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Polymer structure impact on adsorption of the ionic polyamino acid homopolymers and their diblock copolymers on the colloidal chromium (III) oxide

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Abstract

The aim of the presented studies was investigation of the polymers structure and ionic nature influence on the adsorption layer architecture. As an adsorbent the chromium (III) oxide was used. What is important, the surface behaviour of different polyamino acids or polyethylene glycol diblock copolymers addition were analyzed as a function of the solution pH. The analysis of the data obtained from the adsorption and electrokinetic measurements allowed to propose the most probable structures of the polymer adsorption layers found at the solid particles – aqueous polymer solution. Moreover, the application of the stability measurements enabled determination of the interaction between the system constituents. Additionally, investigating the adsorbed polymer chains architecture on the solid particles is essential for further applications of the studied macromolecular compounds.

Keywords

Adsorption; block copolymers; chromium (III) oxide; polyamino acids; suspension stability.

Introduction

Polymers adsorption at the solid – liquid interface is a very sophisticated process depending on various factors but at the same time this phenomenon finds numerous applications in many industrial branches as well as in human activities[1-4]. The macromolecules structure is one of the factors which has a dominant influence on the type and strength of interactions with the adsorbent surface. A slight polymer chain modification contributes to the studied system interfacial properties changes on account of differences in the adsorbent - adsorbate interactions nature. In such a way, solid particles can be modified. Moreover, it is possible to obtain the suspensions exhibiting specific properties (among others, the desired stability). The adsorption process is also strongly affected by the solution pH as well as the adsorbent surface properties [5,6].

Interactions between various metal oxides and polymers containing only one type of the functional groups in the chain structure were repeatedly tested[7-10]. Searching for new stabilizers, the suspension destabilizing agents or the surface modifiers have led to the increased interest in copolymers – the compounds consisting of two (or more) types of structural units of the specified character connected via a covalent bond. These substances show considerably different properties compared to those of proper homopolymers which are their building blocks [11].

Due to the differences in the ionic nature, polarity or structure of the macromolecule block, the copolymers exhibit diverse interactions with the solid surface. In relation to the applied solution pH conditions, the ionic blocks may achieve a variety of conformations at the solid-liquid interface depending on the electrostatic forces occurring in the studied sample. Usually under appropriate conditions one of the polymer structural units undergoes a strong adsorption (an anchor), whereas the other is extended into the bulk solution (a buoy) [12]. Adsorption of various copolymers at the solid – liquid interface becomes one of the most interesting subjects for researchers of dispersed systems [13-21].

Chromium (III) oxide (Cr_2O_3), used as an adsorbent, is a crystalline solid with an intense green colour. Due to its properties it has a wide range of applications. Cr_2O_3 is used as a stable green pigment, a heterogeneous catalyst as well as a

coating for providing mechanical and thermal protection. In relation to the potential environmental risks associated with the chromium (III) oxide presence in the industrial sewage (especially for the water ecosystems), it is necessary to develop effective methods for its disposal. The polymers adsorption resulting in aqueous suspension destabilization can be one of them. Several papers concerning the usage of natural and synthetic substances have been published [22-30]. But on the other hand, stable Cr_2O_3 suspensions are desirable in the building and paint industries. In relation to the adsorbed layer architecture, it is possible to obtain specific stabilization/ destabilization properties of metal oxide particles. In addition, the polymer chains architecture at the solid – liquid interface can be easily controlled by the solution pH changes.

In the presented paper the analysis of the data obtained from the adsorption and electrokinetic (the potentiometric titration and the zeta potential) measurements of the systems containing colloidal chromium (III) oxide and suitable homopolymers (or PEG-copolymers) is shown. The results were used to determine the most probable structure of the polymer layers formed on the solid particles surface. Because of the fact that the polyamino acid units exhibit different ionic nature (ASP is derived from the anionic poly(L-aspartic acid), whereas the cationic LYS unit originates from poly(L-lysine)), the solution pH impact on the polymer adsorption process on colloidal chromium (III) oxide was investigated. Additionally, the application of modern turbidimetric method enables determination of systems stability. The hydrodynamic values (the TSI coefficient, the average aggregates diameter as well as the average flocs sedimentation velocity) calculated on the basis of the multiple light scattering theory were used for better description of overall processes occurring between the suspension particles (especially formation of hydrogen bonds and hydrophobic interactions). As a result, the polymer adsorption surface layer structure under different solution pH conditions was determined which is a highly innovative element. What is important, polymeric substances used in the measurements are totally biodegradable and non-toxic. These features cause that the selected macromolecules can be safely used in environmental issues as well as in many industrial branches (agrochemistry, cosmetic and food industry).

Experimental

Materials

Chromium (III) oxide (Cr_2O_3) from POCh, Poland was used as an adsorbent. The specific surface area of Cr_2O_3 determined by the BET method was found to be 7.12 m^2/g. The point of charge (pH_{pzc}) of Cr_2O_3 was 7.6 and its isoelectric point (pH_{iep}) was about 6 [22]. The average Cr_2O_3 particles size measured using dynamic light scattering was equal to 265 nm with the polydispersity index value below 0.25.

As a macromolecular compounds two class of polymers were applied (both from Alamanda Polymers, USA). One of them are simple polyamino acids:

- poly(L-aspartic acid sodium salt), denoted as ASP,
- poly(L-lysine hydrochloride) – LYS.

The second one consists of asymmetric diblock copolymers:

- poly(L-aspartic acid sodium salt)–*block*–poly(ethylene glycol) – ASP-*block*-PEG,
- poly(L-lysine hydrochloride)–block–poly(ethylene glycol) – LYS-*block*-PEG.

The polydispersity index (PDI) which is a measure of the molecular weight distribution in the polymer is in the range of 1.02 to 1.2. Therefore, polymers exhibit a uniform chain length. The polydispersity index is measured by gel permeation chromatography (GPC) in DMF with 0.1M LiBr at 60°C, a calibration curve constructed from narrow polydispersity PEG standards is used. The average molecular weight is provided by proton NMR spectroscopy using the amino acid repeating unit to the incorporated initiator peaks integration ratio. Average molecular weights of the polyamino acid units (belonging to both homopolymers and copolymers macromolecules) were 27 000 Da (for ASP) and 33 000 Da (for LYS), whereas the PEG block was characterized by the average molecular weight at the level of 1 000 Da. The studied homopolymers or copolymers structure is presented in Figs. 1 and 2. The dissociation constant values (pK_a) determined by the potentiometric titration were 3.73 and 10.55 for ASP and LYS respectively [23]. All measurements were performed in the pH range 3-10 at room temperature (≈25°C). NaCl of the concentration 0.01 mol/dm^3 was used as a supported electrolyte.

Methods

Adsorption measurements were conducted by the static method. The polymer concentration after the adsorption process was estimated by using the UV-Vis Spectrometer (Cary 100, Varian) at a wavelength of 210 nm. This wavelength was chosen after the UV-Vis absorption tests. The peptide bonds began to absorb at 280 nm and were most sensitive in the range of 210–230 nm. However, in that region, a severe interference from the absorption of OH^- ions was observed. Thus, 210 nm was picked and the absorption of 'blank' samples without polymers at the same pH was subtracted. A linear calibration curve was obtained from the standard solution, and it was used to determine the unknown polymer concentrations in the supernatants [8]. On order to eliminate the interferences originating from the hydroxyl ions, the calibration curves were made as a function of the solution pH. A suitable amount of Cr_2O_3 was added into the Erlenmeyer flasks containing 10 cm^3 of polymer solution with fixed concentrations. After adjusting the appropriate pH values, the samples were shaken in water bath (OLS 200, Grant) for 24 h. Then the sediments were centrifuged twice (MPW-223e, Centrifuge) and 5 cm^3 of the polymer solution was taken for the spectrophotometric analysis.

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:

$$\sigma_0 = \frac{\Delta V c F}{mS} \tag{1}$$

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

In order to obtain the potentiometric curves in the absence of the polymer, 50 cm^3 of the supported electrolyte and 0.2 cm^3 of 0.1 mol/dm^3 HCl were placed into the thermostated Teflon vessel containing 50 cm^3 of supporting electrolyte solution or polymer solution with a fixed concentration. 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 initial pH value in the range of 3 – 3.5. After reaching the equilibrium, 1.5 g of Cr_2O_3 was added. The obtained suspension was titrated by NaOH at a concentration of 0.1 mol/dm^3. The surface charge density of the adsorbent was calculated using the "Titr_v3" program written by W. Janusz.

The zeta potential measurements were made using Zetasizer Nano ZS (Malvern). To obtain a solid suspension in the background electrolyte solution, 0.003 g of Cr_2O_3 was added to a 50 cm^3 beaker containing a suitable amount of NaCl. The suspension was further sonicated for 3 minutes and the test pH was fixed. The zeta potential measurements were carried out up to pH 10. The samples with polymers were prepared in the same way, the polymer concentration range was 0.01 - 1 ppm.

