

## **Influence of the electrolyte type on the adsorption and electrokinetic properties of the ionic polyamino acids – Cr<sub>2</sub>O<sub>3</sub> system**

Iwona Ostolska<sup>a</sup> and Małgorzata Wiśniewska

*Maria Curie-Skłodowska University, Faculty of Chemistry,  
Department of Radiochemistry and Colloids Chemistry,  
M. Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland,  
<sup>a</sup>[i\\_ostolska@wp.pl](mailto:i_ostolska@wp.pl)*

The influence of a kind of support electrolyte on the ionic polyamino acids adsorption at the chromium (III) oxide – polymer solution interface was investigated. The NaCl and CaCl<sub>2</sub> were used as the background electrolytes. In order to determine the effect of the electrolyte, the same value of ionic strength of the test solutions were taken. It was proved that formation of intermolecular and intramolecular complexes in the presence of divalent calcium ions is responsible for essential changes in polymer adsorption.

Related to the ionic character of polyamino acid two different adsorption behaviours can be observed. The increase of the ASP adsorption amount in the presence of calcium ions may be explained by formation of complexes between the dissociated carboxylic groups and Ca<sup>2+</sup> ions. The opposite situation takes place in the case of polylysine – the application of CaCl<sub>2</sub> results in the dramatic decrease in the polymer adsorption caused by blocking the active sites available for LYS macromolecules. In order to make a comprehensive analysis, the zeta potential and surface charge density measurements were performed taking into account the kind of the background electrolyte. The above-mentioned tests were carried out in the absence and presence of the polyamino acid at two different concentrations – 10 and 100 ppm respectively.

**Key words:** Polyamino acid, polyaspartic acid, polylysine, chromium (III) oxide, polymer adsorption, potentiometric titration, zeta potential.

## 1. INTRODUCTION

Polymer adsorption on the solid surface is a very complicated process, determined by many different factors. One of them is the presence of inorganic impurities. They can influence the polymer behaviour at the solid–liquid interface by changing the macromolecules conformation. Moreover, they may modify the surface properties as a consequence of blocking active centers accessible for polymer macromolecules. Explanation of such a phenomena is essential to many areas of human activity, in which adsorption of both natural and synthetic polymers is applied [1-6].

Chromium (III) oxide ( $\text{Cr}_2\text{O}_3$ ) was applied as the adsorbent. It is a green, amorphous solid.  $\text{Cr}_2\text{O}_3$  is used as a stable, non-toxic dye in the paint and ceramic industries as well as for glass production. A broad application of this oxide causes that  $\text{Cr}_2\text{O}_3$  is a common pollutant in sewages. Because of its intense colour, it is particularly undesirable in an aqueous medium [7, 8].

In the studies two polymers from the polyamino acid group were used: anionic polyamino acid (ASP) and cationic polylysine (LYS). These synthetic macromolecular compounds contain in their structure appropriate amino acids linked by a covalent bond. Due to their structure, these compounds combine the characteristic features of both synthetic (excellent water solubility, stability in a wide pH range) and natural origin polymers (complete biodegradability, a lack of the toxicity). Studies of the adsorption properties of the above mentioned polymers can contribute to a wider use of this class of compounds. Due to the complete biodegradability and nontoxicity of used polymers, the studied systems can find an application mainly in the sewage treatment and water purification processes. Formation of the stable  $\text{Cr}_2\text{O}_3$  suspensions in the presence of the polyelectrolytes is also important in ceramics.

The aim of this paper was to determine the influence of a background electrolyte type and solution pH on the adsorption properties of two polyamino acids of different ionic nature of functional groups. In order to make a comprehensive analysis of the interactions present in the studied systems, the adsorption amount of the macromolecular compounds on the surface of colloidal chromium (III) oxide was measured. Additionally, the surface charge density measurements as well as the zeta potential tests in the absence and presence of the polymers (in a suitable background electrolyte) were performed. These studies allow to determine the

influence of the earlier mentioned factors on the adsorption and electrokinetic properties of the polyamino acid solution/  $\text{Cr}_2\text{O}_3$  systems.

## 2. MATERIAL AND METHODS

Chromium (III) oxide ( $\text{Cr}_2\text{O}_3$ ) produced by POCh Gliwice (Poland) was used as an adsorbent in the experiments. The specific surface area of  $\text{Cr}_2\text{O}_3$  determined by the BET method (analysis of nitrogen adsorption-desorption isotherms; Micromeritics ASAP 2405 analyzer) was found to be  $7.12 \text{ m}^2/\text{g}$ . The solid was washed with doubly distilled water to remove the impurities until the conductivity of the supernatant was smaller than  $2 \text{ }\mu\text{S}/\text{cm}$ . The point of charge ( $\text{pH}_{\text{pzc}}$ ) of chromium (III) oxide was 7.6 (obtained from the potentiometric titration) and its isoelectric point ( $\text{pH}_{\text{iep}}$ ) was about 6 (zeta potential measurements; Zetasizer 3000, Malvern Instruments) [9]. Despite the small surface area, chromium (III) oxide was applied as the adsorbent. It was the consequence of the fact that in the studied pH range on the  $\text{Cr}_2\text{O}_3$  surface can exist surface active groups of different charge (positively charged in acidic pH and negatively charged at higher pH values). Although  $\gamma\text{-Al}_2\text{O}_3$  exhibits considerably higher surface area, the  $\text{pH}_{\text{pzc}}$  point of this material is equal to 8-9. It denotes that the alumina particles become negatively charged above pH 9. The presence of positive charge on the adsorbent surface lead to the situation in which the cationic polylysine do not undergo adsorption at the solid-liquid interface.

