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Influence of a Type of Electrolyte and its Ionic Strength on the Adsorption and the Structure of Adsorbed Polymer Layer in the System: Polyacrylic Acid/SiO$_2$

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Abstract. The influence of ionic strength and the molecular weight of polyacrylic acid (PAA) on its adsorption and the structure of adsorbed polymer layer on SiO$_2$ surface in the presence NaCl and CaCl$_2$ was measured. Thickness of PAA adsorption layers on the SiO$_2$ surface in these two electrolytes were also measured as well as the expansion coefficient (α) of PAA in CaCl$_2$. The increase of: ionic strength, pH, and the polymer molecular weight causes the increase of PAA adsorption layers thickness. However, PAA expansion coefficient increases with the increase of pH and the polymer molecular weight, but decreases with the increase of ionic strength. The influence of a type of electrolyte and its ionic strength on the zeta potential of SiO$_2$ in the presence of polyacrylic acid (PAA) was measured. As it was observed, the zeta potential is much lower in CaCl$_2$ solution in comparison to the zeta potential in NaCl.

Keywords: polymer adsorption, polymer conformation, adsorption layer thickness, polyacrylic acid, ionic strength

INTRODUCTION

A mechanism of polymers adsorption on a solid surface is a very sophisticated process, determined by very different factors. The most important ones are: character of interactions between the adsorbent and the adsorbat, polydispersity of used polymer, the presence of inorganic impurities, which may block active centres on the oxide surface, a type of used electrolyte, ionic strength and pH of the solution. The determined polymer conformation on the interface is a result of the influence of above-mentioned factors on the adsorption process. It is the polymer conformation, which indicates both the amount of adsorbed polymer and the thickness of adsorption layer. Researches of the polymer adsorption on solid surfaces are carried out in two aspects: theoretical and practical one.[1–3] The interest in the polymers adsorption on the metal oxide/polyelectrolyte solution interface results from the fact that the polymer adsorption is completely different from the adsorption of small particles and ions. Polymer chains may form lots of different conformations in both the bulk phase and the interface, while the ions and the small particles have invariable, defined shape.[4] The practical aspect of the polymer adsorption on the solid surface is associated with the polymer usage in the stabilisation and flocculation processes. So-called sterical stabilisation of the system is caused by addition of low-molecular weight polymer into the dispersion. This process can be applied in the production of: drugs, cosmetics, paints, varnishes and also in the production of paper. On the other hand, high molecular weight polymers adsorbed onto colloid particles cause their flocculation. This process is widely used in utilisation of industrial wastes occuring as water suspensions.

The aim of this paper was to define the influence of a type of electrolyte, ionic strength, pH of the solution on polyacrylic acid (PAA) adsorption on SiO$_2$ surface. Some additional information about the polymer conformation at the interface were obtained by measuring the thickness of PAA adsorption layer on SiO$_2$ surface as well as the expansion coefficient (α) of PAA macromolecules.

SiO$_2$ was used as an adsorbent in all measurements. This oxide takes up very special place among inorganic adsorbents.[5] The amount of its production as well as the range of its applications is much wider in comparison to other oxide adsorbents. This fact results from both SiO$_2$ high mechanic hardness and its low

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sensitivity to the temperature changes. Moreover, SiO_2 is chemically neutral. This feature lets using it as an adsorbent in the adsorption processes of many chemical compounds. Owing to its properties, SiO_2 is one of the most popular used carriers for chemical seeds. What is more, silica has the well-defined interface: SiO_2/polyelectrolyte solution as well as stability in a broad pH range.

Polyacrylic acid was used as a polyelectrolyte in all measurements. This polymer was chosen with a view to the wide spectrum of its applications.[6] It is used as a supplement to surfactants, compound used in the production of paper, inhibitor of fur formation, concentrators in cosmetics and components of drugs: artificial tears.

EXPERIMENTAL

In all measurements SiO_2 produced by POCh-Gliwice was used as an adsorbent. The specific surface area of silica, calculated using the BET (Brunauer, Emmet, Teller) method was $132\ m^2\ g^{-1}$. Before the measurements SiO_2 was washed by doubly distilled water to the conductivity of the supernatant smaller than $2\ \mu S\ cm^{-1}$. The electron microscopy was used to estimate the SiO_2 particles size and shape. The average SiO_2 particles diameter was 460 nm. All particles were of spherical shape.

NaCl as well as $CaCl_2$ were used as background electrolytes. As a polyelectrolyte polyacrylic acid (molecular weights: 2 000 and 60 000) produced by Aldrich was used. All measurements were made at 25 °C.

