electrolyte solution) was put into the Teflon vessel. The added volumes of polymer and electrolyte solutions led to their required final concentrations (C_{PAA} = 100 ppm and C_{NaCl} = 1 × 10⁻² mol dm⁻³). Initial pH of the solution (3-3.5) was adjusted by the use of HCl (1 × 10⁻¹ mol dm⁻³). 0.1 g of the solid was added into the prepared solutions. The following appliances were used for the potentiometric titrations: a burette Dosimat 665 (Methrom), thermostat RE204 (Lauda), a 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 the silica particles in the presence and absence of PAA were measured with the Zetasizer 3000 laser zetameter (Malvern Instruments). There was prepared a suspension containing 0.05 g of SiO₂ in 500 mL of the supporting electrolyte or polymer solution (C_{PAA} = 0.01 ppm). This suspension was sonicated (ultrasonic processor XL, Misonix) and divided into 8 parts of 60 ml volume. Next, the appropriate pH value (ranging from 3–10) was adjusted in each sample. All the samples were thermostated at the time of their preparation.

Results and discussion

Due to the fact that polyacrylic acid is an anionic polymer, the solution pH has the significant influence on its adsorption on the silica surface. Figure 1 presents the adsorbed amounts of PAA as a function of solution pH at 25 °C. For all examined molecular weights of PAA, the

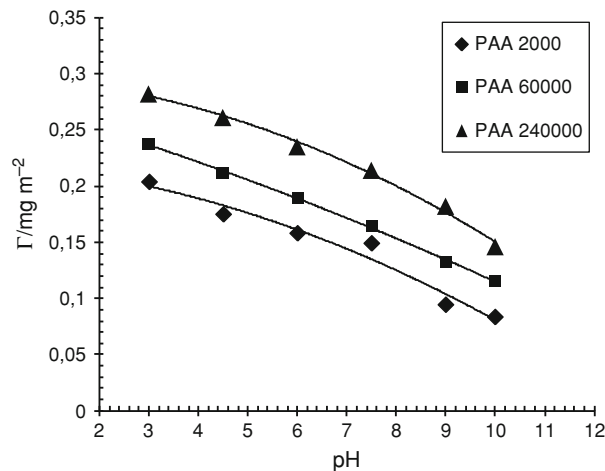


Fig. 1 Adsorbed amounts of PAA on the SiO₂ surface as a function of solution pH, C_{NaCl} = 1 × 10⁻² mol dm⁻³, C_{PAA} = 100 ppm, 25 °C

adsorbed amounts decrease with the increasing pH of the solution.

The analysis of degree of ionization of PAA carboxylic groups and the solid surface charge (Figs 2, 3, 4) with the rise of pH is necessary to explain the obtained dependencies. The increase of pH causes the dissociation of PAA functional groups. The degree (α_d) of their groups dissociation at pH = 3 equals 0.03. At pH = 4.5 (pK_{PAA} = 4.5 [14]) α_d = 0.5 and at pH = 7.5 practically all carboxylic groups in the PAA chains are dissociated (α_d = 0.999).

On the other hand, pH_{pzc} of silica equals approximately 3 for all examined temperatures (Figs 2, 3, 4). It means that the surface of SiO₂ is negatively charged in the whole studied pH range changing from 3 to 10. For example, at 25 °C (Fig. 3), the surface charge density of the silica ranges from -0.2 (at pH = 3.2) to -15 μC cm⁻² (at pH = 10). In such situation, the electrostatic repulsion between the solid surface and PAA chains appears.

pH increase causes the decrease of polymer adsorption because repulsion between the dissociated carboxylic

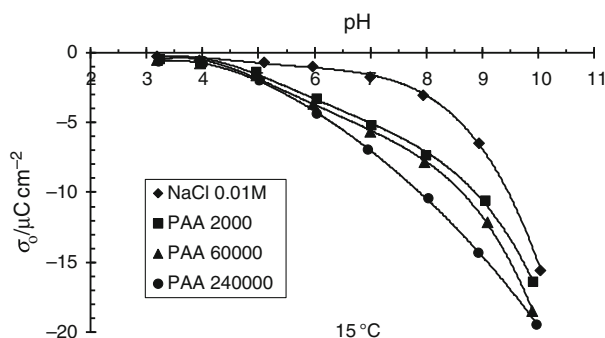


Fig. 2 Surface charge density of SiO₂ in the presence and absence of PAA as a function of the solution pH at 15 °C, C_{NaCl} = 1 × 10⁻² mol dm⁻³, C_{PAA} = 100 ppm

