

STABILITY OF METAL OXIDE SUSPENSION IN THE CATIONIC POLYACRYLAMIDE PRESENCE

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ARTICLE INFO	ABSTRACT
<p>Article History: Received: 28 March 2018 Accepted: 04 April 2018</p>	<p><i>In this study, electroanalytical technique was developed for the quantitative analysis of clomipramine hydrochloride from its commercial tablet dosage forms based on its oxidation behavior. The electrochemical determination of clomipramine hydrochloride was easily carried out on glassy carbon electrode (GCE) by two voltammetric techniques. The electrochemical measurements were carried out on GCE surface in different buffer solutions in the pH range from 2.00 to 12.00 by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The effect of pH on the anodic peak current and peak potential was investigated. Phosphate buffer (pH 6.50) was selected for analytical purposes. The diffusion-controlled nature of the peak was obtained. A linear calibration plot for DPV analysis was constructed in the clozapine concentration range from 5×10^{-6} mol L⁻¹ to 3×10^{-5} mol L⁻¹. Limit of detection (LOD) and limit of quantification (LOQ) were obtained as 2.8×10^{-7} mol L⁻¹ and 8.4×10^{-7} mol L⁻¹ respectively.</i></p>
<p>Keywords: metal oxide, cationic polyacrylamide, electrokinetic properties, suspension stability, polymer adsorption.</p>	
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1. INTRODUCTION

The main reaction of cationic polyacrylamide (PAM) synthesis is free radical copolymerization of acrylamide with the cationic monomer (Jiang and Zhu, 2014). The monomer containing positively charged functional groups used for synthesis of polymer applied in this study is dimethyldiallyl ammonium chloride (DMDAAC). As a result, the quaternary amine groups are introduced to the macromolecules. Contrary to polymer amide groups, these amine groups undergo ionization in aqueous solutions with the changes in solution pH value and are the source of positive charge of polymeric chains.

The most important field of cationic polyacrylamide application is the flocculation process of undesirable solids characterized by high dispersion in aqueous solutions. Long polymeric chains (with molecular weight of the order of several and dozen million Daltons) have ability to form polymeric bridges between the solid particles and their effective aggregation (easily sediment flocs are formed). Moreover, PAM is widely used in removal of polyvalent metal ions, organic compounds (i.e. dyes) and microorganisms from aqueous solutions. For such reasons ionic polyacrylamide finds application in the procedures of industrial waste water purification and drinking water treatment (Entry and Sojka 2000, Amuda *et al.* 2006, Barakat 2011). Cationic polyacrylamide is also used as the rain erosion control agent in agriculture (Sojka *et al.* 2007). By binding loose solid particles the polymer improves considerably the consistency of the soil (simultaneously maintaining surface roughness and continuity of pores).

Thus, such long polymeric chains containing charged functional groups are effective modifiers of the surface properties of solid particles dispersed in liquid medium. The specific structure of polymeric layers covering colloidal particles determines directly such systems stability.

Suspensions of metal oxides are colloidal systems very often encountered in practice. Metal oxides play an important role in adsorptive removal of a great variety of hazardous substances (Wawrzkiwicz *et al.* 2015). They are also used in production of cosmetics, pharmaceuticals and mineral pigments (Simpson *et al.* 2011, Vargas-Reus *et al.* 2012). To obtain the required surface properties of metal oxide particles they were often modified by adsorbed polymers. The specific conformation of polymer chains adsorbed at the solid-liquid interface can be obtained by appropriate selection of among others polymer kind (ionic, nonionic) and metal oxide type, temperature, solution pH, as well as supporting electrolyte type and its concentration (Wiśniewska 2012).

The main aim of studies presented in the manuscript was comparison of stability of three selected metal oxides suspensions (chromium(III) oxide – Cr₂O₃, zirconium(IV) oxide – ZrO₂ (zirconia) and aluminum(III) oxide – Al₂O₃ (alumina) in the presence of cationic polyacrylamide (PAM). The obtained changes in these systems stability (turbidimetry method) after polymer addition were explained based on the analysis of adsorption (spectrophotometry method), surface charge density of the solid (potentiometric titrations) and zeta potential of metal oxide particles (laser microelectrophoresis technique) data.

