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INFLUENCE OF A KIND OF ELECTROLYTE AND ITS IONIC STRENGTH ON THE CONFORMATION CHANGES OF POLYACRYLIC ACID DURING ITS COMING FROM THE BULK SOLUTION TO THE SURFACE OF MnO_2

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Changes in PAA 2000 macromolecules conformation in the bulk solution as well as on the surface of MnO_2 as a function of a kind of electrolyte (NaCl, $CaCl_2$), electrolyte ionic strength (I=0.01, 0.1) and pH (3, 6, 9) of the solution were measured. In order to determine the influence of electrolyte on PAA conformation in the bulk solution the expansion coefficient (α) was measured. Such quantities as: the square root of the mean of the square distance between ends of polymer chain ($\sqrt{\overline{r^2}}$), the square root of the mean of square radius of polymer coil rotation ($\sqrt{\overline{\mathbf{s}^2}}$) and hydrodynamic radius of polymer coil in the bulk solution (R_h) were measured to describe changes in PAA macromolecule conformation during its coming from the bulk solution to the surface of MnO_2. Moreover, PAA adsorption layer thickness in the presence of two various electrolytes, NaCl and $CaCl_2$ (I=0.01, 0.1) was measured. From the obtained results it is clearly visible that researched factors: kind of electrolyte, its ionic strength and pH of a solution have great influence on the conformation of the polymer macromolecules.

Key words: polymer conformation, polymer adsorption, expansion coefficient, adsorption layer thickness

INTRODUCTION

Research on the polymer adsorption on the solid surfaces is carried out in two aspects: theoretical and practical (Fleer et al., 1993; Markovic, 1996; Pan et al., 2001).

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Interest in the polymers adsorption on the metal oxide/polyelectrolyte solution interface results from the fact that the mechanism of polymer adsorption is completely different from the mechanism of small particles and ions adsorption. Polymer chains may form lots of different conformations in both the bulk of solution and in the interface, while the ions and the small particles have invariable, defined shape (Cohen Stuart et al., 1991). Changes in the polymer conformation in the bulk solution and at the interface as well as changes in the structure of polymer chain during its coming from the solution to the surface of the solid are the most important problems in the description of polymers adsorption process. In the bulk solution polymer chains are flexible. It helps them to create coil type structures. The shapes and the dimensions of above-mentioned structures depend on a few factors. Among them the most important ones are interactions between polymer segments and solvent particles, molecular weight of used polymer and polymer concentration. Moreover, polymer coils might permeate each other. The result of that is a very complicated and hard to explain thermodynamic system. When polymer particles are being adsorbed on the surface of the adsorbent, their conformation changes radically. Because of the fact that the concentration of the polymer is always higher in the surface layer than in the bulk solution, the co-permeating process of polymer chains takes place in by-surface layer. The evidence for that is the presence of trains, loops and tail structures. Trains are whose segments that are adjoined to the surface of the adsorbent. Loops and tails are so called spacious polymer structures. They can interact with each other and there are two effects of this interaction: one is their expansion towards the bulk of the solution and the second one is the creation of closely packed polymer coils. The kind of produced polymer conformation has the influence on some parameters describing polymer macromolecule in the solution as well as on the surface. The above-mention parameters are: expansion coefficient (α), thickness of adsorbed polymer layer (δ), square root of the mean of the square distance between ends of polymer chain ($\sqrt{\overline{r^2}}$), square root from the mean of square radius of polymer coil rotation ($\sqrt{\overline{s^2}}$), hydrodynamic radius of polymer coil in the bulk solution (R_h).

Polyacrylic acid was used as a polyelectrolyte because of wide range of its practical applications (Szlezyngier, 1998). It is used as supplement to surfactants, compound used in the production of paper, inhibitor of fur formation, concentrators in cosmetics and components of drugs, artificial tears. There are also some measurements which explain the fact of stability changes of phase colloids in the presence of polyacrylic acid.

Manganese dioxide was chosen as an adsorbent. This oxide is chemically inert, insoluble and stable in a broad pH range. These features as well as well-defined interface allow to use it as an adsorbent. Manganese dioxide finds applications in the production of matches, in glass-making industry to decolourization of glass and as a depolarizer in voltaic cells (Trzebiatowski, 1979).