Polyamino acids: sodium salt of polyaspartic acid (ASP) and poly(lysine hydrochloride) – LYS were produced by Alamanda-Polymers (USA). The average molecular weights of the polymers in question were: 27.000 for ASP and 33.000 for LYS. The polyamino acids exhibit ionic character (anionic and cationic for ASP and LYS respectively) These polymers contain one type of functional groups in their macromolecule chains which is able to dissociate in the aqueous solution. The structures of polymeric substances are shown in Fig. 1. The polydispersity index data (obtained from the producer) were in the range from 1.02 to 1.05. As a supporting electrolyte sodium chloride or calcium chloride (Fluka) were used. The concentration of  $\text{NaCl}$  was  $0.01 \text{ mole}/\text{dm}^3$  whereas the concentration of  $\text{CaCl}_2$  was equal to  $0.003 \text{ mole}/\text{dm}^3$ . Such concentrations of the salts give demanded ionic strength of the solutions ( $I = 0.01$ ) for both electrolytes. The experiments were carried out in doubly-distilled water at room temperature ( $\approx 25^\circ\text{C}$ ).

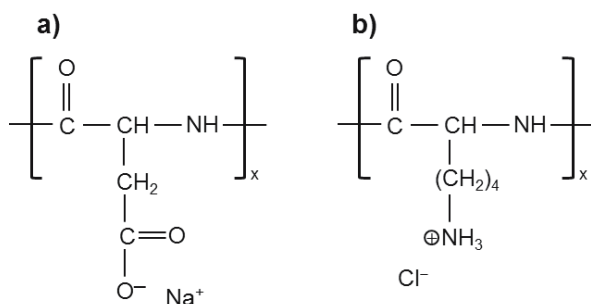


Fig. 1. Structures of used polymers: a) ASP, b) LYS.

### 2.1. Adsorption measurements

Adsorbed amount ( $\Gamma$ ,  $\text{mg}/\text{m}^2$ ) of the applied polyamino acids was measured by the spectrophotometric method with a UV-Vis Spectrophotometer Carry 100 (Varian) connected to the computer with the use of ASP and LYS absorption spectra. Experiments were carried out for the two different pH values for each polymer: 3 and 10 for ASP as well as 7.6 and 10 for LYS. Previous studies shown that LYS does not adsorb on the  $\text{Cr}_2\text{O}_3$  surface at  $\text{pH} = 3$ . The concentrations of both polymers ranged from 10 to 120 ppm. All samples were prepared by diluting the stock solution of macromolecular compounds whose concentrations were determined by the gravimetric method. The concentration of the supporting electrolyte ( $\text{NaCl}$  or  $\text{CaCl}_2$ ) was constant.

To determine the adsorption amount of polyamino acids, the following procedure was applied. 0.1 g of chromium (III) oxide was added to  $10 \text{ cm}^3$  of polymer solution in the supporting electrolyte with suitable concentration. Next pH was adjusted to the desired value using  $\text{HCl}$  and  $\text{NaOH}$  at a concentration of  $0.1 \text{ mole}/\text{dm}^3$ . To achieve adsorption – desorption equilibrium, the suspension was shaken for 20 hours in a thermostated stirrer ( $25^\circ\text{C}$ ). Then, the suspension was centrifuged twice for 10 minutes and 5 ml of clear solution was taken for further analysis. The absorbance of ASP and LYS was measured at a wavelength 210 nm. The extent of polymer adsorption was calculated from the calibration curves measured in solutions of different pH values. The measurement uncertainty in the analysis was up to 3%.

### 2.2. Potentiometric titration

The surface charge on the metal oxide is formed as a result of reactions between the surface hydroxyl groups and electrolyte ions. The

most important factor in the surface charge formation process is the concentration of hydrogen and hydroxide ions as well as ions of background electrolyte. Hydrogen ions influence the surface charge density through the reactions of surface hydroxyl groups:



Depending on the considered theory of the electric double layer, supporting electrolyte ions could undergo specific adsorption as well as bind to the surface through non-specific interactions. Ions become specifically adsorbed as a result of short-range interactions. It is assumed that non-specifically adsorbed ions can be in contact with the metal oxide surface due to long-range coulombic interactions (repulsion or attraction).

Surface charge density of chromium (III) oxide was determined by potentiometric titration. The surface charge density was calculated from the dependence between the volume of base added to the suspension in order to obtain desired pH value:

$$\sigma_0 = \frac{\Delta V c F}{m S} \quad (3)$$

where:  $\Delta V$  – the difference between volume of acid/base added to the suspension to obtain the desired pH of the solution,  $c$  – the molar concentration of acid/base,  $F$  – the Faraday constant ( $9.648 \cdot 10^4$  C/mole),  $m$  – the mass of the metal oxide,  $S$  – the specific surface area of applied metal oxide.

Chromium (III) oxide surface charge density in the presence and absence of polyamino acid (ASP and LYS) in a suitable supporting electrolyte was measured. The influence of the polymers concentration on the surface charge was investigated. The polymer concentrations were 10 and 100 ppm. 1.5 g of  $\text{Cr}_2\text{O}_3$  was added to a thermostated Teflon vessel containing  $50 \text{ cm}^3$  of supporting electrolyte solution or polymer solution with a fixed concentration. The suspensions were titrated with the NaOH solution with a concentration of  $0.1 \text{ mole/dm}^3$ . A thermostated Teflon vessel with a stirrer, an automatic burette (Dosimat 765, Methrom), glass and calomel electrodes (Beckman Instruments), the pH meter PHM 240 (Radiometer) were the parts of the measurements set. The process was controlled by a computer. The surface charge density was calculated using the “Titr\_v3” program written by Władysław Janusz.