The adsorption of PAA (Γ, expressed in $mg\ m^{-2}$) in the mass fraction range from 30 ppm to 200 ppm on SiO_2 surface was carried out using the static method[7,8] presented below.

Into the Erlenmeyer flasks, which contained 10 ml of the polymer solution (chosen concentration of the polymer, electrolyte and pH) SiO_2 was added. These suspensions were shaken for 24 hours. Then silica was centrifuged and 5 ml of the clear solution were taken for further analysis. The adsorption was calculated from the difference between PAA concentration before and after the adsorption. The base of that was the reaction between polyacrylic acid and hyamine, proposed by Crumette and Hummel.[9] The absorbance that increases after hyamine addition to the solution was measured turbidimetrically using a spectrophotometer (Specord M42, Carl Zeiss) with a special computer programme M500. The used wavelength was 500 nm.

PAA expansion coefficient (α) in the presence of $CaCl_2$ as a background electrolyte was determined using the viscosity method.[10] Viscosity of the polymer solutions with various mass fractions (50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm) was measured by a rotational viscometer (CVO 50, Bohlin Instruments). On the basis of above mentioned the reduced viscosity (η_r) for all samples was calculated using the formula:

$$\eta_r = \frac{\eta_{sp}}{w} = \frac{\eta_{rel} - 1}{w} = \frac{\frac{\eta_1}{\eta_0} - 1}{w} \qquad (1)$$

where η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, η_1 is the polymer solution viscosity, η_0 is the solvent viscosity and w is the polymer mass fraction.

From the dependence between the reduced viscosity of polymer solution and its concentration, the intrinsic $[\eta]$ was determined using the extrapolation method ($[\eta] = \lim_{c \to 0} \eta_r$).These measurements were made for various ionic strengths of the solution (1, 0.1, 0.01) and for various pH values (3, 6, 9). The expansion coefficient of PAA chains was calculated from the following formula:

$$\alpha = \left(\frac{[\eta]}{[\eta_\Theta]} \right)^{1/3} \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution at a given temperature, $[\eta_\Theta]$ is the intrinsic viscosity of the polymer solution at the temperature $\Theta(\mathrm{PAA}) \approx 14$ °C.[11]

Due to obtain $[\eta_\Theta]$ values (the intrinsic viscosities of polyacrylic acid at theta temperature) the polymer solution viscosity (η_1) and the solvent viscosity (η_0) at $\Theta(\mathrm{PAA}) \approx 14$ °C were measured using rotational rheometer. When the polymer solution concentration is known, $[\eta_\Theta]$ value can be obtained from the above dependencies.

Thickness of PAA adsorption layer (δ) was also measured by the viscosity method,[12] using a rotational rheometer (CVO 50, Bohlin Instruments). To this end, the SiO_2 suspensions with its various volume fractions (φ_0) were prepared. The volumetric fraction of the solid was determined from the formula:

$$\varphi_0 = \frac{m}{dv} \qquad (3)$$

where m is the solid mass, d is the solid density, v is the suspension volume.

Next, the suspensions were shaken for 24 hours and their viscosity (η_1) as well as that of the reference solutions (η_0) were measured using a rotational viscometer. In this way, the dependency of η_1/η_0 on φ_0 was calculated (calibration curve). Calibration curves were prepared at each pH value and salt concentration. In the same way the viscosity of the suspensions with the adsorbed polymer (η_p) as well as the viscosity of the polymer solution without the oxide (η_{p0}) was measured and the dependency of η_p/η_{p0} was determined. Value η_{p0} was obtained by viscosity measurements of the polymer solutions (initial polymer mass fractions: 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm) under required conditions: pH, ionic strength and type of electrolyte. Next, from the appropriate calibration curve the volumetric fraction of a solid (φ_p) was estimated. When the radius of SiO_2 particles is known, the thickness of the adsorption layer can be calculated from the following formula:

$$\delta = r[\left(\frac{\varphi_p}{\varphi_0}\right)^{1/3} - 1] \tag{4}$$

where r is the radius of the metal oxide particle, φ_p is the volumetric fraction in the presence of polymer, φ_0 is the volumetric fraction in the absence of the polymer.

Thickness of the polymer adsorption layer (δ) on the metal oxide for various ionic strengths (1, 0.1, 0.01, expressed in mol dm^{-3}) and for various pH values (3, 6, 9) was determined.