2. MATERIAL AND METHODS

2.1. Adsorption system characteristics

In the experiments three metal oxides were used as adsorbents - chromium(III) oxide: Cr₂O₃ (*POCH*), zirconium(IV) oxide: ZrO₂ (*Sigma-Aldrich*) and aluminium(III) oxide: Al₂O₃ (*Merck*). They were characterized by the specific surface area (S_{BET}) equal to: 7.12, 21.7 and

155 m²/g, respectively. S_{BET} was determined using the low-temperature nitrogen adsorption-desorption isotherm method (*Micromeritics ASAP 2405 Analyzer*).

The cationic polyacrylamide – PAM (*Korona*) with the weight average molecular weight 7 000 000 Da and the content of quaternary amine groups 50% was applied as an adsorbate (Fig. 1). The pK_b value of this polymer is equal to 9.9 and was determined using the potentiometric titration method. Knowing pK_b value, the ionization degree (α) of the PAM cationic groups can be calculated (Wiśniewska *et al.* 2015). At pH 3 α=99.9 %, at pH 6 it assumes the value 99.9 %, whereas at pH 9 the ionization degree is equal to 88.8 %.

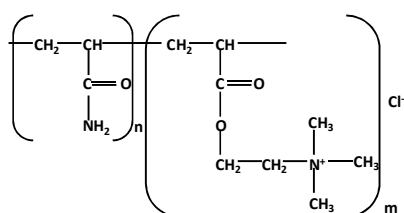


Figure 1. Chemical formula of cationic polyacrylamide.

All measurements were made in the pH range 3-9 at 25°C in the presence of NaCl (as supporting electrolyte) with the concentration 1·10⁻² mol/dm³.

2.2. Stability measurements

The stability measurements of metal oxide suspensions in the absence and presence of PAM were performed using the turbidimetry method (Terpiłowski *et al.* 2015). For this purpose, the apparatus Turbiscan Lab^{Expert} with the cooling module TLab cooler (*Formulation, France*) was applied. The suspension of 0.2 g of oxide in 20 cm³ of NaCl solution (or PAM-NaCl, C_{PAM} 100 ppm) was prepared. Each experiment of suspension stability lasted 15 h and every 15 min the respective data (light transmission and backscattering level) were collected. TLab EXPERT 1.13 and Turbiscan Easy Soft computer programs enabled calculations of stability coefficients TSI (*Turbiscan Stability Index*). The limit values of TSI are 0 (very stable suspensions) and 100 (extremely unstable systems). Moreover, knowing the aggregate migration velocity (on the basis of the changes of transmission or backscattering in time), the aggregate size was calculated using the general law of sedimentation – Stokes law extended on concentrated dispersions (Snabre and Mills 1994).

2.3. Adsorption measurements

Adsorption measurements were performed using the static method in the polymer concentration range 10-150 ppm. The reaction of cationic polyacrylamide with a saturated solution of bromine, sodium formate and starch (in acetate buffer) (Scoggins and Miller 1975) was applied. It enables determination of the polyacrylamide concentration in the solution after the adsorption process (equilibrium concentration). The formed complex gives blue colour of the solution of different intensity depending on the polymer concentration. The solution absorbance was measured after 5 min with the UV-VIS spectrophotometer (Carry 1000; Varian) at 585 nm. Using the calibration curve, the amount of the adsorbed polymer (in unit's mg/m² and mg/g) was determined from the difference between the PAM concentration in the solution before and after the adsorption process.