Stability measurements were conducted using a turbidimeter Turbiscan Lab^{Expert} connected to the cooling module TLab Cooler and specialized computer software. The obtained results are presented in the form of transmissions and backscattering curves as a function of time. The analysis of the turbidimetric data allows to assess dynamics of occurring in the sample during the measurement. Moreover, due to the specialized computer software connected with Turbiscan, it was possible to calculate the TSI parameter (Turbiscan Stability Index) that is very useful in the evaluation of colloidal system stability. The TSI coefficient is calculated from the following formula:

$$TSI = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}} \qquad (2)$$

Where: x_i denotes the average backscattering for each minute of measurement, x_{BS} – the average value of x_i, n is the number of scans.

The coefficient is in the range from 0 (for highly stable systems) to 100 (in the case of very unstable suspensions). Based on the transmission and backscattering data, it was possible to determine the stability parameters such as the diameters of formed aggregates (particles, flocks) [μm] and the rate of particles (aggregates,

flocks) migration [µm/min]. These data were calculated using the programs TLab EXPERT 1.13 and Turbiscan Easy Soft. The measurement lasted 15 hours, during which data were collected every 15 minutes.

The particle velocity rate was calculated on the basis of the multiple light scattering theory. The particles diameter was determined using the general law of sedimentation, which is Stokes' law extended to the concentrated dispersions [31]:

$$V(\varphi, d) = \frac{\left| \rho_p - \rho_c \right| \cdot g \cdot d^2}{18 \cdot v \cdot \rho_c} \cdot \frac{[1 - \varphi]}{\left[1 + \dfrac{4.6\varphi}{(1 - \varphi)^3} \right]} \tag{3}$$

Where: V – the particles migration velocity [µm/min], ρ_c – the continuous phase density [kg/m^3], ρ_p – the particle density [kg/m^3], d – the particle mean diameter [µm], v – the continuous phase viscosity [cP], φ – the volume of the dispersed solid fraction [%].

The studies involve determination of changes of aqueous suspensions stability in the absence and presence of the studied macromolecular compounds. The samples without the polymer were prepared by adding 0.02 g of Cr_2O_3 to 20 cm^3 of the supporting electrolyte at a concentration of 0.01 mol/dm^3, then the suspensions were sonicated for 3 min. The next step was adjusting the required pH value of the samples. The suspensions containing polymers were prepared in an analogues way. The polymeric substance at a concentration of 100 ppm was added to the solid suspension after the sonication process. In order to investigate the effects of solution pH on the suspension stability, the measurements were performed at pH equal to 3 (or 4 for LYS and LYS-*block*-PEG), 7.6 and 10.

Results and Discussion

As can be seen from the chromium (III) oxide TSI parameter changes analysis (Tables 1 and 2), both the solution pH and the polymer functional groups ionic nature have an essential influence on the polymer adsorption layer structure found on the adsorbent surface. As a consequence, the above mentioned factors affect the metal oxide aqueous suspensions stability. Cr_2O_3 in the supporting electrolyte forms stable suspensions at pH 3 – the positively charged solid particles repel electrostatically. In the remaining solution pH values, the mineral oxide samples exhibit a considerable lower durability (the lowest value is reached in the isoelectric point at pH_{pzc} = 7.6). This is related to the attraction forces between the oppositely charged surface active groups located on the adjacent adsorbent particles.

Mechanism of polymers adsorption on the chromium (III) oxide surface

The poly(L-aspartic acid) and ASP-*block*-PEG copolymer adsorption isotherms on the chromium (III) oxide particles surface are presented in Fig. 3 (a-c). The studied polymers adsorption amount changes come from the differences in the adsorption mechanism. At pH 3 the Cr_2O_3 surface is positively charged. Under these conditions, a larger number of the diblock copolymer macromolecules is adsorbed at the solid interface compared to the homopolymer ASP. This is associated with the mixed adsorption layer formation. Under these conditions, both copolymer blocks undergo the adsorption process on the Cr_2O_3 surface. Moreover, the nonionic PEG segments can create the hydrogen bonds with the nondissociated carboxylic groups (the dissociation degree α_{ASP}=16%) belonging to the adjacent ASP chains, which additionally stabilize the structure. The PEG chains presence in the metal oxide surface layer provides the screening of charges originating from the neighbouring adsorbed polyamino acid units. Under the same conditions, the poly(L-aspartic acid) macromolecules can interact with the solid surface only due to the hydrogen bridges and the electrostatic attraction forces.

With the solution pH growth, the order of isotherms is changed. The diblock copolymer adsorption undergoes a gradual reduction related to ASP. The reason for such a behaviour are the mutual repulsion forces between the ASP block segments and the Cr_2O_3 particles surface as well as between the adjacent strongly extended polymer chains. At pH 10 the nonionic copolymer structural unit acts as a buoy, it is directed toward the bulk solution. Due to a lack of affinity for the mineral oxide

surface, it does not participate in the adsorption process at the solid – liquid interface. Additionally, the PEG block contributes to blocking of the adsorbent active sites resulting in an apparent decrease in the adsorption compared to ASP.

From the analysis of the adsorption amount data obtained for poly(L-lysine) and poly(L-lysine)-*block*-polyethylene glycol copolymer (Fig. 4 (a-c)), it is clearly visible that in both cases the adsorption maximum is reached in the alkaline environment. At pH 4 the quantity of the adsorbed polymer macromolecules is considerably lower. Besides the presence of PEG fragment in the copolymer chains, this compound does not undergo binding to the Cr_2O_3 surface at pH 3. The order of the curves is also important. The PEG block appearance in the macromolecules structure provides the copolymer adsorption growth compared to the homopolymer in the alkaline or neutral medium. The reverse order of the adsorption isotherms is observed at pH 4, which is directly related to the changes in both polymers binding mechanisms on the Cr_2O_3 surface.

The LYS-*block*-PEG adsorption growth at pH 10 and 7.6 (compared to the homopolymer with a similar molecular weight) could be explained by the PEG unit influence on the copolymer chains structure. As it was mentioned before, under the alkaline conditions the nonionic block does not exhibit affinity for the adsorbent surface and it can only interact with the lysine segments forming the hydrogen bonds. At pH_{pzc} equal to 7.6, the copolymer adsorption causes that at the solid – aqueous solution interface there can appear a mixed polymer layer (both structural units may be bounded on the Cr_2O_3 surface). In this case the PEG block can act in two ways. Firstly, the nonionic polymer segments participate in the LYS- *block*-PEG adsorption by forming the hydrogen bonds with the positively charged or amphoteric Cr_2O_3 surface groups. Moreover, these connections can be created between the LYS and PEG chains belonging to the other macromolecules [32]. At pH 4 the LYS homopolymer is strongly adsorbed on the Cr_2O_3 surface. Under these conditions, the fully ionized poly(L-lysine) chains adopt a highly stretched conformation and the electrostatic repulsion forces between the system constituents play the crucial role. Placing in the structure a short nonionic PEG block which would constitute an "anchor" should significantly increase the amount of the adsorbed copolymer macromolecules. The reduction of the LYS-*block*-PEG linked with the Cr_2O_3 surface

can be related to the active sites blocked by the substantially longer, expanded LYS fragment.

Surface charge density changes in the presence of the analyzed polymers

The Cr_2O_3 particles surface charge density (σ_0) changes as a function of the solution pH and the analyzed polymer contents are presented in Fig. 5 (a,b). As follows from the data analysis, the concentration of compounds consisting of the anionic polyamino acid unit has an essential impact on the potentiometric titration curves course. It is worth noting that due to the lack of the functional groups capable of electrolytic dissociation, the PEG block does not affect the σ_0 value changes. In the system without the macromolecular compounds, the solid particles point of zero charge (pH_{pzc}) is equal to 7.6 [22].

The polymer adsorption results in the chromium (III) oxide particles surface charge density reduction throughout the solution pH values (except for ASP at a concentration of 10 ppm, where the curves overlap). The σ_0 differences observed for the systems with lower macromolecular compounds concentration come from various chains conformation on the adsorbent surface. No apparent surface charge values alternation in the presence of ASP provides a "flatter" conformation compared to the diblock copolymer. In the acidic solution the coiled anionic polyamino acid chains interact with a limited number of the Cr_2O_3 surface groups. Only in the alkaline environment, the carboxylic groups dissociation degree growth (and associated with it development of the adsorbed polymer coils) ensures slight σ_0 value changes. The addition of the ASP-*block*-PEG copolymer to the studied system significantly decreases the solid particles surface charge density in the pH range 3-10. This is related to the insertion of a larger number of compound macromolecules on the phase boundary on account of the nonionic PEG unit presence. As a consequence, more ASP block dissociated functional groups are assembled in the metal oxide particles surface layer, which contributes to the effective reduction of σ_0 values. Overlapping of curves measured for Cr_2O_3 in the background electrolyte solution and in the presence of ASP-*block*-PEG above pH 10 is connected with considerable drop of the analyzed substance adsorption amount.