SiO_2 surface charge density in the presence and absence of polyacrylic acid was determined using the potentiometric titration method. NaCl concentrations were: 0.01 mol dm^{-3}, 0.1 mol dm^{-3}, 1 mol dm^{-3}.Whereas concentrations of $CaCl_2$ were: 0.003 mol dm^{-3}, 0.033 mol dm^{-3}, 0.333 mol dm^{-3}. These concentrations provided demanded ionic strengths (0.01, 0.1 and 1mol dm^{-3} respectively) for both electrolytes. A thermostated, teflon vessel with a shaker, an automatic burette (Dosimat 665, Methrom) and a pH-meter were the parts of the measurement set. The titration process was controlled by a computer. The density of SiO_2 surface charge was determined using the special "Miar_t" programme.

The zeta potential measurements were made using a zetameter (Zetasizer 3 000, Malvern Instruments). The samples were prepared by ultrasonification of 0.05 g SiO_2 with 500 ml of solution and carefully defined: electrolyte (NaCl, $CaCl_2$), ionic strength (0.01, 0.1 and 1 mol dm^{-3}), polymer concentration (0.01 ppm, 0.1 ppm, 1 ppm) and pH. The zeta potential was measured in the presence and absence of the polymers (PAA 2 000, PAA 60 000).

RESULTS AND DISCUSSION

Adsorption of PAA on the metal oxide surfaces is still one of the most interesting subject for researchers of dispersed systems. Adsorption behaviour of anionic PAA is widely known.[13] This polymer contains acidic carboxylic groups. As it is known, carboxylic groups may dissociate when pH of the solution changes. Foissy *et al.*[14] reported that polyacrylic acid is uncharged at pH = 3. This fact was also confirmed by Cesarano and Aksay.[15] These scientists found that PAA starts becoming charged above pH = 3.4. Gebhardt and Fuerstenau who examined PAA adsorption on silica[16] came to very important conclusions. The first one is that in pH = 4.5 fifty per cent of PAA carboxylic groups is ionized and the second one is that PAA macromolecules do not adsorbed onto silica surface due to electrostatic repulsion. This finding causes the rise of question: what is PAA adsorption mechanism? Ravishankar *et al.*[17] suggested that at lower pH values undissociated carboxylic groups adsorb on Al_2O_3 surface by hydrogen bond between surface hydroxyl and PAA carboxyl groups while at higher pH values the predominant effect of dissociated carboxylic groups adsorption on the surface of alumina is chelation between Al^{3+} surface groups and COO^- ones. This PAA adsorption mechanism was confirmed by Santhiya *et al.*[18] and by Elfarissi.[19] On the basis of above findings a few conclusions may be drawn. First of there are two major PAA adsorption mechanisms: hydrogen bond at low pH values and creation of complexes between metal surface groups and dissociated carboxylic groups at higher pH values. According to the literature pH is the most important factor influences PAA adsorption mechanism. The aim of this paper is to prove that not only pH but also ionic strength and type of electrolyte have a great influence on PAA adsorption mechanism on the surface of metal oxide. Figures 1–4 present PAA 2 000 and PAA 60 000 adsorption isotherms on SiO_2 surface. The influence of such factors as: type of electrolyte, ionic strength, pH of a solution, molecular weight of PAA on its adsorption on SiO_2 surface is presented. The increase of polymer adsorption amount with the increase of ionic strength is observed for all measured systems (Figures 1–3). Such PAA adsorption behaviour is a consequence of changes in carboxylic groups' dissociation degree, modifications of polymer chain conformation at the interface as well as changes in quality and quantity of oxide surface groups. The fact that polyacrylic acid adsorption is observed in pH above pH_{pzc} (for SiO_2 pH_{pzc} equals from 3 to 4)[20] suggests an existence of specific, nonelectrostatic interactions between the adsorbent surface and carboxylic groups[21]. If the electrostatic interactions were predominant the decrease of PAA adsorption with the increase of pH should be observed.[22] The above-mentioned specific interactions are mostly hydrogen bond type or as Vermöhlen suggests,[6] bidental complexes between carboxylic groups of

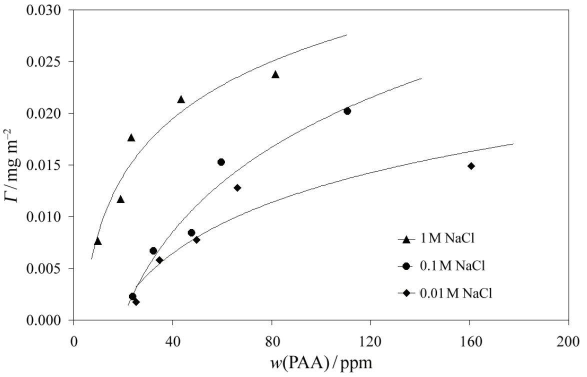

Figure 1. Isotherms of PAA 2 000 adsorption onto SiO_2 at pH = 3 in the presence of NaCl.