2.4. Solid surface charge density determination

The potentiometric titration method (Janusz 1999) was used for the solid surface charge density determination. The appropriate mass of metal oxide was added into the thermostated (*thermostat RE204, Lauda*) Teflon vessel containing 50 cm³ of polymer solution (100 ppm) in the NaCl electrolyte (or only to NaCl electrolyte solution). Such systems were titrated with base NaOH with the concentration 1·10⁻¹ mol/dm³ using the automatic burette Dosimat 665 (*Methrom*). The changes in the pH values during titration were monitored with the pH-meter 71 pHmeter (*Beckman*). The special program Titr_v3 (author W. Janusz) was applied to solid surface charge density calculation from the difference in the base volume added to the suspension and the supporting electrolyte solution that leads to the specific pH value. These measurements enable also determination of point of zero charge (pzc) values for all examined systems.

2.5. Zeta potential determination

The electrophoretic mobility of metal oxide particles (without and covered with polymer) was measured using the Zetasizer Nano ZS with the universal dip cell and MPT-2 titrator (*Malvern Instruments*). The Doppler laser electrophoresis technique was applied and the zeta potential value was calculated with the special computer program using the Henry equation (Hunter 1981). Metal oxide suspensions (without and with PAM) were prepared adding appropriate mass of the solid to 100 cm³ of NaCl solution or PAM-NaCl solution (polymer concentration 10 ppm). After the sonification process the obtained suspension was divided into 6 parts of the same volume. Then in each of them the pH value was adjusted to: 3, 4.5, 5.5, 6.5, 8.5 and 10±0.1, respectively and their electrophoretic mobility were measured. The values of isoelectric points (iep) of metal oxides were determined from obtained curves presenting dependencies of zeta potential as a function of solution pH.

3. RESULTS AND DISCUSSION

As can be seen in Fig. 2 cationic polymer has the great impact on the metal oxide suspension stability at pH 6.

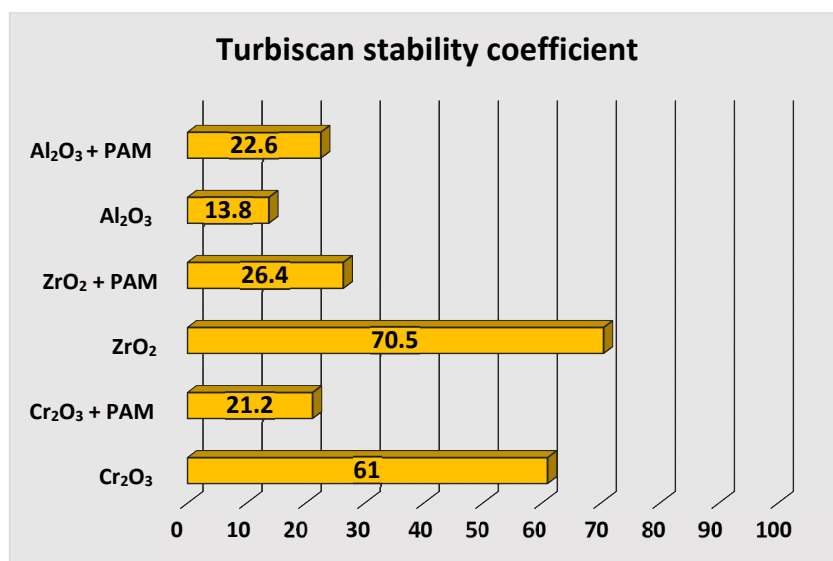


Figure 2. TSI stability coefficients of the metal oxide suspension without and with polyacrylamide at pH 6.