The increase in the anionic polymers concentration in the solution leads to the higher reduction of the σ_0 values with respect to the $Cr_2O_3/$ NaCl system. Simultaneously, reverse of the obtained dependencies is observed. Under the acidic pH conditions (in the range 3-5.5) the potentiometric curves received for both polymers coincide. This comes from the mutual cancellation of two effects associated with the interactions between the negatively charged polymer functional groups and the solid particle surface active species. First of all, the occurrence of numerous carboxylic groups near the metal oxide surface due to the adsorption process leads to σ_0 values decrease. However, on the other hand, the groups directly linked to the Cr_2O_3 surface contribute to the positive charges induction according to Eq.4 (where: S denotes the surface active group):

$$\equiv SOH + R - COOH \leftrightarrow \equiv SOH_2^+ COO^- - R \tag{4}$$

In the pH range from 3 to 5.5, the interactions between a few copolymer dissociated carboxylic groups with the Cr_2O_3 particles are responsible for the positively charged surface groups appearance. The remaining anionic polyamino acid segments are located at a certain distance surrounding Cr_2O_3. In turn, in the case of ASP a greater number of the $-COO^-$ is present on the solid surface leading to the less effective reduction of the surface charge. As the solution pH rises, the amount of copolymer macromolecules adsorbed on the Cr_2O_3 surface gradually drops on account of active sites blocking. Hence, under these conditions the surface charge density changes follow from the lower number of the negatively charged polymer functional groups assembled in the mineral oxide surface layer.

The impact of the homopolymer and copolymer containing the cationic poly(L-lysine) in the chains structure on the chromium (III) oxide surface charge density is presented in Fig.6 (a,b). The addition of any of the tested polymers leads to the point of zero charge (pH$_{pzc}$) shift toward more acidic pH values. Moreover, the adsorption of both polymers results in the surface charge density reduction in the whole measured pH range (except for LYS-*block*-PEG after exceeding pH 10). It is worth noting that regardless of compounds concentration, larger σ_0 values drop is observed in the system involving the poly(L-lysine) macromolecules.

The metal oxide particles surface charge values in the presence of the polymers whose macromolecules contain the cationic functional groups, are affected

by two competitive effects. The decrease in the surface charge density, compared to the system without a polycation, is a consequence of the negatively charged surface groups induction as a result of the electrostatic interactions between the ionized polymer amino groups directly bounded to the solid surface according to Eq.5 [33].

$$\equiv SOH + NH_3^+ - R \leftrightarrow \equiv SO^- NH_3^+ - R + H^+ \tag{5}$$
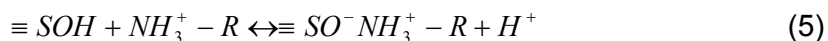
When a number of the positive charges accumulated nearby the particles surface exceeds those of the induced surface active groups amount, the total surface charge rises.

The Cr_2O_3 particles surface charge density reduction in the LYS presence comes from the accumulation of a large number of amino groups in the immediate vicinity of the adsorbent surface. The occurrence of the short PEG fragment in the macromolecule structure results in the less effective σ_0 values drop. In the solution pH range from 4 to 7.6, the nonionic block segments act as the polymer anchor, therefore a few NH_3^+ groups are located in a certain distance from the solid surface. Their small number is bounded to the Cr_2O_3 surface due to the hydrogen bonds formation (causing the σ_0 decrease). Above pH 10 the PEG chains practically lose the affinity for the adsorbent particles but the positive charges number in the metal oxide surface layer is larger enough to predominate the induction effect, and hence, the overall surface charge density increases compared to Cr_2O_3/NaCl. In the system including the poly(L-lysine), the number of the induced charges at the solid-polymer aqueous solution interface is considerably higher as a result of mutual attraction forces appearance. In the case of the cationic macromolecular compounds, the polymers concentration increase does not influence the surface charge density curves course.

Zeta potential measurements of Cr_2O_3 particles in the presence of different ionic nature polymeric substances

The zeta potential changes in the absence and presence of the studied compounds involving anionic poly(L-aspartic acid) are shown in Figs 7 (a-c). It should be noted that the PEG chains occurrence in the macromolecules can impact the electrokinetic potential values as a consequence of the slipping plane offset. The

adsorption of this block may also result in shift of the counter ions from the Stern layer.

For the systems characterized by the lowest polymer concentration (0.01 ppm), the electrokinetic potential in the presence of ASP does not differ from the values obtained for Cr_2O_3 in the supporting electrolyte. The ζ potential reduction is practically observed throughout the pH range for the system with the ASP-*block*-PEG macromolecules.

Similar to the case of the data originating from the potentiometric titration, for the low polymer concentrations this behaviour follows from the increase in the number of the negatively charged copolymer functional groups (in relation to ASP) in the solid particles diffusion layer. Rise of the studied anionic compounds concentration contributes to the essential Cr_2O_3 particles zeta potential values drop. The curves order reversing is observed – the ASP homopolymer more effectively decreases the zeta potential compared to the ASP-*block*-PEG copolymer. Initially in the acidic medium, the nonionic PEG block attendance causes the growth of the ASP-*block*-PEG macromolecules adsorption on the adsorbent surface. This leads to increase in the number of counter ions removed from the Stern layer and, as a result, the zeta potential reaches higher values than those for the corresponding ASP. Moreover, the formation of the densely packed mixed adsorption layer contributes to a weaker slip plane repulsion. As the solution pH rises, the polyamino acid chains in both substances adopt more stretched conformation. Simultaneously, beyond the point of zero charge (pH_{pzc}=7.6), the copolymer adsorption amount decreases in relation to the anionic homopolymer mainly through the adsorbent active centres blocking. Under these conditions a greater number of the dissociated carboxylic groups in the diffusion part of the solid particles covered by ASP is a direct reason for the electrokinetic potential reduction. The adsorption of the stretched anionic homopolymer macromolecules leads to the formation of the polymer layer consisting of numerous loops and tails at the solid-liquid interface. This results in a larger number of positively charged counter ions displacement out of the slipping plane (decreasing the ζ potential).

The zeta Cr_2O_3 potential changes in the absence and presence of the cationic polymers (c= 0.01, 0.1 as well as 1 ppm) are presented in Fig.8 (a-c). The zeta

dependencies analysis as a function of the solution pH allows to determine the diffusion part structure of the mineral oxide particles covered by the polymer film. From the listed data, one can easily draw a conclusion that the structure of the adsorbed polymer macromolecule substantially affects the course of the solid particles electrokinetic potential. The poly(L-lysine) addition leads to the sharp increase in the ζ potential values in the entire solution pH range. As it was mentioned before, the diblock copolymer binding mechanism changes depending on the presence of short, nonionic PEG unit in the chains. Regardless of the LYS-*block*-PEG concentration, for the initial pH values the zeta potential decreases compared to the Cr_2O_3 – NaCl system.

The electrokinetic potential differences, resulting from the presence of the compounds containing the cationic poly(L-lysine), can be explained on the basis of the two opposite effects. The zeta potential reduction is induced by the slipping plane offset by the adsorbed macromolecules. The more extended chains, the stronger influence is. On the contrary, numerous positively charged functional groups introduced to the diffusion part of the solid particles provide the zeta growth.

The reasons for the significant zeta potential changes obtained at pH 4 for both cationic polymers are the differences in the adsorption layer formed at the solid – liquid interface. The block copolymer adsorption is almost twice lower compared to LYS though fewer amino groups are located in the Cr_2O_3 particles diffusion layer. In addition, the ζ potential reduction in relation to the adsorbent in the supporting electrolyte solution indicates a large contribution of the slipping plane shift effect. The strongly stretched adsorbed chains can successfully screen the access to the other adsorbent active centres for the succeeding macromolecules. At $pH \geq pH_{pzc}$ the Cr_2O_3 surface charge density drop favours the increase in the copolymer adsorption amount on account of a larger number of the electrostatic interactions. Under these conditions both polymers contribute to the zeta potential values rise, but this tendency is less distinct in the case of LYS-*block*-PEG. This is related to the positive counter ions removal from the Stern plane by the closely packed copolymer macromolecules.

Cr$_2$O$_3$ suspension stability in the presence and absence of analyzed polymers

On the basis of the hydrodynamic parameters analysis (the TSI values, the average Cr$_2$O$_3$ aggregates diameter and the average sedimentation velocity) as well as the adsorption and electrokinetic data, the appropriate solid suspension stabilization (or destabilization) mechanism can be determined. The values obtained by the turbidimetric measurements carried out in the presence of suitable polyamino acids or their PEG diblock copolymers (Tables 1 – 4) can be very useful to describe the interactions existing between the adjacent adsorbent particles coated with the polymeric film.

The comparison of both the TSI values and the average aggregates diameter formed on account of the ASP (or ASP-*block*-PEG) adsorption at the Cr$_2$O$_3$ – aqueous polymer solution interface exhibits distinct influence of the polymer adsorption layer on the systems durability. The flocks size at pH 3 in the anionic diblock copolymer presence sharply increases in relation to those for homopolymers. Simultaneously, the stability of both suspensions is deteriorated. The reason for such behaviour is the Cr$_2$O$_3$ surface charge neutralization by the adsorbed polymer chains. Moreover, the low carboxylic groups dissociation constant value promotes the hydrogen bonds formation between the adjacent adsorbent particles, which are responsible for increasing the average aggregates diameter as well as their sedimentation velocity (Table 3). In the system containing the diblock copolymer, the nonionic PEG unit ability of the hydrogen bridges formation is responsible for the sample instability.