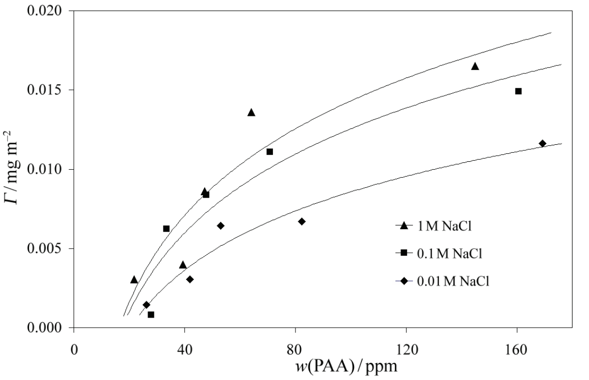

Figure 2. Isotherms of PAA 2 000 adsorption onto SiO_2 at pH = 6 in the presence of NaCl.

polymer chain and silica atoms. The existence of $SiOH_2^+$ surface groups and nondissociated COOH groups favours hydrogen bond type interactions. Considerably large number of both $SiOH_2^+$ and COOH groups in pH = 3 is observed (Table 1). However, screening of repulsive forces between identically charged adsorbent surface and polymer chains has the essential influence on the increase of PAA adsorption with the increase of salt concentration. What is more, the increase of ionic strength causes the increase of the dissociation of carboxylic groups.[23,24] On the other hand, the polymer chain charge, which originates from dissociated carboxylic groups, is much more screened as the ionic strength increases. A result of that is a reduction of repulsion forces between the negatively charged polymer segments and negatively charged surface groups. In such a case polymer chain may form conformation rich in coil-type structures with a large number of loops. What is more, the increase of electrolyte concentration is responsible for large flexibility of PAA chain, what also favours polymer conformation rich in loops structures. These facts lead to the increase of polymer adsorption amount.[25,26]

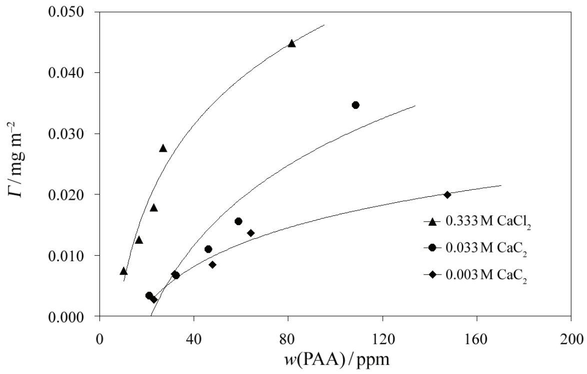

Figure 3. Isotherms of PAA 2 000 adsorption onto SiO_2 at pH = 3 in the presence of $CaCl_2$.

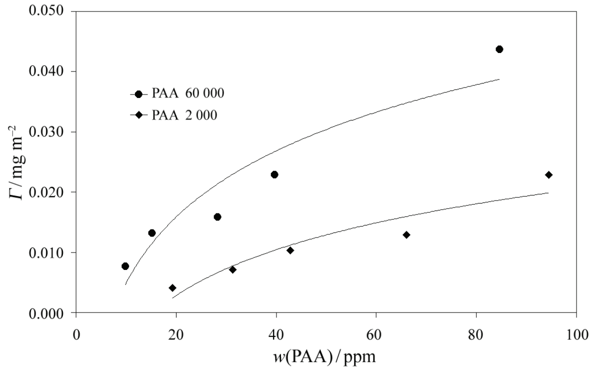

Figure 4. Isotherms of PAA 2 000 and PAA 60 000 adsorption onto SiO_2 at pH = 6 in the presence of 0.333 mol dm^{-3} $CaCl_2$.

Figures 5 and 6 present degree of PAA 2 000 dissociation (α_d) as a function of solution pH for various ionic strength of NaCl (Figure 5) and $CaCl_2$ (Figure 6). As may be seen from these figures not only solution pH but also ionic strength of the electrolyte has the impact on PAA dissociation degree. Moreover, the ratio of concentration of neutral/ionized groups in PAA 2 000 chain ($(1 - \alpha_d) / \alpha_d = [COOH] / [COO^-]$) as a function of solution pH for different electrolytes was measured (Table 2, Table 3).