### 2.3. Zeta potential measurements

The zeta potential measurements were carried out in the absence and presence of polyamino acids in the pH value range of 3 – 10 (Zetasizer 3000, Malvern Instruments). In this case, a suspension of 500 cm<sup>3</sup> containing 0.03g of Cr<sub>2</sub>O<sub>3</sub> in the supporting electrolyte solution with suitable concentration was prepared. After the suspension was sonicated for 3 minutes (Ultrasonic Processor XL, Misonix) and the required pH value in the samples was adjusted by adding an appropriate amount of 0.1M HCl or 0.1M NaOH. In order to study polymer adsorption influence on the zeta potential of the chromium (III) oxide colloidal particles, 0.03 g of the solid was added to the NaCl solution with a fixed polymer concentration (ranging from 0.01 to 1 ppm). The electrokinetic potential was measured with the zeta meter connected with the computer. Each average zeta value is the result of eight repetitions. The measurement error did not exceed 3 %.

## 3. RESULTS AND DISCUSSION

### 3.1. Adsorption measurements

As it can be seen from the analysis of Figs. 2 and 3, a kind of the supported electrolyte has a great influence on the ionic polyamino acids adsorption process. Concentrations of the applied electrolytes were chosen to provide the constant ionic strength (I) equal to 0.01. In the presence of CaCl<sub>2</sub>, the increase in the adsorption amount of the anionic polymer both at pH 3 and 10 is observed. The opposite situation takes place in the case of the cationic polylysine, where in the studied pH range the addition of the calcium chloride leads to reduction of the polyamino acid adsorption amount. The reason for such polymers behaviour at the Cr<sub>2</sub>O<sub>3</sub> – aqueous solution interface are the coordination complexes formed between the macromolecules and calcium ions, which affect changes of the interactions present in the system. Moreover, Ca<sup>2+</sup> ions can undergo adsorption on the Cr<sub>2</sub>O<sub>3</sub> surface and block the active sites which become inaccessible to the polymer macromolecules.

The adsorption measurement results indicate that in the presence of CaCl<sub>2</sub>, the amount of ASP adsorbed on the Cr<sub>2</sub>O<sub>3</sub> surface rises compared to the values obtained for NaCl (Fig. 2). The reason for such a behaviour is the appearance of the complexes between the calcium ions and the dissociated carboxylic groups present in the polymer chain. The above

mentioned complexes can be created between the  $-\text{COO}^-$  groups belonging to the same or different macromolecules (Fig. 4). The formation of a given type of connections results in the significant macromolecules conformation changes on the solid surface [10]. The previous studies of ASP in the presence of NaCl as the support electrolyte proved that adsorption of the polymer at pH 3 is mainly driven by electrostatic attraction forces and hydrogen bonds [11].

Table 1. Degree of dissociation of studied polyamino acids [11].

pH	ASP dissociation degree	LYS dissociation degree
3.0	0.157	1.00
6.0	0.995	0.998
7.6	0.999	0.997
10.0	1.00	0.780

What is more, ASP shows the tendency to formation of the associated macromolecular pairs due to the interactions between the undissociated carboxylic groups of the adjacent chains [12]. In turn, with the increasing solution pH, the decrease in the ASP adsorption amount is significant. It follows from the repulsion forces occurring between the strongly ionized polyamino acid chains and the negatively charged surface active groups. Under these conditions, the polymer adsorption can be explained mainly by the hydrogen bridges formation. The use of  $\text{CaCl}_2$  as the background electrolyte increases the magnitude of the ASP adsorption in both studied pH values. This fact is a consequence of probable formation of the complexes between the functional groups belonging to two different ASP macromolecules and  $\text{Ca}^{2+}$  ions.

Due to the strong adsorption of the anionic polymer at pH 3 and the repulsion forces occurring between the positively charged adsorbent surface and  $\text{Ca}^{2+}$  ions ( $\text{pH}_{\text{pzc}} = 7.6$  in NaCl), one of the macromolecules undergoes binding to the solid surface, while the other one must be directed toward the bulk solution. Moreover, formation of the complexes between the dissociated carboxylic groups placed to the same polymer chain and the calcium ions (intramolecular complexes) in the solution is also possible. As a result, the polymer macromolecules exhibit the conformation of the more densely packed coil [13]. In both cases the obtained polymer conformation allows to adsorb a larger number of ASP macromolecules per unit of the adsorbent surface area, which explains the

increase in the adsorption in the higher polymer concentrations range. In the acidic solutions, the differences in the amount of the polymer bounded to the metal oxide surface are negligible (in comparison to NaCl). It is obvious that the increase in the polymer concentration accompanies the rise in the  $-\text{COO}^-$  groups and the probability of the formation of the complexes between the groups belonging to the same chain is also larger. At low ASP levels, the number of polymer- $\text{Ca}^{2+}$  ions complexes is small due to a lack of a sufficient number of carboxylic groups capable of creating this type of connections (ASP dissociation degree at pH 3 is equal to 16%, see Table 1). The proposed ASP adsorption mechanism in the  $\text{CaCl}_2$  environment is presented in Fig. 5.

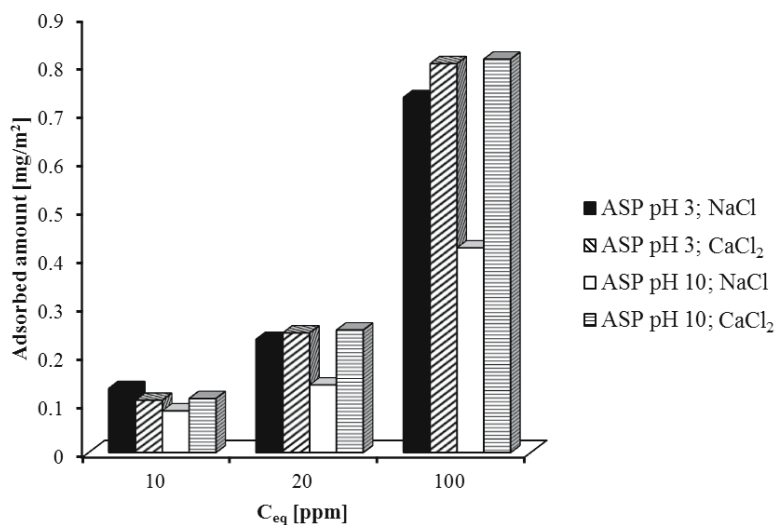


Fig. 2. Adsorption of ASP 27 000 on the  $\text{Cr}_2\text{O}_3$  surface as a function of solution pH in the presence of various background electrolytes.