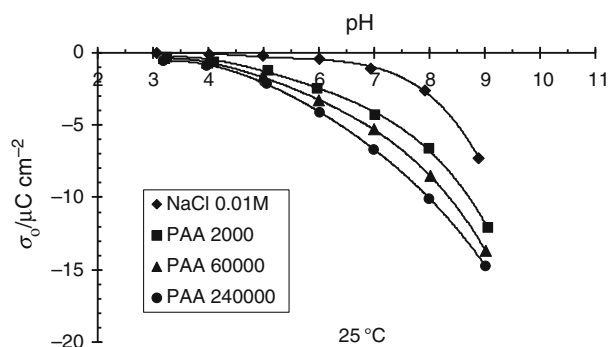


Fig. 3 Surface charge density of SiO₂ in the presence and absence of PAA as a function of the solution pH at 25 °C, $C_{\text{NaCl}} = 1 \times 10^{-2}$ mol dm⁻³, $C_{\text{PAA}} = 100$ ppm

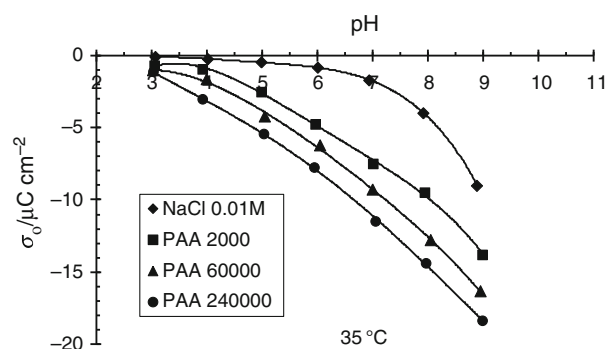


Fig. 4 Surface charge density of SiO₂ in the presence and absence of PAA as a function of the solution pH at 35 °C, $C_{\text{NaCl}} = 1 \times 10^{-2}$ mol dm⁻³, $C_{\text{PAA}} = 100$ ppm

groups in PAA macromolecules and the negatively charged silanol groups on the solid surface is strong. Despite this fact, adsorption of polyacrylic acid on the silica surface occurs in the whole range of pH, even at the highest values of pH. As follows, different non-electrostatic forces have to be responsible for PAA adsorption process on the SiO₂ surface. Otherwise, the adsorption of negatively charged polymer chains on the negatively charged solid surface should not take place.

Besides pH, temperature influences the adsorption process of polyacrylic acid on the SiO₂ surface.

Figures 5, 6, 7 present the adsorption isotherms of PAA on the silica surface at 15, 25 and 35 °C. These adsorption measurements were carried out under the same pH conditions (pH = 6). The analysis of these isotherms leads to the conclusion that polymer adsorption on the solid surface increases with the temperature rise for all examined molecular weights of PAA.

The obtained isotherms were fitted to the Langmuir adsorption model according to Eq. 1. These linear dependencies enable calculation of the free energies of polymer adsorption from Eq. 2. The obtained results are placed in Table 1 where the values of free energy of PAA adsorption

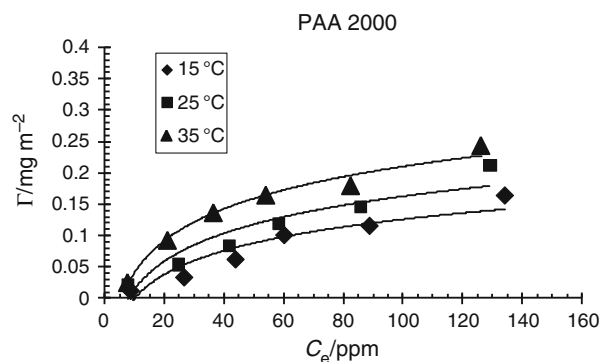


Fig. 5 Adsorption isotherms of PAA 2000 on the SiO₂ surface for different temperatures, $C_{\text{NaCl}} = 1 \times 10^{-2}$ mol dm⁻³, pH = 6

