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INFLUENCE OF A KIND OF ELECTROLYTE AND ITS IONIC STRENGTH ON THE ADSORPTION AND ZETA POTENTIAL OF THE SYSTEM: POLYACRYLIC ACID/MnO₂/ELECTROLYTE SOLUTION

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The influence of a kind of electrolyte (NaCl, KCl, CaCl₂ and MgCl₂), its ionic strength (0.01; 0.1; 1) and pH of a solution (3; 6; 9) on the adsorption of polyacrylic acid (PAA 2 000 and 60 000) on the surface of manganese dioxide (MnO₂) was measured. PAA adsorption was the highest in the presence of calcium chloride. Adsorption of polyacrylic acid increased also with ionic strength but decreased with the increase of pH of the solution. These results are consistent with theoretical findings concerning adsorption of anionic polyelectrolytes on surface of metal oxides. The influence of a kind of electrolyte and its ionic strength on the zeta potential in the presence of PAA was also measured. It was proved, that the zeta potential of MnO₂ is highest in the presence of calcium chloride as a background electrolyte. Moreover the zeta potential increased with ionic strength of all measured systems.

key words: polyacrylic acid, manganese dioxide polymer adsorption, polymer conformation, zeta potential

INTRODUCTION

Adsorption of high molecular weight substances arouses an increasing interest over the past few years. It is the results of the fact that the adsorption of polymer is completely different from the adsorption of small particles and ions. Polymer chains may form lots of different conformations in both the bulk phase and the interface,

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while the ions and the small particles have invariable and defined shape (Cohen Stuart et al. 1991). The practical aspect of the polymer adsorption on solid surfaces is related to two processes: stabilisation and flocculation that are applied in many different branches of industry (Fleer et al. 1993, Fleer et al. 1993, Pan et al. 2001). The addition of low-molecular weight polymers to a dispersion causes sterical stabilisation of the dispersed system. This process is applied in production of: drugs, cosmetics, paints, varnishes and also in production of paper. On the other hand, the addition of high molecular weight polymers to a dispersion causes flocculation, widely used in treatment of industrial wastes occurring as water suspensions. Measurements of polymers' adsorption on the solid surfaces are determined by many different factors. Among them the most important ones are: the character of interactions between an adsorbent and an adsorbate, a type of used electrolyte, ionic strength and pH of the solution, polydispersity of the used polymer and the presence of impurities.

Manganese dioxide has been chosen as an adsorbent. It occurs in nature as a mineral called battery manganese or pyrolusite. Manganese dioxide forms a few polymorphic modifications (α , β , γ) but none of them has a stoichiometric composition (Kolditz 1994). Under standard conditions MnO_2 is insoluble and has amphoteric properties. Moreover MnO_2 has a also well-defined interface MnO_2 /polyelectrolyte solution is stable in broad pH range. This dioxide finds applications in production of matches, in glass-making industry to decolourization of glass and as a depolarizer in voltaic cells (Trzebiatowski 1979).

Polyacrylic acid has been used as a polyelectrolyte in all measurements. This polymer has been chosen because of the wide spectrum of its applications (Szlezyngier 1998). It is used as: a supplement to surfactants, a compound used in production of paper, an inhibitor of fur formation, a concentrator in cosmetics and a component of drugs.

The aim of this paper is to define the influence of a type of used electrolyte, its ionic strength and pH of the solution on polyacrylic acid (PAA) adsorption on MnO_2 surface. Another important information about electrokinetic properties of manganese dioxide in the presence of PAA has been obtained by measurements of zeta potential in the presence and absence of polymer.

MATERIALS AND METHODS

MnO_2 produced by POCh-Gliwice was used as an adsorbent in all measurements. The specific surface area of manganese dioxide, calculated using the BET method was $38 \text{ m}^2 \text{ g}^{-1}$ and the average diameter of this oxide particles was equal to 280 nm. MnO_2 average pores diameter, also calculated using the BET method, was equal to 4.6 nm. Before the measurements MnO_2 was washed with doubly distilled water until the conductivity of the supernatant was smaller than $2 \mu\text{S cm}^{-1}$.

NaCl, KCl, MgCl₂ and CaCl₂ were used as background electrolytes. Concentrations of these electrolytes were chosen so as to provide a desired ionic strength (0.01; 0.1; 1). Polyacrylic acid (molecular weights: 2 000 and 60 000) produced by Aldrich was used as a polyelectrolyte.