The comparison between PAA adsorption isotherms on SiO_2 surface in the presence of different electrolytes, but with the same ionic strength leads to the conclusion about the influence of the electrolyte type on polymer adsorption. Higher adsorption amount in the presence of $CaCl_2$ as a background electrolyte is observed in comparison to adsorption in the presence of NaCl for all measured systems. Negatively charged polyacid segments are better neutralised by divalent calcium cations than monovalent sodium ones. It probably results from a creation of intermolecular complexes ($R–COO–Ca^{2+}–COO–R$) between calcium ions and

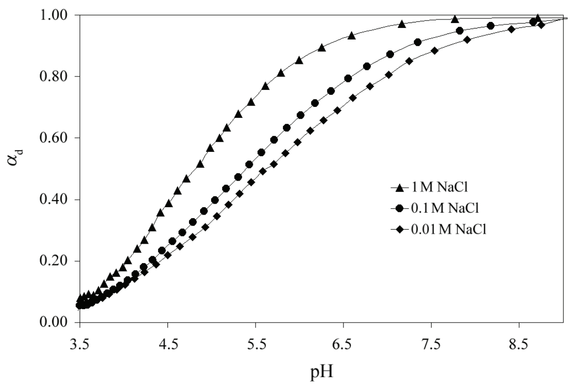

Figure 5. Degree of PAA 2 000 dissociation (α_d) as a function of solution pH for various ionic strenght of NaCl.

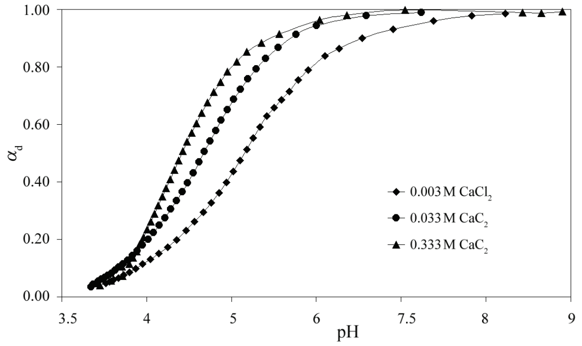

Figure 6. Degree of PAA 2 000 dissociation (α_d) as a function of solution pH for various ionic strenght of $CaCl_2$.

carboxylic groups. Such fact favours the polymer conformation rich in loops and tails, what obviously causes the increase of adsorption amount.[27] What is more, divalent calcium cations effectively screen repulsive forces between polymer and the surface of SiO_2. This effect also causes the increase of polymer adsorption in the presence of $CaCl_2$.

The comparison between polymer adsorption isotherms for different PAA molecular weights points out that the biggest adsorption amount is observed for higher PAA molecular weight (Figure 4). Such an adsorption behaviour results from the differences in long and short polymer chain affinity to the oxide surface.[28]

One of the quantities describing polymer macromolecule in a solution is the expansion coefficient (α). Table 4 presents the influence of ionic strength, pH of a solution and polymer molecular weight on the polyacrylic acid expansion coefficient in the presence of $CaCl_2$ as a background electrolyte.

Presented data point out that the PAA expansion coefficient decreases with the increase of ionic strength. The most important reason for this phenomenon is a reduction of repulsion forces between polymer chain segments. This is a consequence of screening of the $-COO^-$ groups charge by ions of electrolyte. Polymer chain forms the conformation, which resembles a coil. In such a situation linear dimensions of macromolecules decrease with the increase of ionic strength. On the

Table 1. Concentration of different surface groups ($SiOH_2^+$, SiO^-, SiOH) onto SiO_2, μC cm^{-2} at the presence of NaCl of different concentrations.

	pH	$SiOH_2^+$	SiO^-	SiOH
0.1M NaCl	4	0.001	0.000	135.306
	5	0.000	–0.004	135.305
	6	0.000	–0.061	135.247
	7	0.000	–0.400	134.898
	8	0.000	–2.333	132.914
	9	0.000	–7.717	126.863
1M NaCl	4	0.001	–0.001	135.289
	5	0.000	–0.005	135.303
	6	0.000	–0.039	135.261
	7	0.000	–0.0415	134.794
	8	0.000	–3.949	130.789
	9	0.000	–25.948	109.124

Table 2. The ratio of neutral : ionized groups concentration in PAA 2 000 chain ($(1-\alpha_d)/\alpha_d$ = [COOH]/[COO^-]) as a function of solution pH in the presence of NaCl as a background electrolyte

	$(1-\alpha_d)/\alpha_d$ = [COOH]/[COO^-]		
pH	$I_c = 0.01$[(a)]	$I_c = 0.1$	$I_c = 1$
3.5	23.7	18.4	10.5
5	1.88	1.55	1.13
6.5	0.45	0.27	0.11
8	0.0869	0.0638	0.0111

(a) I_c is expressed in mol dm^{-3}

Table 3. The ratio of neutral : ionized groups concentration in PAA 2 000 chain ($(1-\alpha_d)/\alpha_d$ = [COOH]/[COO^-]) as a function of solution pH in the presence of $CaCl_2$ as a background electrolyte