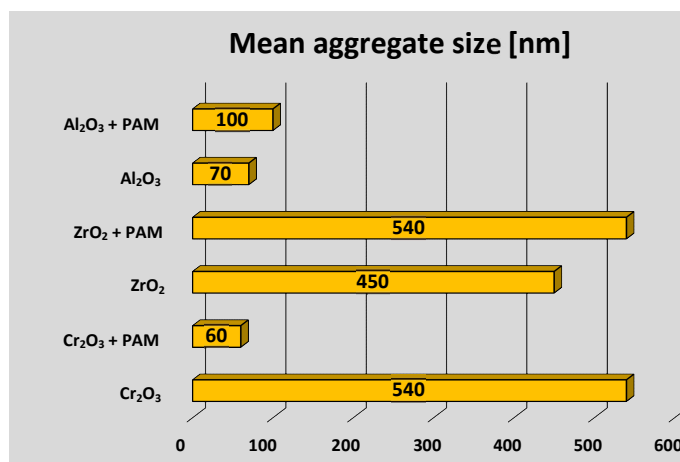


Figure 3. Mean aggregate sizes formed in the metal oxide suspension without and with polyacrylamide at pH 6.

In the case of Cr₂O₃, ZrO₂ systems without PAM and ZrO₂ system with PAM, the suspensions are unstable (high TSI values) and large aggregates are formed – sizes in the range 450 nm – 540 nm, respectively, for chromium(III) oxide and zirconium(IV) oxide (Fig. 3). The polymer addition causes considerable improvement of stability conditions in these systems (TSI values decrease). In the case of Al₂O₃, suspension without cationic PAM is relatively stable and in the polymer presence insignificant decrease of its stability is observed. This is reflected in much smaller sizes of formed aggregates – not exceeding 100 nm (Fig. 3).

In order to explain the obtained changes in solid suspension stability after cationic polyacrylamide addition the analysis of adsorption and electrokinetic results is necessary. Figure 4 presents the PAM adsorbed amounts on the surfaces of applied metal oxides expressed in mg/m² (polymer/metal oxide surface, Fig.4a) and mg/g (polymer/metal oxide mass, Fig.4b), examined at three solution pH values.

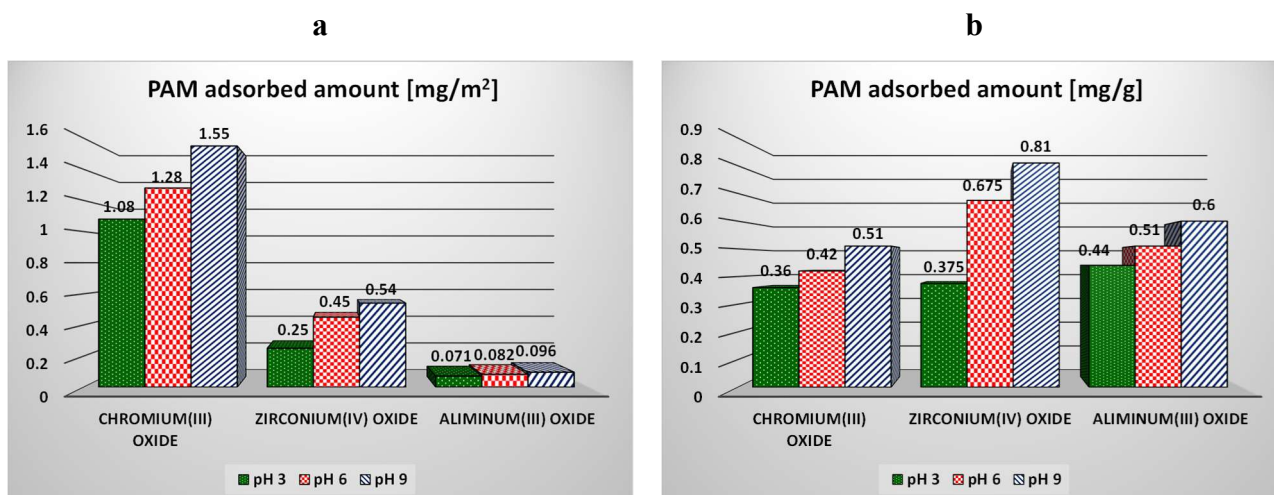


Figure 4. Adsorbed amounts of cationic PAM on the surfaces of examined metal oxides at pH 3, 6 and 9.