The adsorption of PAA (Γ [mg m⁻²]) in the concentration range from 30 ppm to 200 ppm on the MnO₂ surface was carried out using the static method (Chibowski et al. 1999) presented below. Into the Erlenmeyer flasks, which contained 10 ml of the polymer solution (chosen concentration of the polymer, electrolyte and pH) 0.2 g of MnO₂ was added. These suspensions were shaken for 24 hours. Then manganese dioxide was centrifuged and 5 ml of the clear solutions were taken for further analysis. The adsorption was calculated from the difference between PAA concentration before and after the adsorption. The base of analysis was the reaction between polyacrylic acid and hyamine, proposed by Crumette and Hummel (Crummett et al. 1963). The opacity increases after hyamine addition to the solution was measured turbidimetrically using a spectrophotometer (Specord M42, Carl Zeiss) using a special computer programme M500. The wavelength used was 500 nm.

The zeta potential measurements were made using a zetameter (Zetasizer 3 000, Malvern Instruments). The samples were prepared by ultrasonification of 0.05 g MnO₂ with 500 ml of solution and carefully defined: electrolyte (NaCl; KCl; MgCl₂; CaCl₂), ionic strength (0.01; 0.1; 1), polymer concentration (0.01 ppm; 0.1 ppm; 1 ppm) and pH. The zeta potential was measured in the presence and absence of polymers (PAA 2 000; PAA 60 000).

RESULTS AND DISCUSSION

Figure 1 presents the polyacrylic acid (PAA 60 000) adsorption isotherms on the surface of MnO₂ in the presence of four different electrolytes (CaCl₂, MgCl₂, KCl, NaCl) characterized by the same ionic strength (0.1), at pH 6.

Background electrolyte has the great influence on the adsorption of polyacrylic acid. As it can be seen, adsorption of PAA is higher when divalent cation chlorides are used as background electrolytes in comparison to PAA adsorption in the presence of NaCl and KCl. This phenomenon is a consequence of the creation of bidental complexes between Ca²⁺ or Mg²⁺ ions and dissociated carboxylic groups (Vermöhlen et al. 2000). These complexes may be created between two different polyelectrolyte chains or between carboxylic groups from the same macromolecule. It results in a spatial polymer conformation rich in loops and tails structures. Because of the fact, that the number of the adsorption sites on the surface of the metal oxide is constant, formation of such a conformation, built in the direction of bulk solution, causes the increase of polymer adsorption (Chibowski 1988).

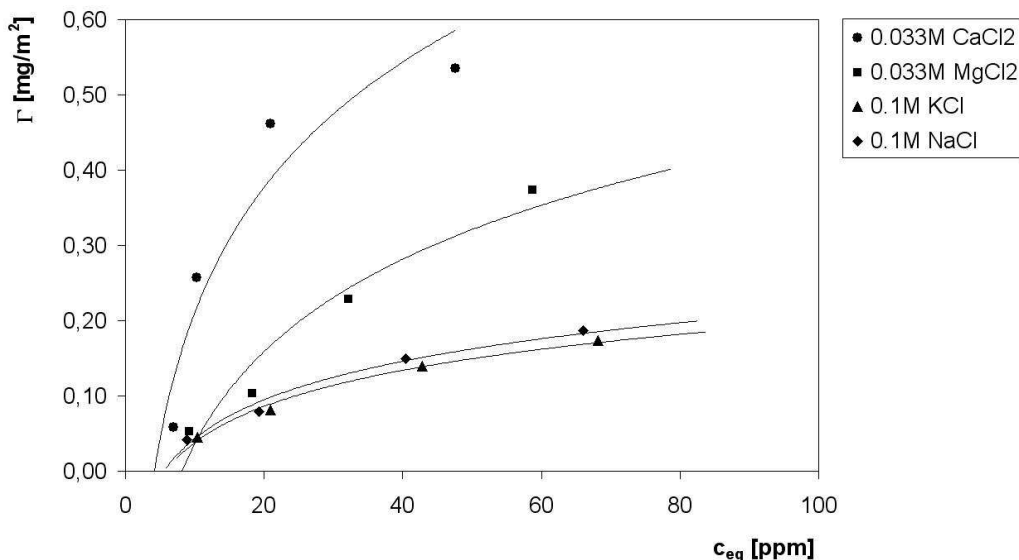


Fig. 1. Adsorption isotherms of PAA 60000 in the presence of different electrolytes, pH=6