At the point of zero charge (pH=7.6) the studied system stability improvement is observed (compared to Cr$_2$O$_3$ in the supporting electrolyte). At the same time, the durability growth varies depending on the macromolecule structure besides the fact that the adsorption level of both polymers is very similar (TSI=13.22 for ASP and TSI=33.11 for ASP-*block*-PEG respectively). What is important, the average diameters of the aggregates are the smallest. This follows from the fact that the PEG block can act as an anchor, while between the ASP chains and the adsorbent the repulsive forces occur. Moreover, numerous hydrogen bridges formed between the ASP and PEG segments of the adjacent particles are responsible for the Cr$_2$O$_3$ particles aggregation. In turn, in the case of ASP the extension of long polymer

chains toward the bulk solution contributes to more effective suspension particles repulsion.

In the alkaline medium, the average flocks size in the ASP-*block*-PEG/ Cr_2O_3 system rises. The opposite tendency is observed in the solid suspension containing the homopolymer ASP. Under these conditions the PEG fragment does not adsorb on the solid surface and is directed toward the solution. Therefore it can interact in the hydrophobic ways or form the hydrogen bonds with both blocks of the copolymer macromolecules adsorbed on the other solid particles. Additionally, the adsorption amount decrease results in the smaller number of the $-COO^-$ groups occurring in the solid surface layer. Likewise at pH 7.6, the existence of one type of monomer units in the homopolymer macromolecule favours the higher Cr_2O_3 suspension stability because of the electrosteric stabilization.

The size changes of the aggregates formed in the presence of the cationic polymers and their sedimentation velocity are listed in Table 4. At pH 4 the addition of both LYS and LYS-*block*-PEG results in a slight Cr_2O_3 suspension stability decrease compared to the system which does not contain any polymeric substances. For two other pH values, the Cr_2O_3 particles are stabilized, wherein the TSI values are higher for LYS-*block*-PEG indicating occurrence of the additional hydrogen bonds interactions.

In the acidic medium the aggregates size (and the migration velocity) in the LYS-*block*-PEG/ Cr_2O_3 system are significantly greater compared to those of the homopolymer despite the lower diblock copolymer adsorption. The LYS-*block*-PEG chains bounded to the solid surface exhibiting the spatially extended conformation (ζ=6.4 mV in relation to 54.9 mV for LYS). In addition, the amino groups localized mainly in the particles diffusion layer are completely ionized, the hydrogen bonds can be formed between the segments belonging to different blocks, which explains the higher TSI value compared to LYS/ Cr_2O_3 (Table 2). In the case of the suspension including the poly(L-lysine), the repulsive forces between various loops and tails contained in different adsorbent particles adsorption layers gain the greater contribution.

At pH_{pzc} and above, both cationic polymers contribute to the increase in the Cr_2O_3 suspensions durability. It should be noted that this improvement is

considerably less evident after application of the block copolymer. Additionally, under these conditions the average aggregates size is smaller than at pH 4, in the basic solutions these values rise inconsiderably. Above the point of zero charge the adsorption of both polymers increases rapidly mainly through the electrostatic attraction forces. Simultaneously, the amino groups dissociation degree value is gradually reduced, thus the adsorbed polyamino acid chains adopt a more compact conformation. In the LYS case a larger number of positively charged loops and tails accumulated in the diffusion layer (ζ=49.7 mV at pH 7.6) results in the increasing repulsive forces between the adjacent solid particles. The slight deterioration of stability, observed in this system with the solution pH rise, follows from the appearance of single polymer bridges (d=0.135 µm). Despite higher copolymer adsorption and the presence of the same length poly(L-lysine) unit in the macromolecule structure, numerous hydrogen bonds formed between both polymer structural units adsorbed on different particles are responsible for the suspension durability drop.

Conclusions

The solution pH has the essential influence on the analyzed macromolecular compounds binding mechanism. The presence of two blocks of different ionic nature in the diblock copolymer macromolecules strongly affects the polymer film structure formed at the solid-liquid interface compared to those built up of one kind of monomeric units. The differences in the polymer chains arrangements are translated into changes in the Cr_2O_3 suspensions stability.

The highest adsorption level for both anionic polymers is found at pH 3. Under these conditions the particles surface charge becomes neutralized by the adsorbed oppositely charged chains. As a result, the solid suspensions in the presence of ASP and ASP-*block*-PEG are relatively unstable. With the solution pH increase, the number of the polymer macromolecules linked to the Cr_2O_3 surface gradually drops. However, the structure impact on the stability of systems containing both polymeric substances is more distinct. The durability reduction observed for the diblock copolymer presence is related to the hydrogen bridges formation between different polymer blocks.

In the case of the compounds containing the cationic poly(L-lysine) part in the macromolecule, the isotherms have the reversed order. The adsorption maximum is reached at pH 10, however, both polymers do not undergo binding at pH 3. Under the acidic pH conditions, the Cr_2O_3 suspensions in the presence of the cationic compound (or PEG copolymer) exhibit lower stability compared to the Cr_2O_3/ NaCl system. The solution pH increase results in the gradual solid samples stabilization. Due to possible interactions between the copolymer chains adsorbed on different adsorbent particles, this polymeric material is a better flocculant agent than poly(L-lysine) at pH≥pH$_{pzc}$.

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Fig. 1.

20

Fig. 2.

c)
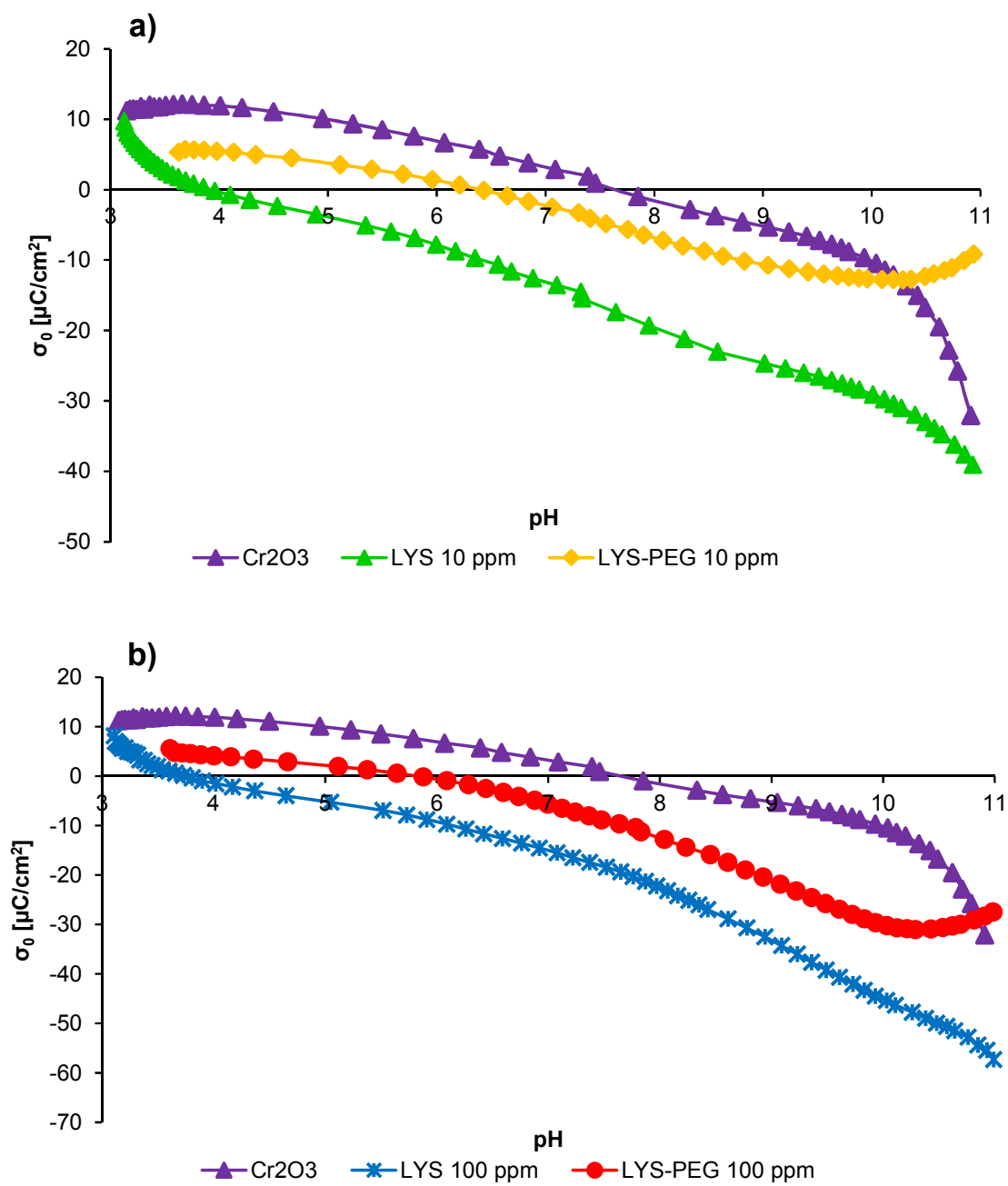
ASP pH 10 (○)   ASP-PEG pH 10 (●)