The influence of  $\text{CaCl}_2$  as the background electrolyte on the ASP adsorption is more clearly visible at  $\text{pH} = 10$ . The divalent calcium ions attendance leads to the considerable growth of the ASP adsorbed amount throughout the measured concentrations range. This allows to draw a conclusion, that under these conditions the polymer adsorption is likely driven by formation of intramolecular complexes. As a result, the highly ionized ASP macromolecule ( $\alpha = 100\%$ ) become more neutralized causing the reduction of the polymer coil dimensions. Decrease in the amount of the negatively charged functional groups placed in the polymer chains reduces the repulsion forces occurring between the polymer coil and the solid surface. In addition, divalent  $\text{Ca}^{2+}$  cations more effectively



screen the repulsive forces between the polymer chains and the  $\text{Cr}_2\text{O}_3$  surface. Specific adsorption of the calcium ions does not inhibit the polymer binding since the remaining carboxylic groups can still create the intermolecular connections. It favours formation of the adsorption layer rich in the loops and tails, which is responsible for the meaningful increase of the ASP adsorption amount compared to the analogous pH value when NaCl is used as the support electrolyte.

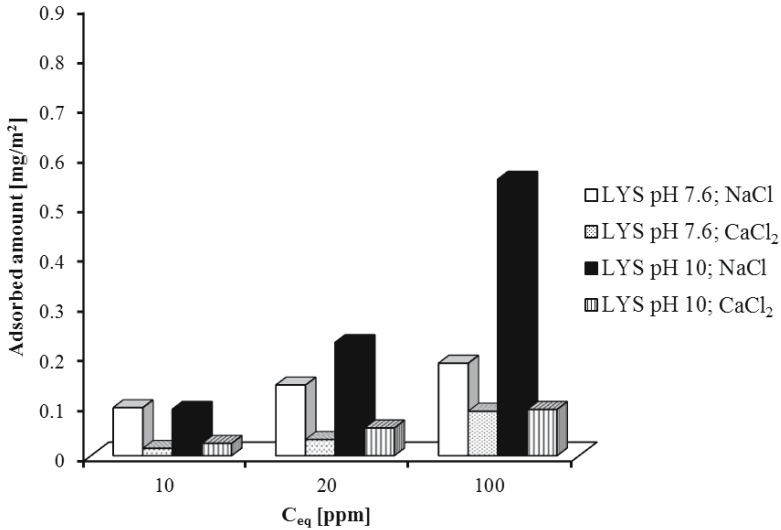


Fig. 3. Adsorption of LYS 33 000 on the  $\text{Cr}_2\text{O}_3$  surface as a function of solution pH in the presence of various background electrolytes.

The comparison between the polylysine adsorption data as a function of the studied background electrolytes (Fig. 3.) indicates that in the presence of calcium chloride, the adsorption amount of the cationic polymer is significantly decreased both at pH = 7.6 and 10. The earlier research proved that electrostatic attraction between the ionized amino groups and the negatively charged  $\text{Cr}_2\text{O}_3$  surface as well as the hydrogen bonds formation are responsible for LYS adsorption under these conditions [11]. Reduction of the polymer adsorption after the addition of  $\text{CaCl}_2$  (Fig. 6) can be explained by strong tendency of  $\text{Ca}^{2+}$  ions to undergo a specific adsorption on the  $\text{Cr}_2\text{O}_3$  surface resulting in a block of the adsorbent active sites accessible to the macromolecules. Another fact that must be taken into consideration during the discussion is the attendance of the quaternary amino groups in the LYS structure, which do not participate in the formation of complexes with the calcium ions. These connections can arise only as a result of the  $\text{Ca}^{2+}$  ions coordination

by the lone electron pairs of nitrogen and oxygen atoms originating from the peptide bond.

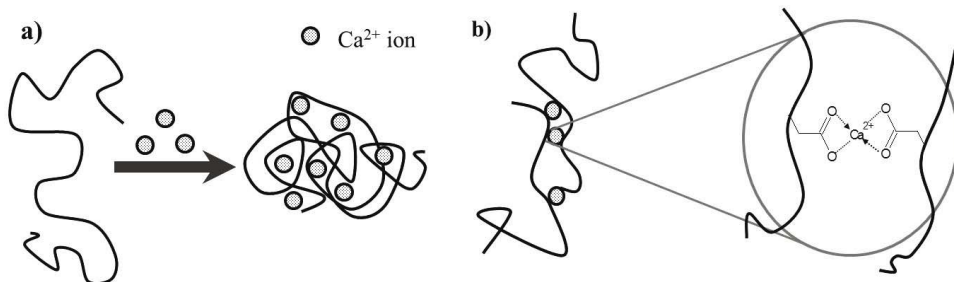


Fig. 4. Interactions between the polymer and  $\text{Ca}^{2+}$  ions: a) intramolecular complexes, b) intermolecular complexes.

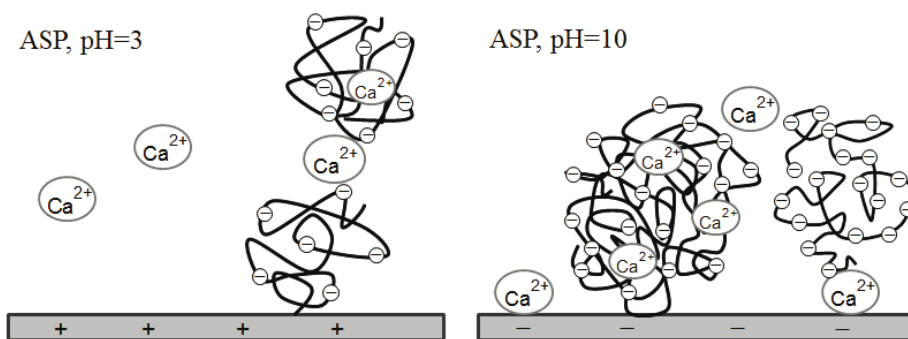


Fig. 5. A proposed mechanism of ASP adsorption on the  $\text{Cr}_2\text{O}_3$  surface in the presence of  $\text{CaCl}_2$  as a function of studied solution pH values.