Moreover, PAA adsorption in the presence of CaCl₂ as a background electrolyte is higher than in the presence of MgCl₂. This is a consequence of differences in desorption energy of calcium and magnesium ions. It is known that calcium cations desorb poorly from the surface of metal oxide, what is the evidence of strong interaction between them and the oxide surface groups. On the other hand, magnesium cations can desorb from the surface quite easily. Therefore, a better contact between PAA macromolecules and oxide surface is observed in the presence of CaCl₂, what increases the polymer adsorption. The presented isotherms shows also the similarity between PAA adsorption in the presence of monovalent metal chlorides. This situation may be explained by similarities in sodium and potassium ions activity and their equal charge.

Figure 2 presents the dependency between PAA adsorption and electrolyte ionic strength. As one can notice, the increase of ionic strength increases the PAA adsorption. This is a consequence of a few effects: changes in dissociation degree of carboxylic groups in PAA chain, conformational changes of polyacrylic acid on the surface of the metal oxide and changes of a kind and number of adsorbent surface groups (Tekin et al 2006). At pH values higher than pH_{pzc} of MnO₂ (~4.5) the screening effect of repulsion forces between negatively charged oxide surface and dissociated PAA chains (pK_a of polyacrylic acid=4.5 (J.E. Gebhardt et al. 1983)) has the most important influence on the increase of PAA adsorption with the increase of salt concentration. As it is known from our previous results the increase of electrolyte concentration as well as the increase of pH both increase the dissociation of polyacrylic acid (Grządka et al. 2008) and result in the appearance

of larger number of dissociated carboxylic groups in the measured system together with the increase of metal cation concentration.

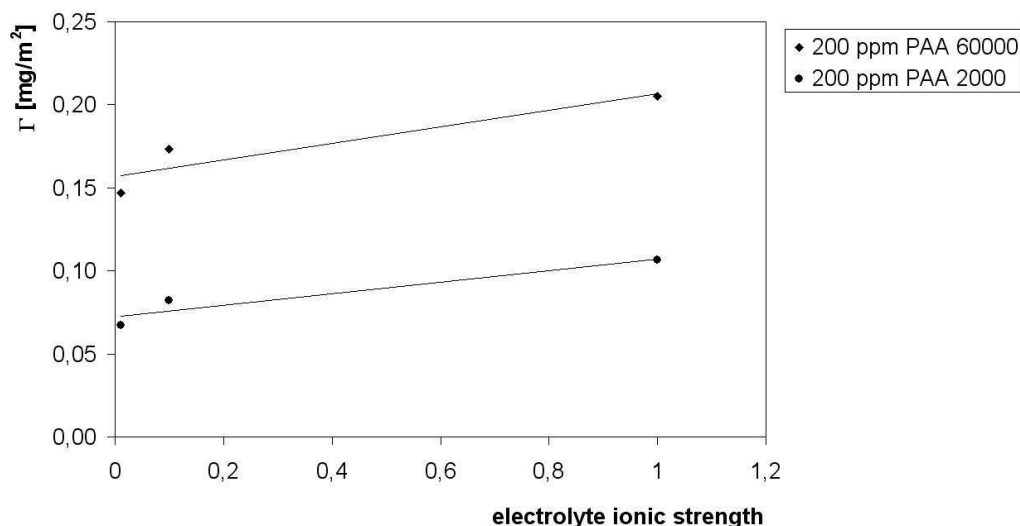


Fig. 2. Dependency between PAA adsorption and KCl ionic strength, pH=6

These cations are able to screen the repulsion between the negatively charged surface. Its consequence is the increase of PAA adsorption on MnO_2 with the increase of electrolyte concentration. Moreover, in solution of high electrolyte concentration polymer chains are much more flexible (Adachi et al. 2002), what favors spacious polymer conformation, rich in loops and tails structures. Creation of such a conformation on the metal oxide surface leads to the increase of the polymer adsorption.