EXPERIMENTAL

MnO_2 produced by POCh-Gliwice was used as an adsorbent in all measurements. The specific surface area of manganese dioxide, calculated using the BET (Brunauer, Emmet, Teller) method was 38 $m^2\,g^{-1}$ and the average diameter of this oxide particles equalled 280 nm. Before the measurements MnO_2 was washed with doubly distilled water until the conductivity of the supernatant smaller than 2μS cm^{-1}.

NaCl, and $CaCl_2$ were used as background electrolytes. Polyacrylic acid (molecular weight 2000) produced by Aldrich was used as a polyelectrolyte.

PAA expansion coefficient (α) in the presence of NaCl and $CaCl_2$ as background electrolytes was determined using the viscosity method (Porejko et al., 1974). Viscosity of the polymer solutions with various concentrations was measured by a rotary rheometer (CVO 50, Bohlin Instruments). On the basis of above mentioned the reduced viscosity (η_r) for all samples was calculated using the formula:

$$\eta_r = \frac{\eta_{sp}}{c} = \frac{\eta_{rel} - 1}{c} = \frac{\frac{\eta_1}{\eta_0} - 1}{c} \tag{1}$$

where: η_{sp} - the specific viscosity, η_{rel} - the relative viscosity, η_1 - the polymer solution viscosity, η_0 - the solvent viscosity and c is the polymer solution concentration.

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

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

where: $[\eta]$ - the reduced viscosity of the polymer solution at a given temperature, $[\eta_\Theta]$ - the reduced viscosity of the polymer solution at the Θ temperature (PAA Θ temperature ≈ 14° C).

From the viscosity measurements some qualities describing polymer coil during its coming from the bulk solution to the surface of the solid were obtained. $\sqrt{\overline{r^2}}$ - square root from the mean of the square distance between ends of polymer chain was estimated using the Flory - Fox equation:

$$[\eta] = \frac{\Phi\left(\overline{r^2}\right)^{3/2}}{M} \tag{3}$$

where: $[\eta]$ - reduced viscosity of the polymer solution, Φ - Flory-Fox constant = 2.1×10^{21}, M - molecular weight of measured polymer.

From $\sqrt{\overline{r^2}}$ square root of the mean of square radius of polymer coil rotation ($\sqrt{\overline{\mathbf{s}^2}}$) was calculated using the formula:

$$\left(\overline{s^2}\right) = \frac{\left(\overline{r^2}\right)}{6}\ . \tag{4}$$

Hydrodynamic radius of polymer coil in the bulk solution (R_h) was estimated from the equation:

$$R_h = f\sqrt{\overline{s^2}} \tag{5}$$

where: f - polymer constant for PAA = 0.66.

Thickness of PAA adsorption layer (δ) was also measured by the viscosity method (Pandou et al., 1987), using a rheometer. The MnO_2 suspensions with its various volumetric fractions (ϕ_0) were prepared. The volumetric fraction of the solid was determined from the formula:

$$\phi_0 = \frac{m}{dv} \tag{6}$$

where: m - the solid mass, d - the solid specific gravity, v - the reference solution volume.

Next, the suspensions were shaken for 24 hours and their viscosity (η) as well as that of the reference solutions (η_0) were measured using a rheometer. In this way, the influence of ϕ_0 on η/η_0 was calculated (calibration curve). In the same way the viscosity of the suspensions with the adsorbed polymer (η_p) as well as that of the polymer solution (η_{p0}) was measured and the influence of η_p/η_{p0} was determined. Next, from the calibration curve the volumetric fraction of a solid (ϕ_p) was estimated. When the radius of MnO_2 particles is known, the thickness of the adsorption layer can be calculated from the following formula:

$$\delta = r\left[\left(\frac{\phi_p}{\phi_0}\right)^{1/3} - 1\right] \tag{7}$$

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

Thickness of the polymer adsorption layer (δ) on the metal oxide in the presence of NaCl and $CaCl_2$ for various electrolytes ionic strengths (0.01, 0.1) and for various pH values (3, 6, 9) was determined.

RESULTS AND DISCUSSION

Table 1 shows the obtained values of the expansion coefficient (α) of PAA 2000 in the presence of NaCl and $CaCl_2$ (I= 0.01, 0.1). Measurements were made for various pH values (3, 6, 9) of the solution.