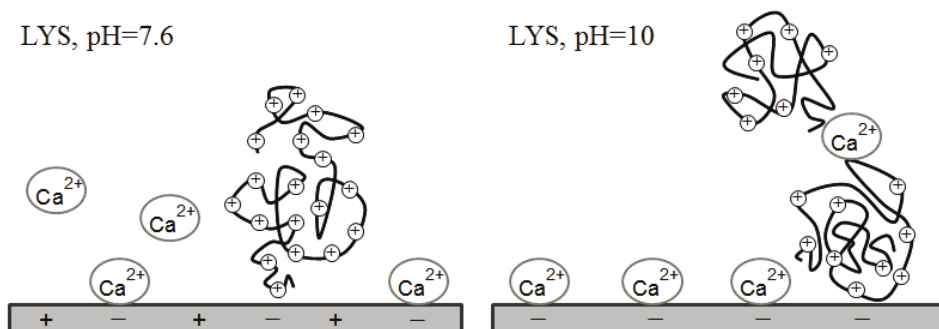


Fig. 6. A proposed mechanism of LYS adsorption on the  $\text{Cr}_2\text{O}_3$  surface in the presence of  $\text{CaCl}_2$  as a function of studied solution pH values.

Moreover, the calcium ions bring about the growth of the electrostatic repulsion between the LYS chains and the positively charged surface active groups. A slight increase in LYS adsorption at pH 10 (in comparison to pH = 7.6) is a consequence of a number of the intermolecular and intramolecular complexes appearance resulting from the interactions between  $\text{Ca}^{2+}$  ions and a lone electron pair of nitrogen atoms present in the undissociated amino group (the increase of solution pH accompanies the reduction of the LYS dissociation degree, Table 1).

### 3.2. Potentiometric titration

The analysis of the data obtained from the potentiometric measurements points out that the presence of the divalent cations has great influence on the surface charge density of chromium (III) oxide. As follows from the run of these dependencies, changes in the surface charge of the  $\text{Cr}_2\text{O}_3$  particles, when  $\text{CaCl}_2$  is used as the background electrolyte, are more visible in comparison to the values obtained in the presence of  $\text{NaCl}$ . The specific adsorption of  $\text{Ca}^{2+}$  cations induces the surface negative charges formation and therefore it is a cause of the surface charge density reduction in the whole measured solution pH range. These results are in good agreement with the theoretical predictions. In order to investigate the influence of the ionic polyamino acids attendance, the potentiometric measurements at the polymer concentrations of 10 and 100 ppm were conducted. The distinct changes in the  $\sigma_0$  were noted only for the concentration at the level of 100 ppm. The reason for such a behaviour can be found in the insignificant adsorption of the macromolecules in the low polymer concentration system.

It is clearly seen from Fig. 7 that the addition of ASP leads to the decrease of the surface charge density when  $\text{CaCl}_2$  or  $\text{NaCl}$  is used as the background electrolyte. As a result of the anionic polymer adsorption, near the solid surface there is formed a negatively charged adsorption layer containing numerous loops and tails. The observed changes come from the simultaneous occurrence of two effects. The adsorbed negatively charged polymer segments contribute to the induction of the positive charges on the  $\text{Cr}_2\text{O}_3$  surface. However, the dominant number of the dissociated carboxylic groups is located in the metal oxide by-surface layer (in the form of loops and tails) and it is responsible for the total reduction of the  $\text{Cr}_2\text{O}_3$  surface charge density values. The considerable decrease in the  $\sigma_0$  values when  $\text{CaCl}_2$  is used as the background electrolyte comes from ASP –  $\text{Ca}^{2+}$  ions complexes formation and their adsorption on the solid surface. On account of the interactions between

the calcium ions and the carboxylic groups belonging to one or more polymeric chains, the densely packed adsorption layer is created. The presence of a larger number of the negatively charged carboxylic groups in the by-surface part of solid reduces the surface charge density. In addition, the increase of solution pH accompanies the growth of ASP dissociation degree, which favours the formation of a larger number of the complexes. Increase in the number of the  $-\text{COO}^-$  groups placed near the  $\text{Cr}_2\text{O}_3$  surface due to  $\text{CaCl}_2$  attendance results from the more effective screening of the negative polymer charge by the divalent calcium ions compared to the monovalent sodium ions.

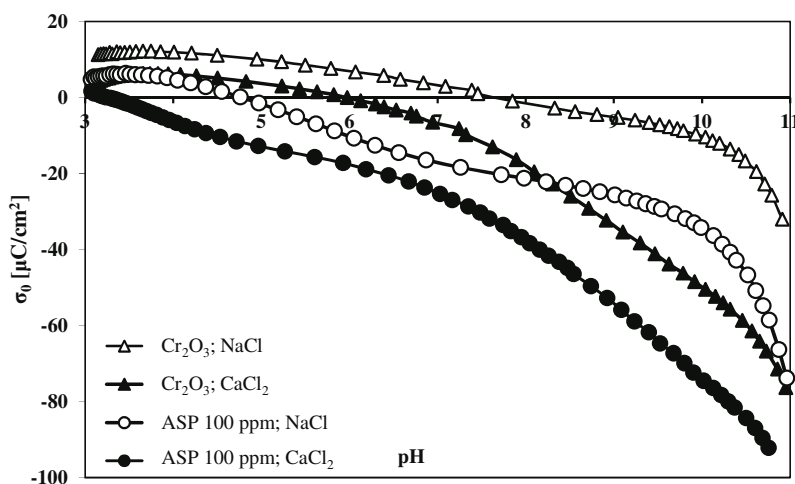


Fig. 7. Chromium (III) oxide surface charge density as a function of pH in the presence of different electrolytes ( $I = 0.01$ ) and ASP 27 000.