The analysis of the data presented in Fig. 4 indicated that adsorption of cationic polyacrylamide increases with the pH increase for all examined metal oxides. Moreover, adsorbed amounts of the polymer per unit area of the solid is the greatest in the case of chromium(III) oxide (Fig. 4 a). It is probably connected with concentration of different types of solid hydroxyl groups on the unit of solid surface area (Chibowski and Wiśniewska 2001). In the case of Cr₂O₃ the concentration of these groups must be the highest and the polymer adsorption is the greatest. Due to the fact that Cr₂O₃ is characterized by the smallest specific surface area the adsorbed amounts of the polymer per unit weight of the solid is the smallest (Fig. 4 b), but comparable with those obtained for Al₂O₃ (with the highest specific surface area). This proves the high adsorption affinity of the ionic polyacrylamide to the surface of chromium (III) oxide compared to other examined adsorbents.

The PAM adsorption changes with the solution pH increase is the result of changes in both the solid surface charge and ionization of the PAM carboxyl groups with the pH rise. The total surface charge of the solid assumes zero value (point of zero charge - pzc) at specific pH for each system containing metal oxide. The determined values of pH_{pzc} points for all examined systems are presented in Fig. 5. Below pH_{pzc} the solid surface is positively charged and above this value, the solid surface assumes negative charge. Thus, the most favorable electrostatic conditions for adsorption of cationic polymer on the surface of given metal oxide is above its pH_{pzc} value.

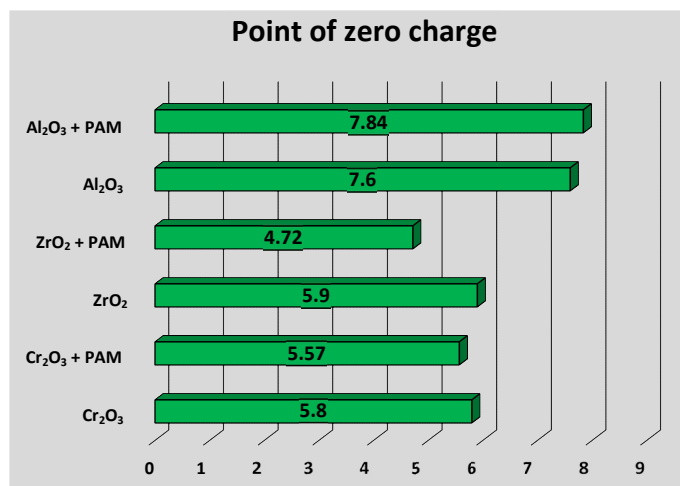


Figure 5. pH_{pzc} values of the metal oxide systems without and with cationic polyacrylamide.

As can be seen in Fig. 5 the points of zero charge for Cr₂O₃, ZrO₂ and Al₂O₃ oxides are equal to 5.8; 5.9 and 7.6, respectively. For this reason, the greatest adsorption of positively charged PAM macromolecules is observed at pH 9 at which the electrostatic attractions between adsorbate and adsorbent takes place. The polyacrylamide adsorption has the lowest level at pH 3 due to the repulsion between the totally ionized PAM macromolecules and the positively charged surface of the solid. The polymer binding with the metal oxide surface undergoes through the hydrogen bridges under these disadvantageous conditions. Although the charged active solid sites can contribute to formation of these bonds, the neutral ones are mainly responsible for it. This results from the fact that ≡MeOH⁰ surface groups are much more numerous than ≡MeOH₂⁺ and ≡MeO⁻ ones (Chibowski and Wiśniewska 2001).

Very important parameter related to solid suspension stability is electrokinetic potential zeta. The specific pH value at which potential zeta of solid particles is equal to zero is called isoelectric point (iep). As can be seen in Fig. 6, the isoelectric points of metal oxides without the polymer are located at pH values 6, 6.4 and 8.4 for Cr_2O_3 , ZrO_2 and Al_2O_3 , respectively. Some differences between the pH_{pzc} and pH_{iep} values of applied oxides are a result of overlapping of the electrical double layers formed in the pores present in the applied solids structure (Skwarek 2015).