Table 1. PAA expansion coefficient in the presence of NaCl and $CaCl_2$

	pH	0.01M NaCl	0.1M NaCl	0.003M $CaCl_2$	0.033M $CaCl_2$
PAA 2000	3	1.33	1.16	1.42	1.23
	6	1.34	1.32	1.45	1.32
	9	1.45	1.45	1.51	1.48

Analysis of the obtained data, which describe the dimensions of a singular polymer coil in the bulk solution, shows that the expansion coefficient is always higher in the presence of $CaCl_2$. This situation might be explained by the influence of divalent cations on the degree of carboxylic group dissociation. In the presence of Ca^{2+} PAA is more dissociated than in the presence of monovalent cation. Because of a larger number of negatively charged carboxylic groups which repel each other, polymer coil becomes more stretched and the expansion coefficient of PAA increases.

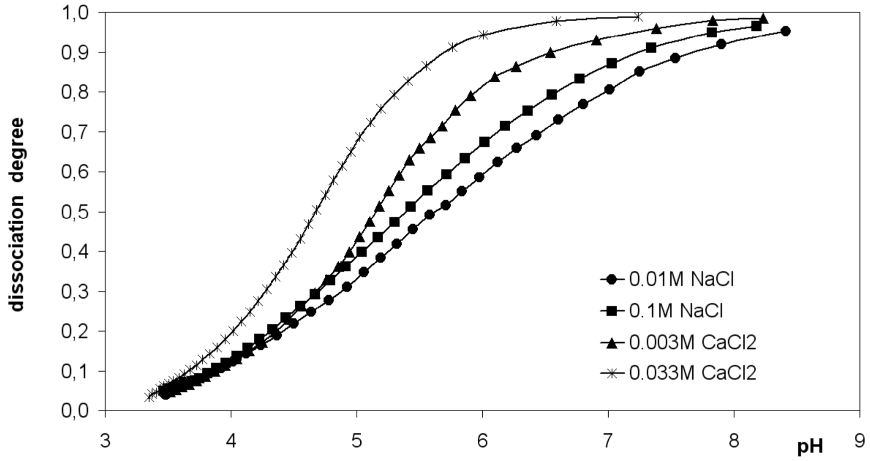

Fig. 1. PAA 2000 dissociation degree as a function of pH in the presence of NaCl and $CaCl_2$.

Linear dimensions of polymer coil also increase with the increase of pH. This fact is a consequence of the increasing number of carboxylic groups in the polymer chain with the increase of pH of the solution. The repulsion forces between -COO$^-$ groups cause the stretching of the polymer chain and the increase of PAA expansion coefficient.

Table 2. The ratio of concentration of neutral/ionized groups in PAA 2000 chain as a function of solution pH in the presence of NaCl and $CaCl_2$

pH	$(1-\alpha_d)/\alpha_d$=[COOH]/[COO$^-$]			
	0.01M NaCl	0.1M NaCl	0.003M $CaCl_2$	0.033M $CaCl_2$
3.5	25	17	20	14
4.5	3.5	2.8	3.3	1.3
5.5	1.2	0.8	0.51	0.15
6.5	0.43	0.26	0.11	0.095
7.5	0.13	0.09	0.042	0.031
8.5	0.033	0.020	0.014	0.011

One of the most surprising facts is that the increase of ionic strength causes the decrease of α. This fact is a consequence of three factors: the increase of dissociation of carboxylic groups (Chibowski et al., 2003), the decrease of PAA solubility and the increase of carboxylic groups screening effect by electrolyte cations. The first from the above-mentioned effects causes the increase of α while two others cause the decrease of this value. It seems that the summary effect of the influence of these factors on the expansion coefficient causes small decrease of α values.

Table 3 presents PAA 2000 adsorption layer thickness on the surface of MnO_2 in the presence of NaCl and $CaCl_2$.

Table 3. PAA 2000 adsorption layer thickness on the surface of MnO_2 in the presence of NaCl and $CaCl_2$

electrolyte	pH	δ [nm]	electrolyte	pH	δ [nm]
0.01 M NaCl	3	1.8	0.003 M $CaCl_2$	3	5.1
	6	2.4		6	8.4
	9	3.5		9	12.6
0.1M NaCl	3	2.5	0.033 M $CaCl_2$	3	8.0
	6	3.5		6	13.6
	9	7.0		9	15.3

Analysis of the data presented in Table 3 confirms that both the kind of used electrolyte and its ionic strength have the influence on the adsorption layer thickness. Comparison between these data leads to the conclusion that the presence of divalent metal chloride as the electrolyte causes larger increase of the adsorption layer thickness than in the presence of NaCl. This fact is a consequence of a few phenomena.