	$(1-\alpha_d)/\alpha_d$ = [COOH]/[COO^-]		
pH	$I_c = 0.01$[(a)]	$I_c = 0.1$	$I_c = 1$
3.5	19.9	14.2	8.2
5	1.29	1.11	0.97
6.5	0.11	0.08	0.04
8	0.0141	0.0137	0.0106

(a) I_c is expressed in mol dm^{-3}

Table 4. PAA expansion coefficient (α) in the presence of NaCl as a background electrolyte[30]

		$c(NaCl)/mol\ dm^{-3}$		
	pH	0.01	0.1	1
PAA 2 000	3	1.33	1.16	1.09
	6	1.34	1.32	1.20
	9	1.45	1.45	1.32
PAA 60 000	3	1.34	1.17	1.09
	6	1.36	1.33	1.24
	9	1.48	1.44	1.34

Table 5. PAA expansion coefficient (α) in the presence of $CaCl_2$ as a background electrolyte

		$c(CaCl_2)/mol\ dm^{-3}$		
	pH	0.003	0.033	0.333
PAA 2 000	3	1.42	1.23	1.11
	6	1.45	1.32	1.24
	9	1.51	1.48	1.37
PAA 60 000	3	1.44	1.37	1.19
	6	1.48	1.44	1.28
	9	1.54	1.52	1.38

Table 6. Thickness of PAA adsorption layers δ/nm on the SiO_2 surface in the presence of NaCl as a background electrolyte

		$c(NaCl)/mol\ dm^{-3}$		
	pH	0.001	0.01	1
PAA 2 000	3	0.99	2.06	4.90
	6	1.03	3.19	5.62
	9	3.43	7.79	13.14
PAA 60 000	3	1.44	2.18	5.21
	6	1.64	4.31	9.17
	9	4.98	8.13	14.83

Table 7. Thickness of PAA adsorption layers δ/nm on the SiO_2 surface in the presence of $CaCl_2$ as a background electrolyte

		$c(CaCl_2)/mol\ dm^{-3}$		
	pH	0.003	0.033	0.333
PAA 2 000	3	4.48	6.36	8.78
	6	7.08	11.88	12.61
	9	10.58	13.32	16.51
PAA 60 000	3	6.20	8.80	9.75
	6	9.44	12.79	15.45
	9	12.93	16.21	21.99

other hand PAA adsorption increases with the increase of electrolyte ionic strength. The reason for that is a formation of the adsorption layer made by closely packed polymer coils. The increase of electrolyte concentration also worsens the quality of a solvent, which results in the decrease of the linear dimensions of the polymer macromolecules.

The PAA expansion coefficient increases with the increase of pH. It is a consequence of the increasing number of dissociated carboxylic groups which follows in a wake of increasing pH. Repulsive forces between $–COO^-$ groups cause the stretching of the polymer chain and they are also responsible for the increase of the PAA expansion coefficient.

It is obvious that the higher PAA molecular weight the higher the expansion coefficient (α) of PAA. It results from the length of the polymer chain.

Very important conclusions about the structure of the adsorbed polymer layers may be drawn from PAA adsorption layer thickness (δ) on SiO_2 surface. Tables 5 and 6 present the influence of ionic strength, pH of a solution and polymer molecular weight on thickness of the polymer adsorption layers.

The increase of PAA adsorption layer thickness with the increase of ionic strength results from both screening of polymer segments charge and screening of the solid surface charge by increasing salt concentration. The effect of that is a gradual reduction of repulsive forces between segments of the polymer chain. Such a situation favours the polymer conformation, which resembles a coil. But it also should be noticed that with increasing electrolyte ionic strength PAA adsorption layer thickness increases with the simultaneous decrease of PAA expansion coefficient. The final values of PAA adsorption layer thickness result from a reduction of repulsion forces between the surface of measured solid and PAA chains and also between segments of PAA. Such a situation leads to a very large packing of adsorbed PAA macromolecules.

Moreover, a very important factor, which has the effect on the increase of adsorption layers thickness with the increase of ionic strength, is a competitive adsorption between polymer segments and electrolyte ions. In high salt concentrations electrolyte ions may block some active centres on the oxide surface. In such a situation polymer coils may compress each other and because of that they have to form the conformation stretched towards the liquid phase.

A type of used electrolyte also influences PAA adsorption layers thickness. For all measured systems the highest adsorption layers thickness were obtained when $CaCl_2$ was used as a background electrolyte. This fact results from phenomenon of a formation of bidental complexes between divalent Ca^{2+} cations and carboxylic groups of the polymer chain. Obtained adsorption layer is thicker than the adsorption layer in the presence of NaCl because larger number of segments may form polymer coils that results in the thicker adsorption layer.