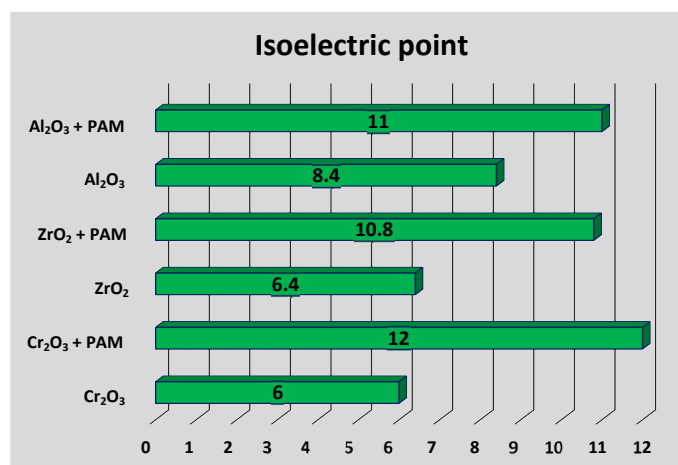


Figure 6. pH_{iep} values of the metal oxide systems without and with cationic polyacrylamide.

The presence of cationic polymer layer around the solid particles results in a significant increase of the zeta potential values and the considerable shift of the pH_{iep} towards the higher pH values. The main reason for zeta potential increase in the cationic polyacrylamide presence is the occurrence of positively charged functional groups of the adsorbed polymer macromolecules in the area of slipping planes around the solid particles (Wiśniewska *et al.* 2016). These groups belong to the polymeric segments located in the loop and tail structures of the adsorbed macromolecules and are not directly bound with the solid surface. They are present in large quantities in the border of the stiff and diffusion parts of the electrical double layers formed on the solid particle surfaces. As a result, such great shift of pH_{iep} values for systems with PAM in comparison to the system without PAM is observed.

Taking adsorption and electrokinetic data into consideration the most probable mechanism of solid suspension stability in the cationic polyacrylamide presence can be proposed. The ionic PAM addition at pH 6 causes considerable improvement of chromium(III) oxide and zirconium(IV) oxide systems stability. These suspensions without polymer are unstable at pH 6 due to the fact that such pH value is very close to points of zero charge and isoelectric points obtained for Cr_2O_3 and ZrO_2 (Figs 5 and 6). The adsorption of completely ionized polymer chains on the solid surface at pH 6 results in appearance of electrosteric repulsion of PAM adsorption layers covered metal oxide particles. The adsorbed polymeric layers prevent the aggregation of solid particles not only due to the steric hindrance presence (PAM macromolecules) and also electrostatic repulsion coming from positively charged groups of the polymer. In the case of Al_2O_3 the polymer addition at pH 6 causes insignificant improvement of solid suspension stability. The alumina system without polymer is relatively stable in comparison to other examined oxides. Under such conditions bare Al_2O_3 particles are positively charged and repulse each other preventing their rapid aggregation. The polymer

adsorption layer presence makes connection of solid particles even more difficult (for electrosteric reasons).

4. CONCLUSIONS

Presented results indicated that high-molecular cationic polyacrylamide, commonly referred to as a polymeric flocculant, can also act as effective stabilizer of aqueous suspensions of metal oxide particles. At specific solution pH value (pH 6) and PAM concentration (100 ppm) it causes considerable improvement of chromium(III) oxide and zirconium(IV) oxide suspensions stability. The total ionization of functional groups of adsorbed macromolecules results in electrostatic repulsion between solid particles covered with polymeric layers. Moreover, it was shown that ionic polymer adsorption changes considerably structure of electrical double layer formed at the solid-liquid interface which is reflected in changes of the surface charge density and zeta potential of metal oxide particles dispersed in aqueous solution.

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