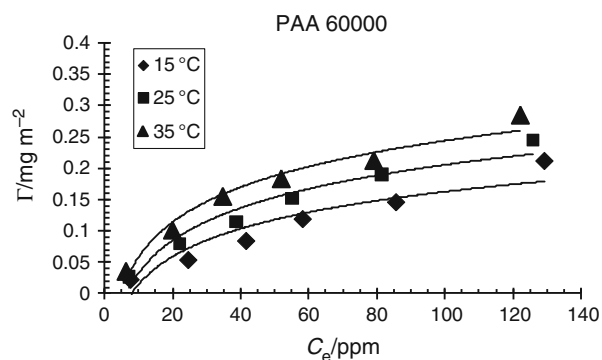


Fig. 6 Adsorption isotherms of PAA 60000 on the SiO₂ surface for different temperatures, $C_{\text{NaCl}} = 1 \times 10^{-2}$ mol dm⁻³, pH = 6

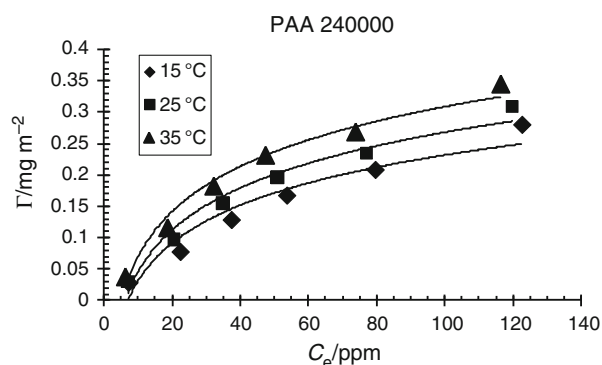


Fig. 7 Adsorption isotherms of PAA 240000 on the SiO₂ surface for different temperatures, $C_{\text{NaCl}} = 1 \times 10^{-2}$ mol dm⁻³, pH = 6

on the silica surface (ΔG_{ads}^0) increase with the increasing temperature. Moreover, the calculated values of ΔG_{ads}^0 ranging from -18.12 kJ mol⁻¹ (for PAA 2000 at 15 °C) to -38.28 kJ mol⁻¹ (for PAA 240000 at 35 °C) correspond to the energies of hydrogen bridges creation. The mean energy of these interactions was in the range of 12–33 kJ mol⁻¹ [15]. The hydrogen bonds can be created between both neutral ($\equiv \text{SiOH}$) and charged ($\equiv \text{SiO}^-$, $\equiv \text{SiOH}_2^+$) silanol groups.

The obtained increase in PAA adsorption on the silica surface and its adsorption free energy with the increasing temperature results from the changes of polymer adsorption layer structure which is determined by specific conformation of adsorbed polymer macromolecules.

At 15 °C (very close to θ temperature of PAA solution), the polymer chains are maximally coiled [16]. It is caused by the fact that under such temperature conditions the interaction energy between the polymer segments and the solvent molecules is the same as that between the segment-segment and the solvent-solvent. The θ solvent (at θ temperature) is characterized by ideally bad quality. Polymer coils are often called the Gaussian coils because their linear dimension can be described by the statistical Gauss theory. These coiled polyacrylic acid macromolecules adsorb on the silica surface causing the effect of blockade of solid active sites. Thus, the adsorption process of other macromolecules becomes impossible. This limited access of PAA to the SiO₂ surface results in the situation in which a smaller number of polymer segments can be bound with the solid surface. As a result at 15 °C, the obtained adsorbed amounts and free energies of adsorption are small.

When temperature increases, the solvent quality usually improves. The attractive interactions between the polymer segments and the solvent molecules start playing a dominant role. As a consequence, the polymer chain conformation at the interface is more stretched due to coils developing. Thus at 35 °C, the polymer adsorption layers are composed of long tail and loop structures, expanding in solution perpendicularly to the solid surface. Such stretched conformation of adsorbed PAA chain does not consume many solid active sites. It gives possibility of adsorption of a greater number of other macromolecules because the accessible surface area is larger. For this reason, a greater number of polymer chains can adsorb on the same surface unit in comparison to flatter conformation at 15 °C. It results in large adsorption and large values of free energy of polymer adsorption.