The course of the surface charge density curves in the presence of LYS as a function of the solution pH is presented in Fig. 8. The collected potentiometric data point out that the distinct reduction of the  $\text{Cr}_2\text{O}_3$  surface charge density is observed when NaCl is used as the electrolyte, whereas in the system containing  $\text{CaCl}_2$ , the influence of the polymer can be seen only in the pH range from 8 to 11 (compared to the values obtained without LYS). This is likely to come from the competitive calcium ions adsorption on the adsorbed active sites. It leads to the situation in which the majority of the cationic polyamino acid macromolecules occur in the bulk solution. Moreover, the attendance of the divalent calcium ions is responsible for the growth of the repulsion forces between the positively charged LYS macromolecules and the  $\text{Cr}_2\text{O}_3$  surface.

The reduction of  $\sigma_0$  values in the presence of  $\text{Ca}^{2+}$  ions observed for the high solution pH can be caused by the formation of a number of the coordination complexes between the amino groups originating from the adsorbed LYS chains and the background electrolyte cations (Fig. 8). This is possible as a result of the decrease in the polymer dissociation degree with the increasing solution pH values. Under these conditions, the polymer adsorption layer composed of a definite number of positively charged amino groups is formed. These groups can interact with the adsorbent surface groups leading to reduction of the solid particles surface charge [14]. The comparison between the potentiometric curves obtained for both electrolytes indicates that in the presence of  $\text{CaCl}_2$ , the less compact LYS adsorption layer with fewer loops and tails in the structure is formed resulting in the slight surface charge density decrease.

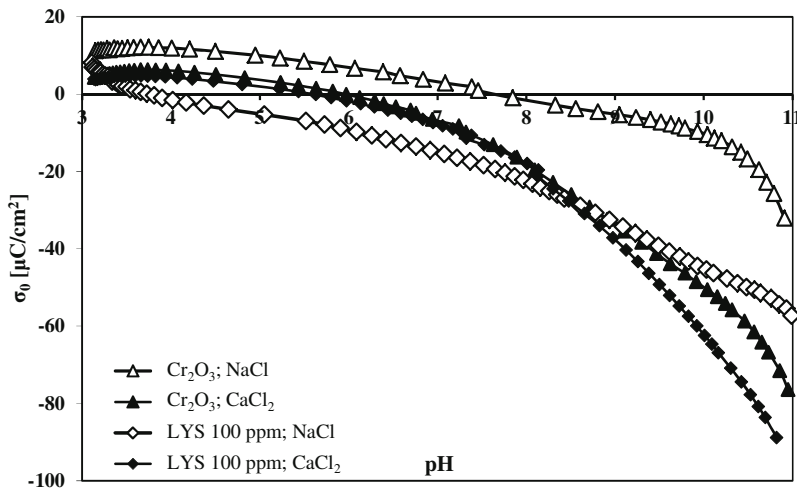
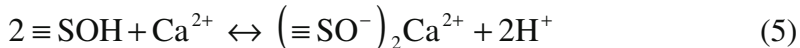
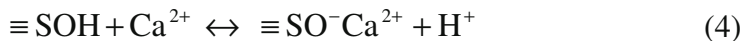


Fig. 8. Chromium (III) oxide surface charge density as a function of pH in the presence of different electrolytes ( $I=0.01$ ) and LYS 33 000.

### 3.3. Zeta potential measurements

The effect of the supporting electrolyte type on the zeta potential of the colloidal  $\text{Cr}_2\text{O}_3$  particles in the absence and presence of the ionic polyamino acids is presented in Figs. 10 and 11. As follows from the run of the curves, the  $\text{Cr}_2\text{O}_3$  zeta potential reaches the lowest values in all measured pH range when NaCl is applied as the background electrolyte. This phenomenon can be explained on the basis of the specific calcium ions adsorption on the  $\text{Cr}_2\text{O}_3$  surface. At the acidic pH values, the number

of negatively charged surface active sites is low and  $\text{Ca}^{2+}$  ions can undergo an ion exchange according to the equations 4-6 [17].



At pH about 6.5, the zeta potential increase follows from the adsorption of the  $\text{CaOH}^+$  ions appearing in the test system. These cations exhibit large affinity for the negative metal oxide surface (Fig. 9). Strong divalent ions binding is responsible for the double electrical layer thickness reduction. As a consequence, the contribution of the slipping plane shift effect is reduced and the zeta potential value rises [15, 16]. Moreover,  $\text{Ca}^{2+}$  ions possess greater charge compared to sodium cations, hence in a consequence of their adsorption on the  $\text{Cr}_2\text{O}_3$  particles leads to acquisition of the positive charge. As follows from the ionic equilibria graph presented in Fig. 9 the calcium hydroxide precipitation do not occur (in the opposite situation, the zeta potential of  $\text{Cr}_2\text{O}_3$  should be observed).