Fig. 3.
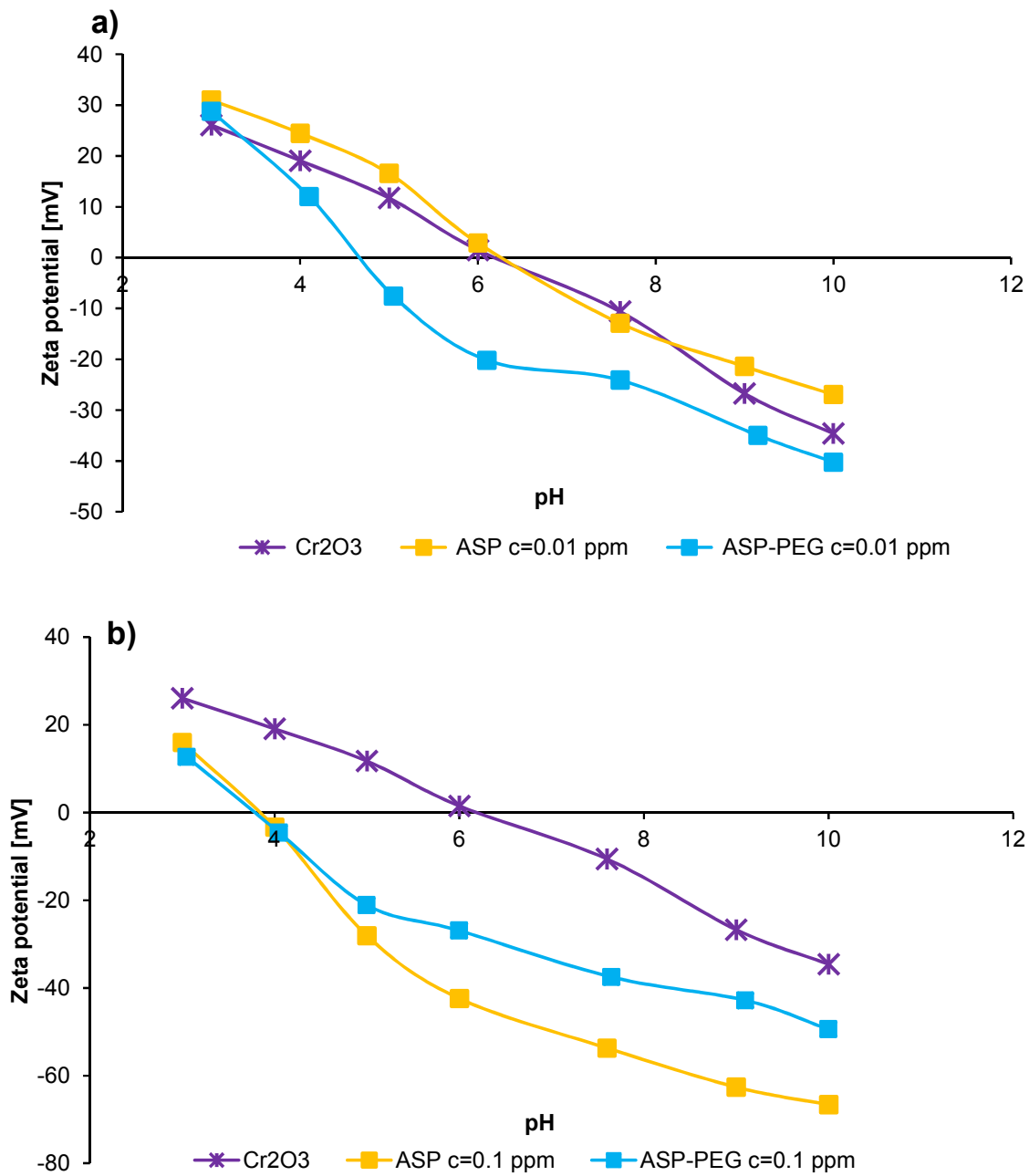

a)