Very important information, which can supplement description of the adsorption mechanism of PAA chains on the silica surface, may be obtained from thermogravimetric measurements. Figures 8 and 9 present the TG and DTG curves for the SiO₂-NaCl, SiO₂-NaCl-PAA 2000 and SiO₂-NaCl-PAA 240000 systems, for which the adsorption process of PAA was carried out at 25 °C. The thermal characteristics of the investigated systems are also placed in Table 2. The analysis of the TG and DTG curves for the silica samples without PAA indicates that the heating process in the range of 20-900 °C results in two stages. The first one (20-200 °C) is associated with desorption of hygroscopically and physically adsorbed water as well. It is the endothermic process with a minimum at 100 °C on the

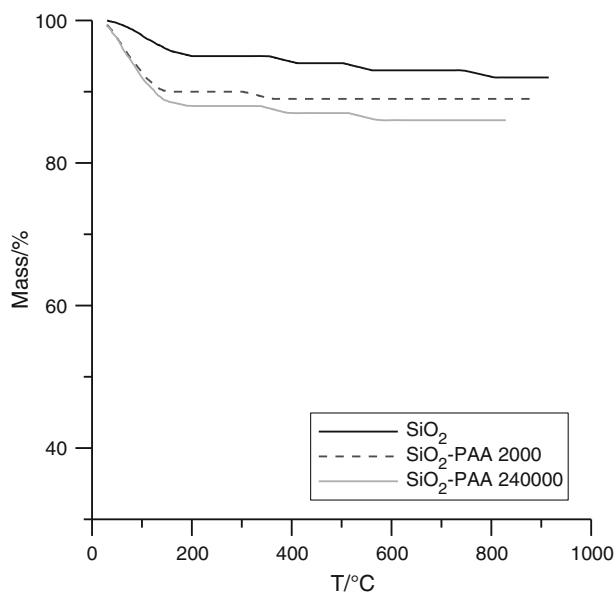


Fig. 8 TG curves for: (a) SiO₂-NaCl, (b) SiO₂-NaCl-PAA 2000 and (c) SiO₂-NaCl-PAA 240000 systems, $C_{NaCl} = 1 \times 10^{-2}$ mol dm⁻³, $C_{PAA} = 100$ ppm, pH = 6, 25 °C

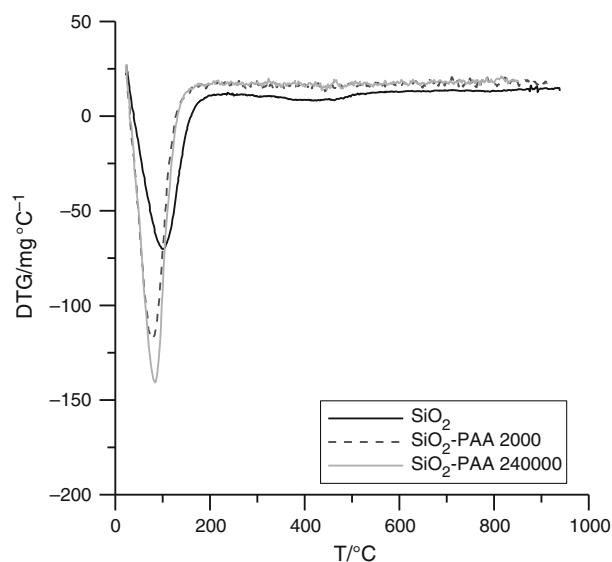


Fig. 9 DTG curves for: a) SiO₂-NaCl, b) SiO₂-NaCl-PAA 2000 and c) SiO₂-NaCl-PAA 240000 systems, $C_{NaCl} = 1 \times 10^{-2}$ mol dm⁻³, $C_{PAA} = 100$ ppm, pH = 6, 25 °C

DTG curve. The other one (200-900 °C) corresponds to the desorption of structural water resulting from silanol condensation of -OH surface groups. The obtained dependencies are in good agreement with literature data [17].

The adsorption of PAA causes both changes in the surface characteristics of silica and the thermal stability of these systems. Similarly, to silica without polymer, for the SiO₂-PAA systems, two characteristic temperature ranges

Table 2 Thermal behaviour of SiO₂-NaCl, SiO₂-NaCl-PAA 2000 and SiO₂-NaCl-PAA 240000 systems, $C_{\text{NaCl}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{PAA}} = 100 \text{ ppm}$, pH = 6