$$[\text{Ca}^{2+}]_{\text{TOT}} = 3.00 \text{ mM}$$

$$I = 0.010 \text{ M}$$

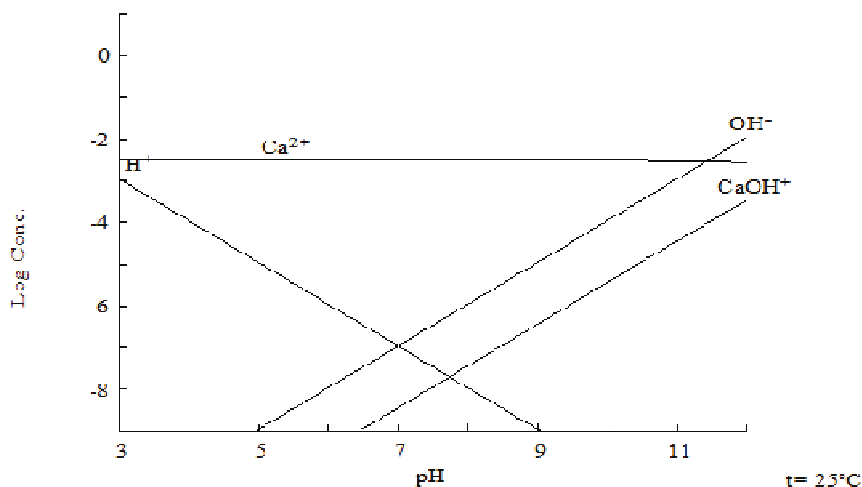


Fig. 9. Type of calcium ions present in the solution as a function of pH [the values were calculated by using the MEDUSA program written by Ignasi Puigdomenech].

Some interesting conclusions on the effect of the background electrolyte type on the zeta potential can be drawn from Fig. 10.

Analyzing the presented data it was found that regardless of the applied electrolyte, ASP reduces the  $\text{Cr}_2\text{O}_3$  zeta potential throughout the measured pH range. However, the observed changes are more visible for NaCl containing systems. Moreover, in the presence of sodium chloride the increase in the ASP concentration contributes to the further zeta decrease, whereas after the addition of  $\text{CaCl}_2$  the ASP concentration change does not affect the  $\zeta$  potential values. The zeta reduction with the rising of the ASP concentration in the  $\text{Cr}_2\text{O}_3/\text{NaCl}$  system comes from the presence of a larger number of negatively charged functional groups in the diffusion part of the solid particles. In addition, the polymer chains adsorbed on the  $\text{Cr}_2\text{O}_3$  surface are responsible for the increase in the slipping plane shift effect. When  $\text{CaCl}_2$  is used as the background electrolyte, the magnitude of the zeta lowering is smaller. As it was mentioned before, the interactions between the ASP segments and  $\text{Ca}^{2+}$  ions conduct to decrease in the ionization degree of the adsorbed macromolecules through formation of the intramolecular complexes (R-COO-Ca-COO-R). As a result, a smaller number of the  $-\text{COO}^-$  groups is located in the diffusion part of the metal oxide electrical double layer. The reduction of the polymer coil dimensions favours formation of the more densely packed polymer adsorption layer, which shifts the slipping plane less effectively. The above mentioned phenomena are the reason for the notable  $\text{Cr}_2\text{O}_3$  zeta decrease.

Fig. 11 presents the  $\zeta$  potential dependencies obtained for the  $\text{Cr}_2\text{O}_3$  particles with and without LYS as a function of the solution pH. In the NaCl containing systems, the presence of the cationic polymer causes a marked increase in the zeta potential in all measured pH (compared to the values drawn in the polymer absence). This is a consequence of numerous positively charged amino groups attendance in the  $\text{Cr}_2\text{O}_3$  diffusion layer. The decrease of the zeta potential at  $\text{pH} > 7$  is related to the slipping plane shift by the adsorbed LYS macromolecules. When  $\text{CaCl}_2$  is applied, the addition of polylysine contributes to less visible growth of the  $\zeta$  potential. It is a clear evidence for the competitive adsorption between the LYS macromolecules and the calcium ions which results in lowering of the polymer binding. Another fact that can be taken into consideration is the occurrence of strong repulsion forces between the LYS adsorbed chains. As can be noticed by analyzing Fig. 11, the lower LYS concentration (0.1 ppm) causes the higher increase of the zeta potential in comparison to the system containing 1 ppm of the polymer. It comes from the appearance of two competitive effects influencing the zeta potential. At the concentration of 0.1 ppm the effect of the positively charged amino groups

presence in the diffusion layer of  $\text{Cr}_2\text{O}_3$  particles predominates. With the increasing LYS concentration a larger number of LYS- $\text{Ca}^{2+}$  ions complexes is formed and shifting the slipping plane becomes the dominant effect.

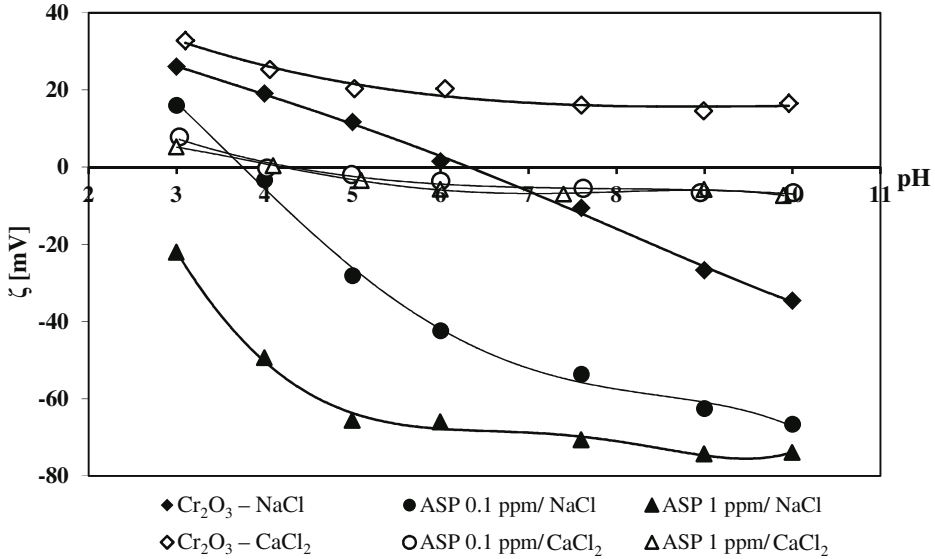


Fig. 10. Influence of the background electrolyte type on the zeta potential of  $\text{Cr}_2\text{O}_3$  particles in the presence and absence of ASP at the concentration of 0.1 and 1 ppm.