LYS pH 4 (◇)   LYS-PEG pH 4 (◆)
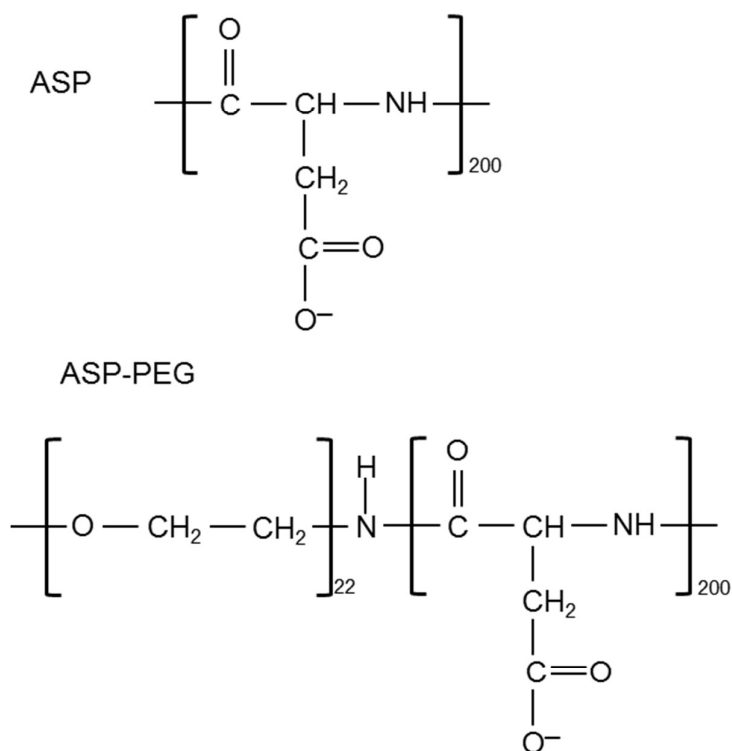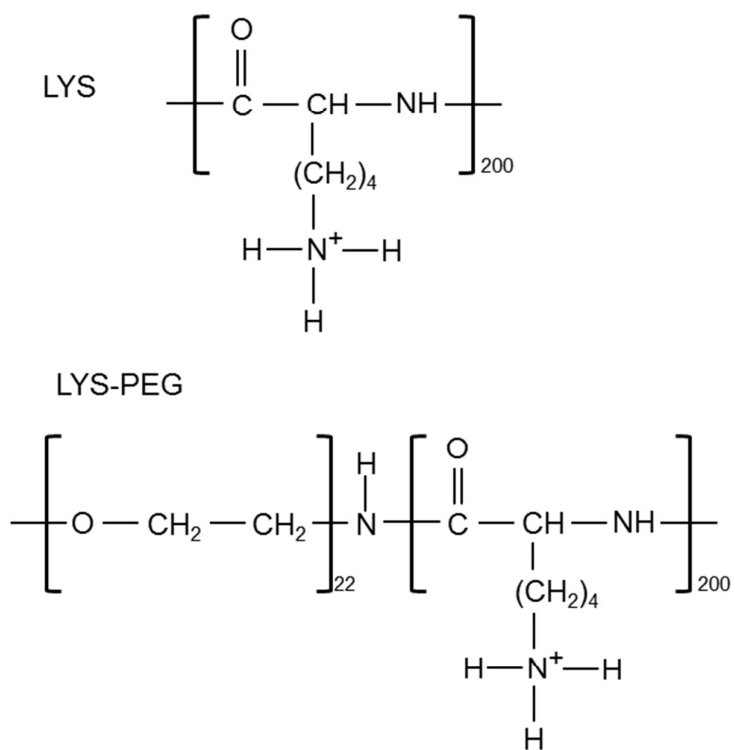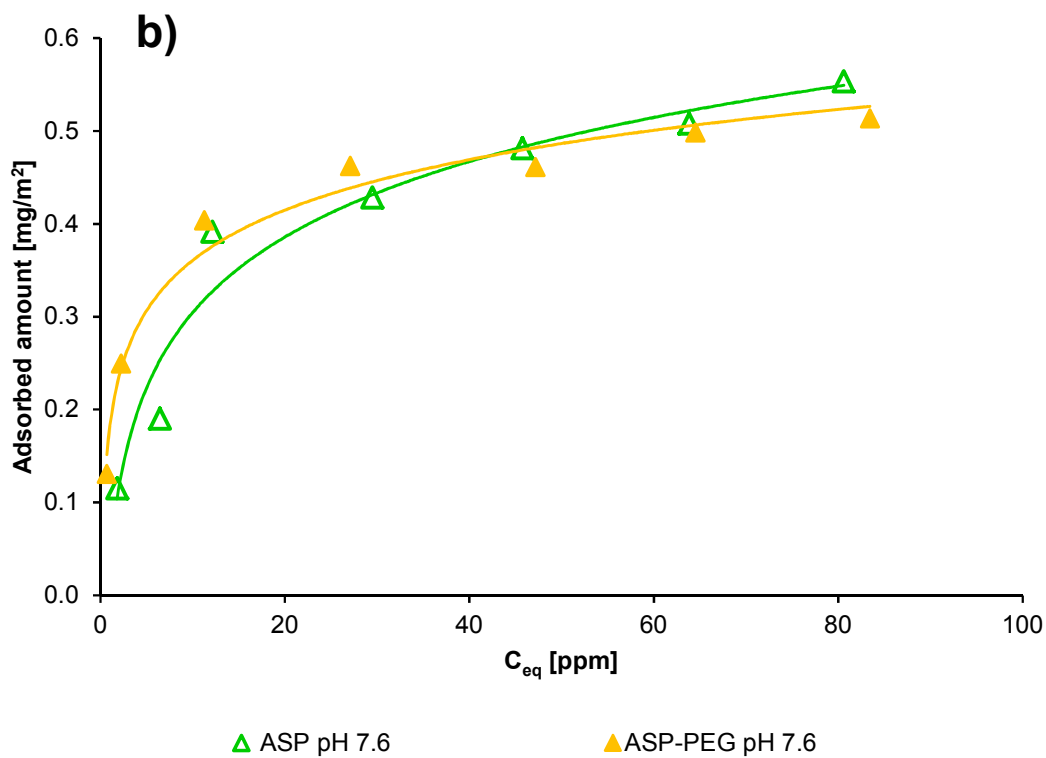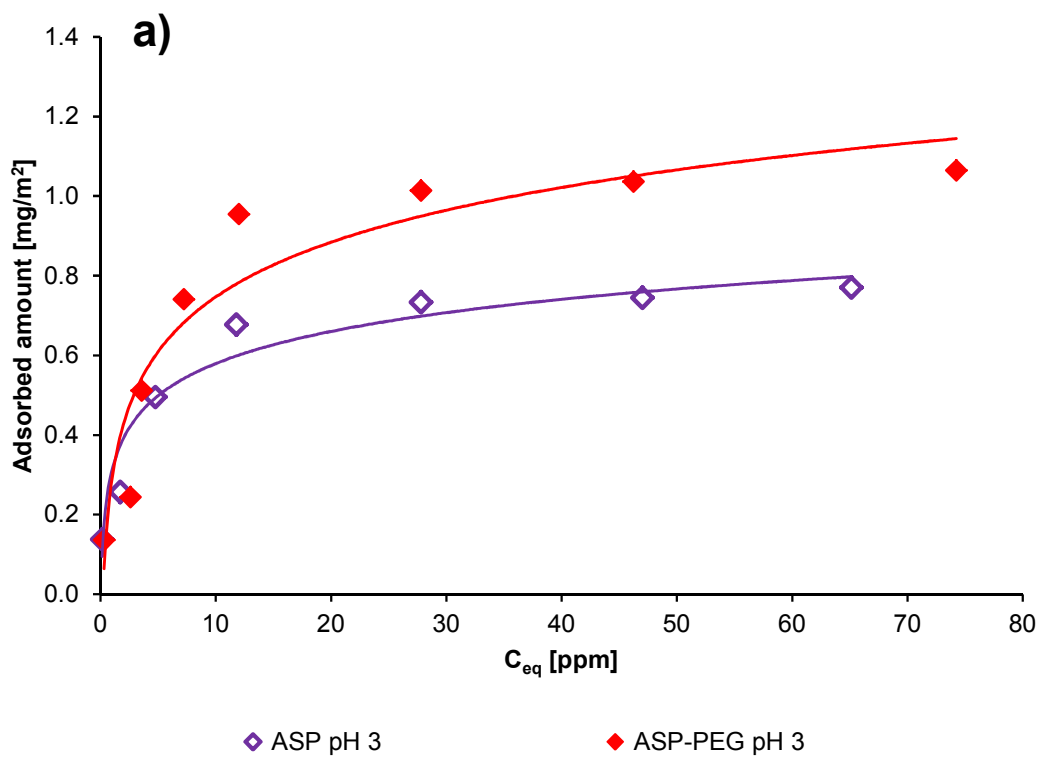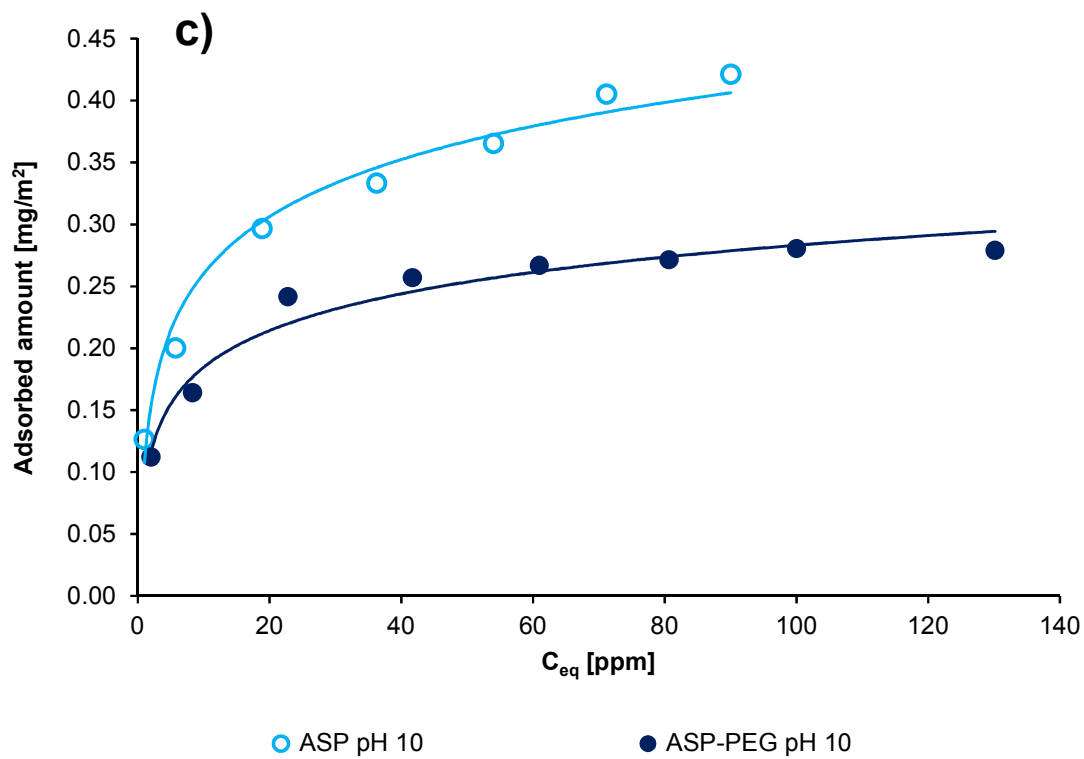