Analysis of the influence of pH on the adsorption layers thickness points out, that the increase of pH causes the increase of adsorption layers thickness. This phenomenon may be explained by the fact, that the increase of the number of dissociated $-COO^-$ groups follows the increase of pH. When pH changes from 3 to 9 the $[COOH]/[COO^-]$ rate decreases several times.[24] In pH above pH_{pzc} a solid surface and polymer chains repel each other. The result of that is the polymer chain conformation expanded towards the liquid phase and what is more the increase of adsorption layers thickness.

The electrokinetic properties of the interface SiO_2/PAA in the presence of NaCl or $CaCl_2$ may be defined by the analysis of the zeta potential measurements (Figures 7–9). These data may also be used to the interpretation of the structure of the adsorbed polymer.

The comparison between ζ potential curves points out that following factors: PAA molecular weights, a type of electrolyte and its ionic strength have the great influence on the zeta potential of SiO_2.

For all measured systems the zeta potential of SiO_2 molecules in the presence of PAA decreases in the whole pH range in comparison to the zeta potential of SiO_2 molecules in the absence of PAA (Figure 7). The most important reason for this phenomenon is the presence of negative charge from dissociated carboxylic groups $-COO^-$ presented in the polymer chain. The number of these groups increases with the increase of polymer concentration and also with the increase of polymer molecular weight. The additional effect which also influences the decrease of the zeta potential in the presence of polyacrylic acid is a possibility of a shift of the slipping plane. The shift is higher when polymer adsorption layer is closely packed. This factor causes a shift of the slipping plane from the surface of the solid what is also responsible for the decrease of the zeta potential.[29] As it is known, high molecular weight polymers have lots of segments in their chains and form the coil-type conformations with a large number of loops and tails structures. Because of that the increase of polymer molecular weight causes that the adsorbed polymer layers is thicker (Tables 5, 6) and a consequence of that is the effective shift of the slipping plane as well as the decrease of the zeta potential.

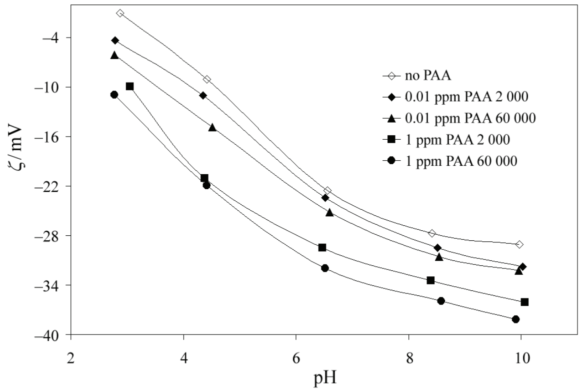

Figure 7. Silica zeta potential as a function of pH values for various concentrations of PAA 2 000 and PAA 60 000; $c(NaCl) = 0.01\ mol\ dm^{-3}$.

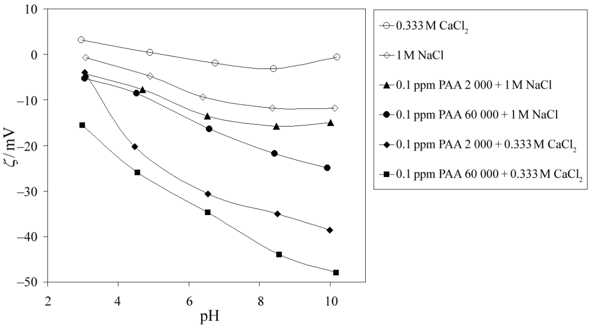

Figure 8. Silica zeta potential as a function of pH values in the presence of 1 mol dm^{-3} NaCl or 0.333 mol dm^{-3} $CaCl_2$ and polyacrylic acid.

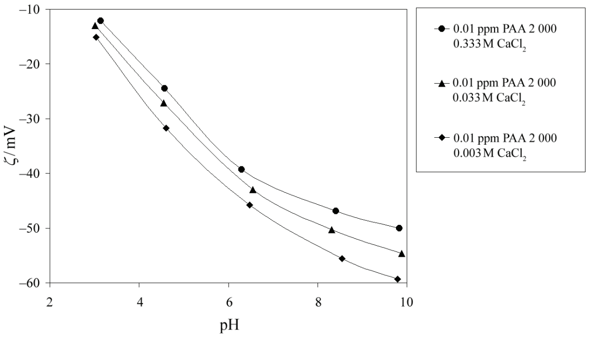

Figure 9. Silica zeta potential as a function of pH values in the presence of 0.01 ppm PAA 2 000 and $CaCl_2$.