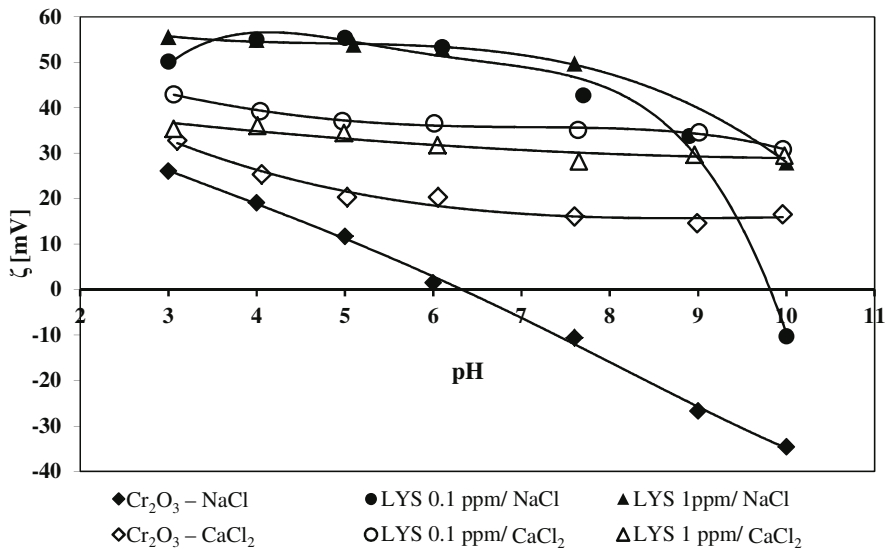


Fig. 11. Influence of the background electrolyte type on the zeta potential of  $\text{Cr}_2\text{O}_3$  particles in the presence and absence of LYS at the concentrations of 0.1 and 1 ppm.



#### 4. CONCLUSIONS

The influence of the type of the background electrolyte on the adsorption and electrokinetic properties of the  $\text{Cr}_2\text{O}_3$ / ionic polyamino acid solution system was investigated. It was pointed out that the adsorption of the studied polymers at the solid – liquid interface depends not only on the presence of  $\text{Ca}^{2+}$  ions. The obtained results showed that both the solution pH and the polymer functional groups type have the essential contribution to the interfacial behaviour of the system. It can be clearly visible that for the anionic polymer (ASP), the use of  $\text{CaCl}_2$  as the supporting electrolyte increases the amount of adsorbed macromolecules irrespective of the solution pH values. This is a consequence of the formation of complexes between the calcium ions and the carboxyl groups belonging to the same or different polymer chains. In turn, the opposite situation takes place in the case of polylysine (LYS), whose the magnitude of adsorption clearly decreases in the presence of  $\text{CaCl}_2$ . It comes from the specific adsorption of the supporting electrolyte ions on the  $\text{Cr}_2\text{O}_3$  surface and growth of the electrostatic repulsion forces between the components of the system.

The potentiometric titration data proved that there is strong influence of the background electrolyte type on the electrokinetic properties of the studied system. The formation of the complexes between the calcium ions and the carboxylic groups of the anionic polyamino acid results in the marked reduction of the surface charge density compared to the values obtained for chromium (III) oxide in the presence of a suitable supporting electrolyte. In the polylysine containing system,  $\text{CaCl}_2$  attendance induces small changes in the  $\text{Cr}_2\text{O}_3$  particles surface charge density as a consequence of the small adsorbed amount of the cationic polymer macromolecules under the alkaline pH conditions.

The type of the electrolyte cation has the essential influence on the metal oxide zeta potential value, but it is can also affect the magnitude of changes obtained in the presence of polyamino acid. It was also found that the addition of anionic ASP causes the zeta potential reduction throughout the measured pH range. The increase in the polymer concentration promotes the further decrease in the electrokinetic potential. The comparison of the data obtained for the studied electrolytes leads to the conclusion that in the presence of  $\text{NaCl}$  these changes are distinct, whereas in the  $\text{CaCl}_2$  environment the zeta potential reduction is not clearly shown. The reason for such a behaviour is the formation of closely packed adsorption layer due to the predominating effect of the slipping

plane shift by the adsorbed polymer macromolecules. The cationic character of LYS functional groups is a main reason responsible for the Cr<sub>2</sub>O<sub>3</sub> particles zeta potential growth regardless of the background electrolyte used in the studies. In the presence of NaCl, large zeta changes are observed. Application of CaCl<sub>2</sub> leads to the insignificant zeta increase in comparison to the values obtained for Cr<sub>2</sub>O<sub>3</sub> without the polymer under the same conditions. Such a behaviour can be explained by the considerable reduction of the polylysine adsorption in the presence of Ca<sup>2+</sup> ions and as a consequence of a small number of created complexes.

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### CURRICULA VITAE



**Iwona Ostolska** was born in 1988, Garwolin, Poland. Graduated from Maria Curie-Skłodowska University in Lublin in 2012 receiving an M. Sc. Degree in chemistry. Since 2012 on Ph. D. studies in Department of Radiochemistry and Colloid Chemistry, UMCS. Her research area is adsorption of homopoly-mers and copolymers at the metal oxide – polymer solution interface and the influence of this process on the suspension stability.



**Małgorzata Wiśniewska** studied chemistry at Maria Curie-Skłodowska University in Lublin and was graduated in 1998 receiving M.Sc. In 1999 she was employed at the Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry. She received Ph.D. in 2002. In 2011 she achieved postdoctoral degree. Main field of her interest is adsorption mechanism of polymer chains at the solid-liquid interface. She published 56 papers.