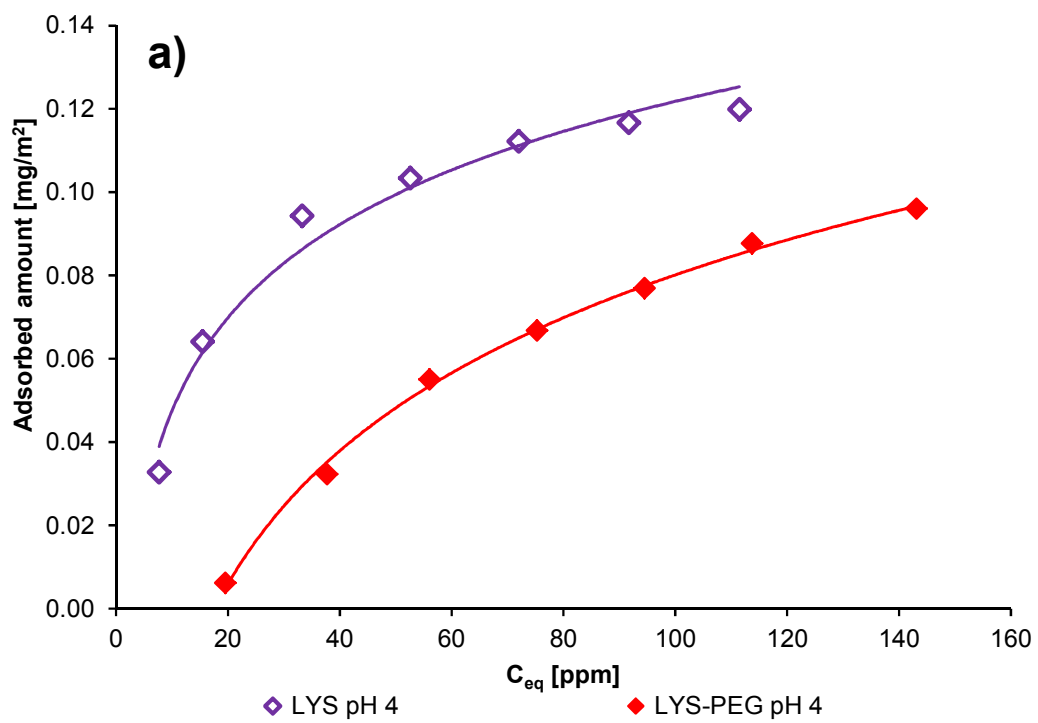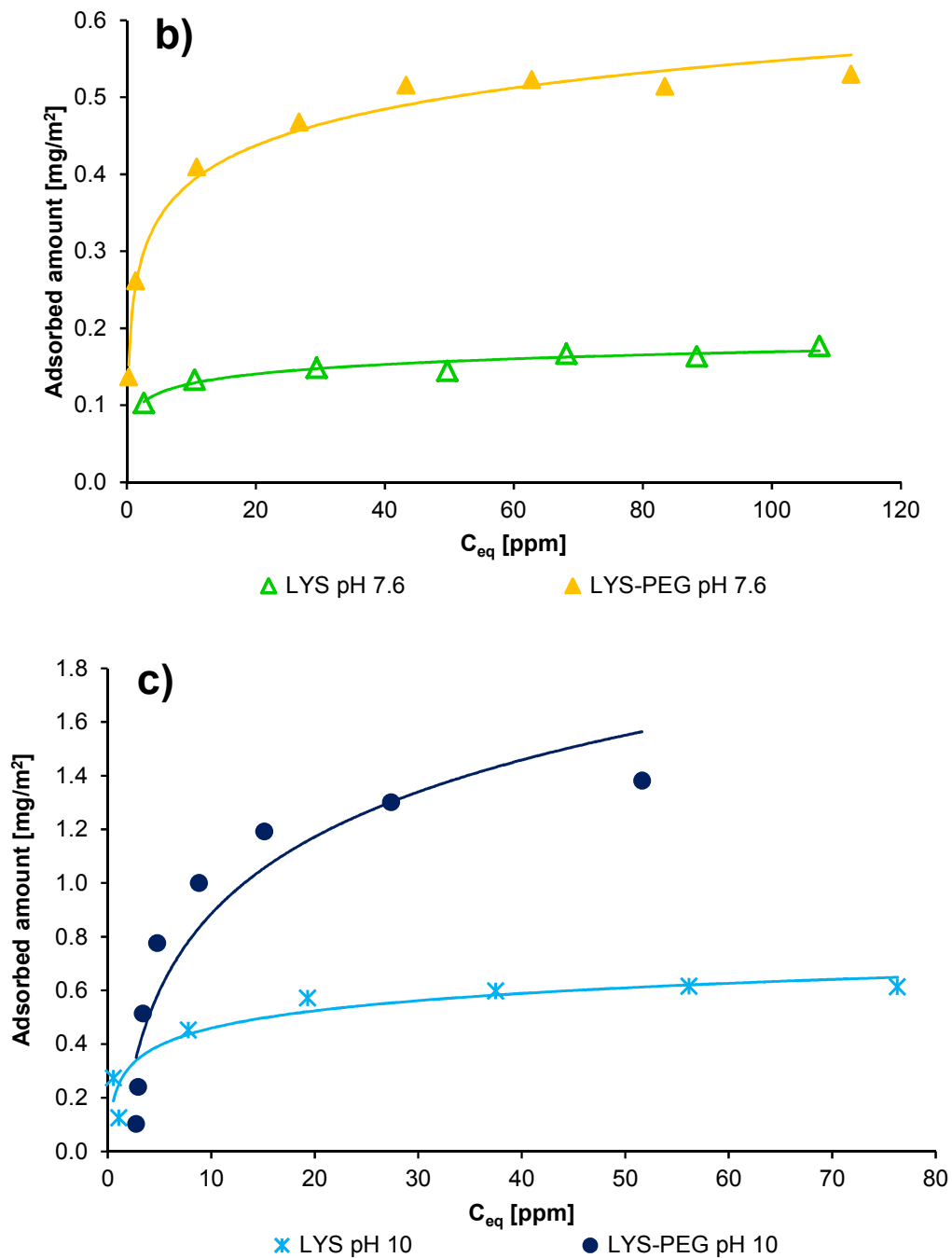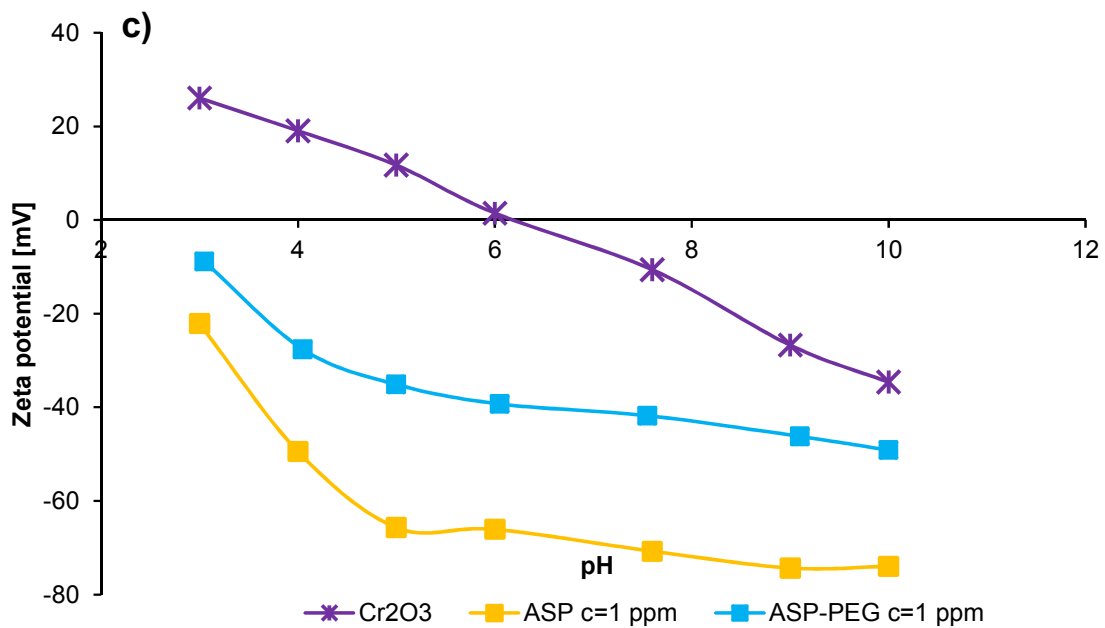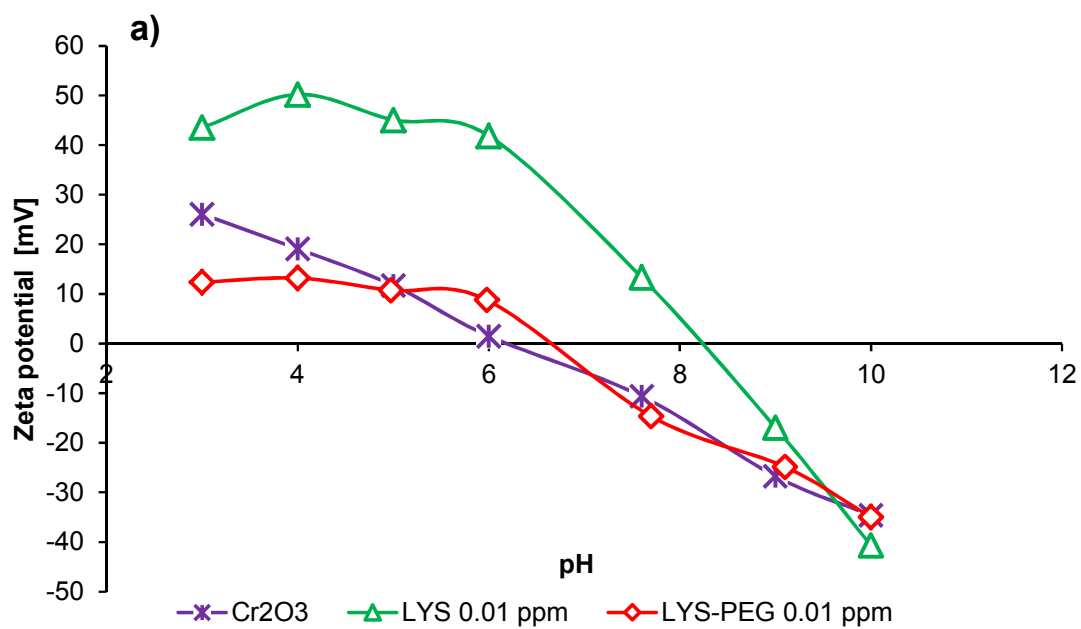
Fig. 4.
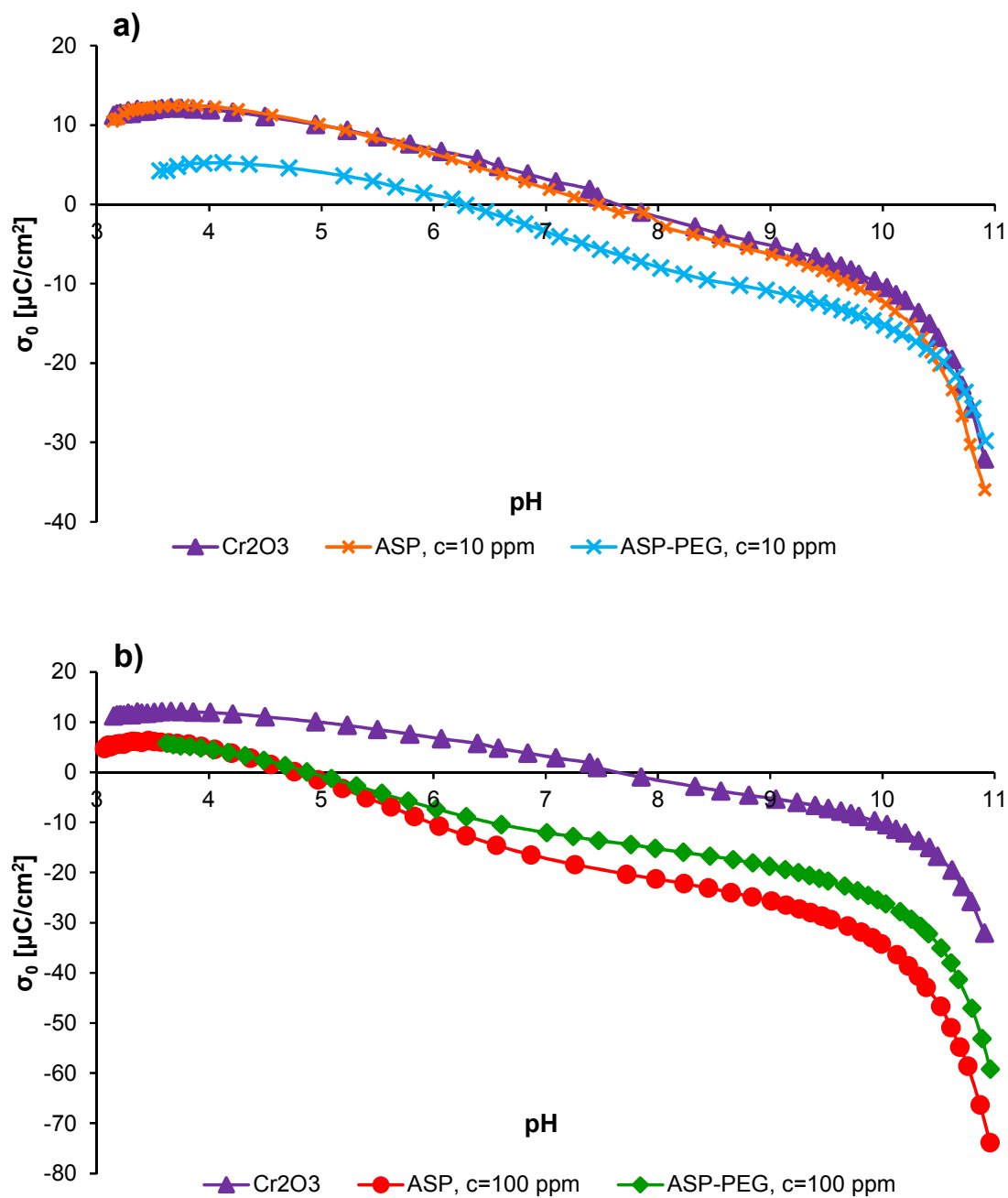
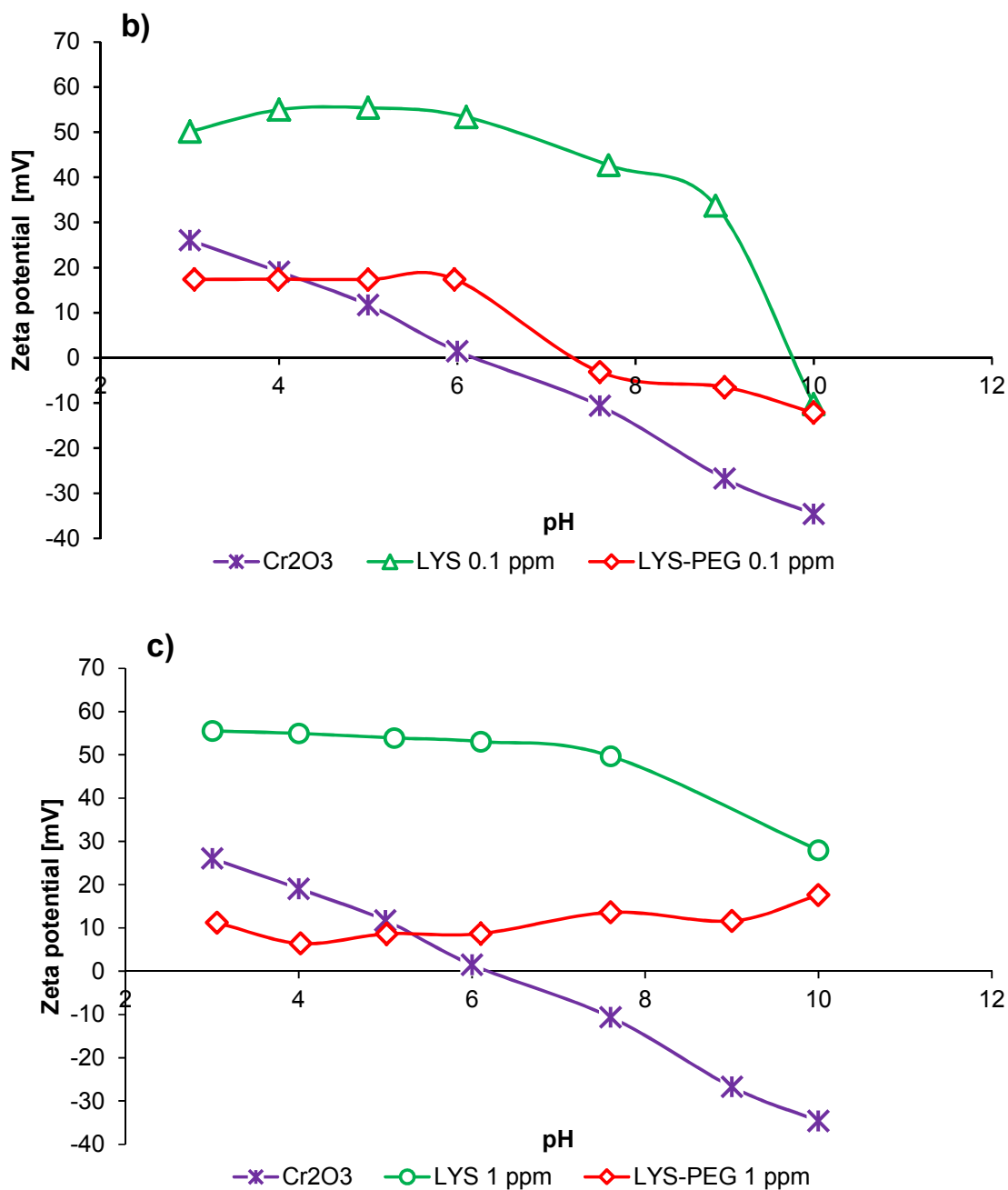Fig. 5 (a-b).