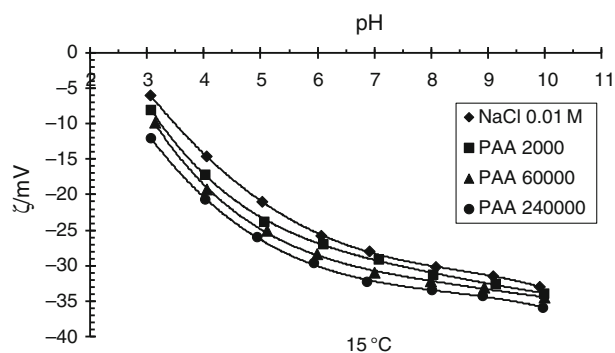
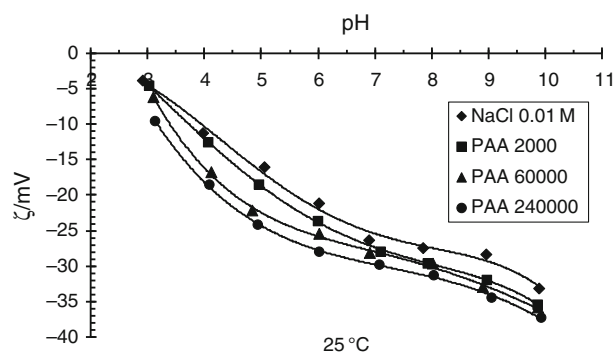
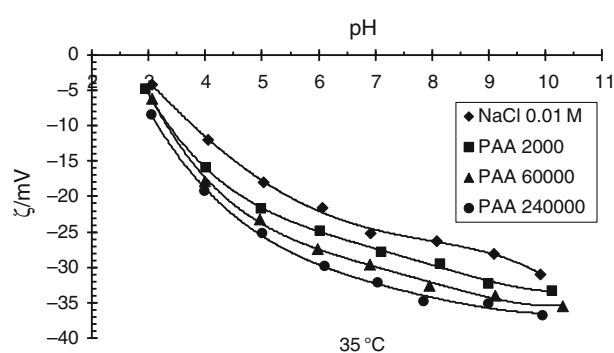
System	DTG peak/°C	Exo↑/endo↓	Mass losses at temperatures/%	
			20-200 °C	200-900 °C
SiO ₂ -NaCl	100	↓	5	3
SiO ₂ -NaCl-PAA 2000	80	↓	9	2
SiO ₂ -NaCl-PAA 240000	84	↓	11	3

can be distinguished. In the temperature range 20–200 °C, the mass losses on the TG curves are significantly higher (about 50%) than or silica without PAA. It can be caused by the loss of weakly bounded silanol groups, which changes of the solid properties from hydrophilic to hydrophobic ones. The peak shift towards a lower temperature (80–84 °C), results from weaker interactions of water molecules with the solid surface and competition between the polymer chains and the water macromolecules for active sites on the adsorbent surface. The polymer carboxylic groups create hydrogen bridges with the silanol groups of silica, but not all polymer functional groups are bonded with the solid surface. The great number of them, existing in tail and loops structures of adsorbed macromolecules, are not bounded with the adsorbent surface. These unadsorbed carboxylic groups can create the hydrogen bridges with the water molecules from solution. The heating of such systems causes removing process of them. For this reason, the dehydroxylation is considerably bigger (greater peak on the DTG curve). This effect is more pronounced in the case of higher molecular weight of PAA (240000), which is connected with the greater number of functional groups in longer polymer chains. In the temperature range 200–900 °C the changes in thermal characteristics of silica in the presence of polymer are noticeably smaller. The changes obtained on the TG and DTG curves in the case of SiO₂-PAA systems are connected with the changes in a number and nature of solid active sites.

Moreover, the process of blockade of pores by the adsorbed polymer takes place, which causes the decrease of the solid specific surface area, similarly to proteins [18].

The analysis of changes of the surface and diffuse layer charge densities of SiO₂ in the presence of PAA can be very helpful for determination of polymer chain conformation on the silica surface.

Therefore potentiometric titrations and zeta potential measurements of SiO₂ without and with polyacrylic acid at 15, 25 and 35 °C were carried out. The obtained data are presented in Figs 2, 3, 4, 10, 11 and 12, respectively.

**Fig. 10** Zeta potential of SiO₂ particles in the presence and absence of PAA as a function of the solution pH at 15 °C, $C_{\text{NaCl}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{PAA}} = 0.01 \text{ ppm}$ **Fig. 11** Zeta potential of SiO₂ particles in the presence and absence of PAA as a function of the solution pH at 25 °C, $C_{\text{NaCl}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{PAA}} = 0.01 \text{ ppm}$ **Fig. 12** Zeta potential of SiO₂ particles in the presence and absence of PAA as a function of the solution pH at 35 °C, $C_{\text{NaCl}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{\text{PAA}} = 0.01 \text{ ppm}$

The analysis of potentiometric titration results (Figs 2, 3, 4) indicates that for all examined temperatures, the surface charge of SiO₂ is negative in the whole studied pH range both in the absence and presence of PAA. Moreover, the adsorption of polyacrylic acid causes the decrease of the silica surface charge. This effect is the greatest in the case of the highest molecular weight of polymer.