Firstly, PAA dissociation degree is higher in the presence of $CaCl_2$ than in the presence of NaCl as the background electrolyte. Because of larger number of dissociated carboxylic groups and because of their repulsion, polymer forms conformation expanded towards the bulk of solution what leads to the increase of polymer adsorption layer thickness. Secondly, divalent metal cations have the tendency to creation of bidental complexes with carboxylic groups from the polymer chains (Vermöhlen et al., 2000), therefore that polymer conformation is rich in loops and tails structures and the adsorption layer thickness increases. The last effect influences the adsorption layer thickness values is the competitive adsorption between Ca^{2+} cations and polymer segments. It is known that there is constant number of active places on the surface of the adsorbent. If some of them are blocked by metal cations, polymer is forced to create conformation on the rest of them. Such a conformation is always rich in loops and tails structures, what increases the PAA adsorption layer thickness (Chibowski, 1988). Moreover, there is an increase of the adsorption layer thickness with the increase of pH. The explanation of such an adsorptive behavior of PAA is the influence of pH on PAA dissociation degree as well as on a kind and the concentration of the metal surface groups. It is known that the increase of pH causes the increase of PAA dissociation degree. When pH of the solution is higher than pK value of polyacrylic acid (pK_{PAA} = 4.5) the increase of the number of dissociated carboxylic groups is observed. The consequence of that is the increase of repulsion between negatively charged carboxylic groups and the increase of the polymer adsorption layer thickness. Because PAA adsorption is higher in low pH values and lower in higher ones (Chibowski et al., 2005) some conclusions about PAA conformation on the interface solid/polyelectrolyte solution might be drawn. If the increase of pH causes straightening of PAA coils, adsorption of negatively charged polymer chain on the negative surface takes place only by a few groups. The rest of the polymer chain stays in the solution and forms brush type conformation. Such a conformation is characterized by low amount of adsorbed polymer but a thick adsorption layer. On the other hand, for low pH values, besides the hydrogen bond type, there are electrostatic attraction forces between positively charged surface and dissociated negatively charged carboxylic groups (Solberg et al., 2003). Under such conditions the polymer adsorption layer is closely packed what leads to lower values of polymer adsorption layer thickness.

The influence of ionic strength on the thickness of PAA adsorption layer can be analyzed from the data presented in Table 3. It can be seen that the increase of electrolyte ionic strength accompanies the increase of adsorption layer thickness. It is a consequence of the fact that in high salt concentration repulsion between the surface groups of metal oxide as well as between polymer segments is better screened by metal cations. The effect of this phenomenon is not only the increase of PAA adsorption amount but also the increase of the polymer adsorption layer thickness. Another reason for the increase of PAA adsorption layer thickness with the increase of electrolyte ionic strength is the above-mentioned competitive adsorption between polymer segments and metal cations. It also should be noticed that the increase of salt concentration leads to the increase of flexibility of polymer chain (Steitz et al., 2000; Adachi et al., 2002). That conduces the increase of the polymer adsorption layer thickness.

Tables 4-5 present characteristics of PAA 2000 macromolecules during their coming from the bulk of electrolyte solution to the surface of MnO_2.

Table 4. Characteristic of PAA 2000 particles during their coming
from the bulk of NaCl solution to the surface of MnO_2.

	pH	$\sqrt{\overline{\mathbf{r}^2}}$ [nm]	$\sqrt{\overline{\mathbf{s}^2}}$ [nm]	R_h [nm]	δ [nm]
0.01 M NaCl	3	14.4	8.9	9.1	1.8
	6	20.5	11,3	11.3	2.4
	9	33.4	17.5	15.2	3.5
0.1 M NaCl	3	16.4	10.8	10.9	2.5
	6	23.1	11.8	12.7	3.5
	9	35.6	17.2	15.9	7.0

Table 5. Characteristic of PAA 2000 particles during their coming
from the bulk of $CaCl_2$ solution to the surface of MnO_2

	pH	$\sqrt{\overline{\mathbf{r}^2}}$ [nm]	$\sqrt{\overline{\mathbf{s}^2}}$ [nm]	R_h [nm]	δ [nm]
0.003 M $CaCl_2$	3	26.8	13.3	11.7	5.1
	6	35.9	17.6	14.5	8.4
	9	49.2	22.8	20.1	12.6
0.033 M $CaCl_2$	3	33.5	16.2	16.1	8.0
	6	46.3	21.7	18.3	13.6
	9	59.8	27.5	24.0	15.3