Fig. 6 (a-b).

a)

b)

Fig. 7 (a-c).

Fig. 8 (a-c).

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Table 2. TSI values for the Cr_2O_3 suspensions in the absence and presence of LYS or LYS-*block*-PEG block copolymer (c=100 ppm).

Table 3. Average size of aggregates and their average velocity in the Cr_2O_3 suspension formed in the absence and presence of ASP or ASP-*block*-PEG.

Table 4. Average size of aggregates and their average velocity in the Cr_2O_3 suspension formed in the absence and presence of LYS or LYS-*block*-PEG.

Table 1.

System	Cr_2O_3	ASP c = 100ppm	ASP-*block*-PEG c=100 ppm
pH	TSI value		
3	12.76	48.71	47.19
7.6	62.91	13.22	33.11
10	49.82	11.94	35.55

Table 2.

System	Cr_2O_3	LYS c = 100ppm	LYS-*block*-PEG c=100 ppm
pH	TSI value		
4	12.76	17.24	26.21
7.6	62.91	14.18	35.21
10	49.82	23.24	44.85

Table 3.

System	Cr_2O_3		ASP c = 100ppm		ASP-*block*-PEG c=100 ppm	
pH	d [μm]	V [μm/min]	d [μm]	V [μm/min]	d [μm]	V [μm/min]
3	0.077	0.830	0.073	0.659	1.70	41.55
7.6	0.051	0.325	0.085	0.906	0.459	3.01
10	0.576	41.52	0.074	0.696	1.68	40.46

Table 4.

System	Cr$_2$O$_3$		LYS c = 100ppm		LYS-*block*-PEG c=100 ppm	
pH	d [μm]	V [μm/min]	d [μm]	V [μm/min]	d [μm]	V [μm/min]
4	0.077	0.83	0.106	1.41	0.359	1.85
7.6	0.051	0.32	0.125	1.97	0.215	0.667
10	0.576	41.5	0.135	2.27	0.239	0.816