Despite the fact that the adsorption of anions causes usually the increase of the solid surface charge density, in the case of anionic PAA, the decrease of the silica surface charge was obtained. Dissociated carboxylic groups of the adsorbed polymer chains not undergoing bonding with the solid surface are responsible for this decrease. These groups are placed at the interface in the tail and loop structures of adsorbed macromolecules.

Obviously, the effect of lowering the solid surface charge is the most pronounced in the case of the largest molecular weight of polymer, because the number of not bonded dissociated carboxylic groups at the interface is the biggest.

The adsorption increase and more stretched conformation of adsorbed macromolecules with the rising temperature produce a greater number of polymer carboxylic groups in the surface area. Thus, the negative charge, coming from them causes the most considerable decrease of the silica surface charge in the presence of PAA at 35 °C.

Figures 10, 11, 12 present the zeta potential of SiO₂ particles in the presence and absence of PAA at 15, 25 and 35 °C.

As can be seen, the potential zeta of solid particles both without and with polymer adsorbed on their surface is negative in the whole studied pH range. Moreover, polyacrylic acid adsorption results in lowering of zeta potential of the silica.

The main reason for the decrease of zeta potential of SiO₂ particles with the adsorbed polymer is an anionic character of polyacrylic acid and the presence of dissociated carboxylic groups of adsorbed chains in the diffuse layer. Besides, the effects of blockade of the solid active sites by adsorbed macromolecules and the shift of slipping plane may be responsible for the changes of the silica zeta potential. The first one is more probable at a low examined temperature, at which the adsorbed polymer chains are coiled. It limits possibility of adsorption of other polymer chains and electrolyte ions, which influences the charges composition in the slipping plane. On the other hand, at higher temperature the effect of the slipping plane shift becomes dominant. At this temperature, the conformation of the adsorbed macromolecules is more stretched. The polymer adsorption layer is rich in loop and tail structures. It leads to significant shift of the slipping plane and reduction of the zeta potential.

In addition, the polyacrylic acid adsorption causes the greatest decrease in zeta potential of the silica particles at 35 °C. Similarly to the solid surface charge, the stretched conformation of the adsorbed macromolecules leading to the largest adsorbed amounts at higher temperature results in the presence of a greater number of dissociated carboxylic groups of PAA chains in the diffuse layer. Their negative charge causes the most noticeable reduction of the silica zeta potential in the presence of PAA at 35 °C.

Conclusions

The temperature increase in the range of 15–35 °C causes the conformational changes of polyacrylic acid macromolecules adsorbed on the silica surface. Their conformation changes from the polymer coils (at 15 °C) to the stretched structure (at 35 °C). These changes in linear dimensions of adsorbed PAA chains lead to the increase of the adsorbed amounts and free energies of adsorption (ΔG_{ads}^0) with the rising temperature.

The analysis of the calculated values of (ΔG_{ads}^0) proves that hydrogen bridge type interactions are responsible for the adsorption process of polyacrylic acid macromolecules on the SiO₂ surface.

The changes obtained on the thermogravimetric curves for SiO₂–PAA systems are connected with the changes in a number and nature of solid active sites and the blockade of pores by the adsorbed polymer resulting in decrease of the solid specific surface area. The nonbounded functional groups of polymer in tail and loop structures of adsorbed macromolecules are responsible for significant dehydroxylation effect of the systems in the presence of PAA.

The main reason for reduction of the silica surface charge and its zeta potential in the presence of PAA is an anionic character of polymer. Dissociated carboxylic groups of polyacrylic acid are placed in the surface and diffuse layers with tail and loop structures of adsorbed macromolecules. Moreover, the effect of blockade of the solid active sites by the adsorbed polymer chains has some influence on electrokinetic properties of the investigated systems at 15 °C (polymer coils adsorption). At 35 °C the effect of the shift of slipping plane, caused by the adsorption of stretched polymer chains, is dominant.

Acknowledgements This work was supported by MNiSW Grant N204 071 32/1869 in years 2007–2010.

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