A comparison between data presented in Table 4 and 5 allows to draw some conclusions about the influence of a kind of electrolyte and its ionic strength on the conformational changes of PAA chain during its coming from the bulk solution to the surface of MnO_2. First of all, R_h values in the presence of $CaCl_2$ are higher those in the presence of NaCl. This fact comes from high affinity of Ca^{2+} cations to PAA carboxylic groups and Ca^{2+} tendency to creation of bidental complexes. In the presence of divalent metal cations dimensions of PAA macromolecule are higher not only in the solution but also on the metal oxide surface (δ values in the presence of $CaCl_2$ are also higher). Changes in $\sqrt{\overline{s^2}}$, R_h, and δ values strongly prove that PAA conformation is changed during its coming from the bulk solution to the surface of the solid. The polymer chains are being adsorbed on the surface of the solid by a few number of functional groups, what dramatically changes their conformation. Because of this fact polymer adsorption layer thickness is lower than the dimensions of polymer macromolecule in the bulk solution. Moreover, because δ values are lower than the polymer coil diameter in the solution (2x$\sqrt{s^2}$), it evidences that adsorbed polymer chains may permeate each other. Such a situation leads to closely packed conformation of PAA in the adsorption layer. It can also be seen from the data presented in Tables 4-5 that not only pH values but also electrolyte ionic strength increase the values of the parameters which characterized the polymer macromolecule during its coming from the bulk solution to the surface of the metal oxide. This is a consequence of the influence of above-mentioned factors on the PAA dissociation degree. As it was said above, the increase of pH and the increase of electrolyte ionic strength both cause the increase of the PAA dissociation degree.

CONCLUSIONS

1. PAA expansion coefficient is always higher in the presence of $CaCl_2$ and at higher pH values. This fact results from larger number of negatively charged carboxylic groups.
2. α of PAA decreases with the increase of ionic strength. This is a summary consequence of three factors: the increase of dissociation of carboxylic groups, the decrease of PAA solubility, and the increase of carboxylic groups screening effect by counterions.
3. The polymer adsorption layer thickness is higher in the presence of divalent metal chloride. There are three explanations of this phenomenon: larger number of dissociated carboxylic groups, creation of bidental complexes between carboxylic groups, and divalent metal cations and competitive adsorption between Ca^{2+} cations and the polymer segments.
4. α of PAA increases also with the increase of pH. The reasons for that are changes in PAA dissociation degree and changes in a kind and a concentration of the metal surface groups.
5. The increase of electrolyte ionic strength accompanying the increase of PAA adsorption layer thickness. It is a consequence of better screening effect in the presence of salt.
6. Changes in $\sqrt{r^2}$, $\sqrt{s^2}$, R_h, and δ values in the presence of different electrolytes strongly prove that PAA conformation is changed during its coming from the bulk solution to the surface.

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Grządka E., Chibowski S.,*Wpływ rodzaju elektrolitu i jego siły jonowej na zmiany konformacyjne kwasu poliakrylowego podczas jego przechodzenia z głębi roztworu na powierzchnię MnO2.* Physicochemical Problems of Mineral Processing, 42 (2008), 47-56 (w jęz. ang)

Zbadano wpływ rodzaju elektrolitu (NaCl i $CaCl_2$) i jego siły jonowej (0.01, 0.1) na zmiany konformacyjne kwasu poliakrylowego PAA 2000 w głębi roztworu, na powierzchni adsorbentu (MnO_2) jak i w trakcie przechodzenia makrocząsteczek z głębi roztworu na powierzchnię ciała stałego. W tym celu przeprowadzono pomiary wiskozymetryczne następujących wielkości: współczynnika ekspansji kwasu poliakrylowego (α), grubości warstewek adsorpcyjnych (δ) oraz parametrów charakteryzujących makrocząsteczkę w trakcie przechodzenia z głębi roztworu na powierzchnię ciała stałego czyli: pierwiastka kwadratowego ze średniej kwadratu odległości między końcami łańcucha ($\sqrt{\overline{r^2}}$), pierwiastka kwadratowego ze średniej kwadratu promienia obrotu kłębka polimerowego ($\sqrt{\overline{s^2}}$) oraz promienia hydrodynamicznego (R_h). Przeprowadzone pomiary pozwoliły uzyskać informacje na temat charakterystyki konformacyjnej PAA w zależności od rodzaju i stężenia elektrolitu podstawowego.

słowa kluczowe: konformacje polimerowe, adsorpcja polimeru, współczynnik rozszerzalności , grubość warstwy adsorpcyjnej