Considering the influence of a type of electrolyte on the zeta potential it may be observed that the zeta potential of SiO_2 in the presence of polyacrylic acid is always lower when $CaCl_2$ is used as a background electrolyte in comparison to the zeta potential values in the presence of PAA and NaCl (Figure 8). This fact results from the changes in PAA conformations in the different electrolytes. As was mentioned before, PAA conformation in the presence of Ca^{2+} ions is more stretched towards the liquid phase than PAA conformation where NaCl was used as a background electrolyte. Such a situation is a consequence of forming bidental complexes between Ca^{2+} ions and carboxylic groups from the polymer chain.[16] The thickness of polymer adsorption layer in the presence of Ca^{2+} ions becomes thicker (Tables 5, 6) what causes two effects. One of them is a presence of large number of dissociated carboxylic groups in by-surface layer of the oxide and the second is a shift of slipping plane towards the liquid phase. These effects both cause the decrease of the zeta potential.

The comparison between the zeta potential values in solutions characterised by various ionic strengths points out that the increase of salt concentration causes the increase of the zeta potential in the presence of polyacrylic acid (Figure 9). It is a result of the screening of the polymer charge from dissociated carboxylic groups by electrolyte ions. When electrolyte ionic strength is higher the polymer charge is better screened and the zeta potential increases.

CONCLUSION

A type of used electrolyte and its ionic strength influences the amount adsorbed polymer. As was proved, PAA adsorption in the presence of $CaCl_2$ as a background electrolyte is bigger in comparison to PAA adsorption in the presence of NaCl. This fact results from spacious PAA conformation in the presence of $CaCl_2$. The reason for this is a formation of bidental complexes between calcium ions and carboxylic groups of PAA chain. The PAA adsorption also increases with increasing salt concentration. Explanations for this fact are changes in dissociation degree of the carboxylic groups in the PAA chain. The increase of pH of the solution lowers the PAA adsorption amount. This fact results from changes in the dissociation degree of functional groups of both polymer and the adsorbent and changes in PAA chain conformation. Moreover, the expansion coefficient of PAA is much higher when $CaCl_2$ is used as a background electrolyte. The reason for that is specious conformation of PAA in the presence of $CaCl_2$. However, the expansion coefficient increases with decreasing ionic strength. It may be explained by the fact that at high salt concentration the repulsion between negatively charged PAA segments decreases. Thickness of adsorbed PAA layers is also higher in the presence of $CaCl_2$. Formation of bidental complexes between calcium ions and carboxylic groups of PAA are responsible for this phenomenon. The increase in thickness of the adsorption layer with increasing ionic strength is also a result of the screening effect of the polymer segments charge by electrolyte counterions as well as the surface oxide charge and changes in PAA dissociation degree.

A type of used electrolyte as well as its ionic strength influences both the zeta potential and the surface charge density of the system: polyacrylic acid/silica. As it was measured the zeta potential of SiO_2 is much lower in the presence of PAA when $CaCl_2$ is used as a background electrolyte than in the presence of NaCl. This fact results from the changes in PAA conformations in the presence of different electrolytes. The zeta potential also increases with increasing electrolyte ionic strength. The explanation for this phenomenon is screening of the polymer charge by electrolyte ions. Moreover, molecular weight of the polymer as well as its concentration has the influence on the zeta potential. With the increase of above-mentioned factors the decrease of the zeta potential is also observed.

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SAŽETAK

Utjecaj vrste elektrolita i njegove ionske jakosti na adsorpciju i strukturu adsorbiranog sloja polimera u sustavu: poliakrilna kiselina/SiO_2

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Ispitan je utjecaj ionske jakosti i relativne molekulske mase poliakrilne kiseline (PAA) na adsorpciju i strukturu adsorbiranog polimernog sloja na površini SiO_2 u prisutnosti NaCl i $CaCl_2$. Mjerena je debljina adsorbiranog sloja PAA na površini SiO_2 kao i ekspanzijski koeficijent (α) za PAA u $CaCl_2$. Povećanje ionske jakosti, pH i relativne molekulske mase polimera uzrokuje debljanje sloja adsorbirane PAA. Međutim, ekspanzijski koeficijent PAA povećava se povećanjem pH i relativne molekulske mase polimera, ali se smanjuje povećanjem ionske jakosti. Mjeren je utjecaj vrste elektrolita i ionske jakosti na zeta potencijal SiO_2 u prisutnosti poliakrilne kiseline (PAA). Primjećeno je da je zeta potencijal mnogo niži u otopinama $CaCl_2$ u usporedbi s zeta potencijalom u otopinama NaCl.