Figure 3 points out that PAA adsorption decreases with the increase of pH. As was mentioned above, PAA macromolecules at pH lower than 4.5 consist mostly of nondissociated carboxylic groups, but with further increase of pH the number of $-\text{COO}^-$ groups increases. The decrease of polyacrylic acid adsorption with the increase of pH results from the above-mentioned increase of negative charge in PAA chain. If the repulsion between adsorbent and adsorbate intensifies, interactions between polymer and surface of the solid are reduced. At low pH values the most possible adsorption mechanism is electrostatic attraction and nonelectrostatic, specific interaction between carboxylic groups and surface metal oxide groups, mostly hydrogen bond type (Solberg et al. 2003). At pH values higher than pH_{pzc} the most important mechanism responsible for PAA adsorption is the formation of complexes between polymer segments and adsorbent surface groups.

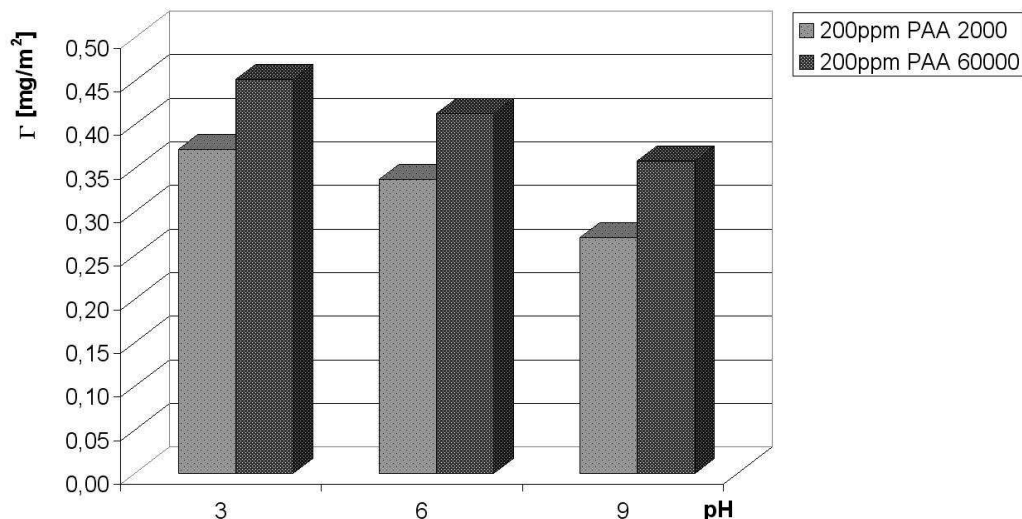


Fig. 3. Dependency between PAA adsorption and pH of the solution in the presence of 0.333M MgCl₂

Figures 4–6 show the dependencies of the zeta potential of MnO₂ on the concentration of polymer, on the type of electrolyte and on electrolyte ionic strength. There are three effects responsible for the changes in values of the zeta potential in the presence of polymer. The first one is the presence of the charge of the dissociated polymer groups in the by-surface layer of the solid. The second one the shift of the slipping plane caused by the polymer adsorption on the metal oxide surface and the last one is the change of position of counterions in the Stern layer, which follows the polymer adsorption process. The first and the second effects cause the decrease of the zeta potential, but the third one causes the increase of this value. It must be underlined that these three effects occur simultaneously. The increase or the decrease of the zeta potential depend only on their quantitative contribution.

As it might be seen from Figure 4 the zeta potential of manganese oxide in the presence of polyacrylic acid is lower in the whole pH range than in the absence of polymer. That results from the presence of dissociated carboxylic groups in polymer chain mainly in the by-surface layer of MnO₂. Moreover, with the increase of pH the PAA dissociation increases. This situation causes not only the decrease of the zeta potential but also the conformational changes in PAA chains are observed (Das et al. 2001). Created conformation causes the shift of the slipping plane towards the bulk solutions, what leads to the decrease of the zeta potential value. The increase of polymer molecular weight and polyelectrolyte concentration both cause that the zeta potential of MnO₂ decreases. Such a behavior is reasonable because the increase of polymer molecular weight and the increase of polymer concentration both

cause two effects: the increase of total negative charge in polymer chain and the increase of the adsorption layer thickness. That causes the shift of the slipping plane in the bulk solutions and the decrease of the zeta potential values is observed.

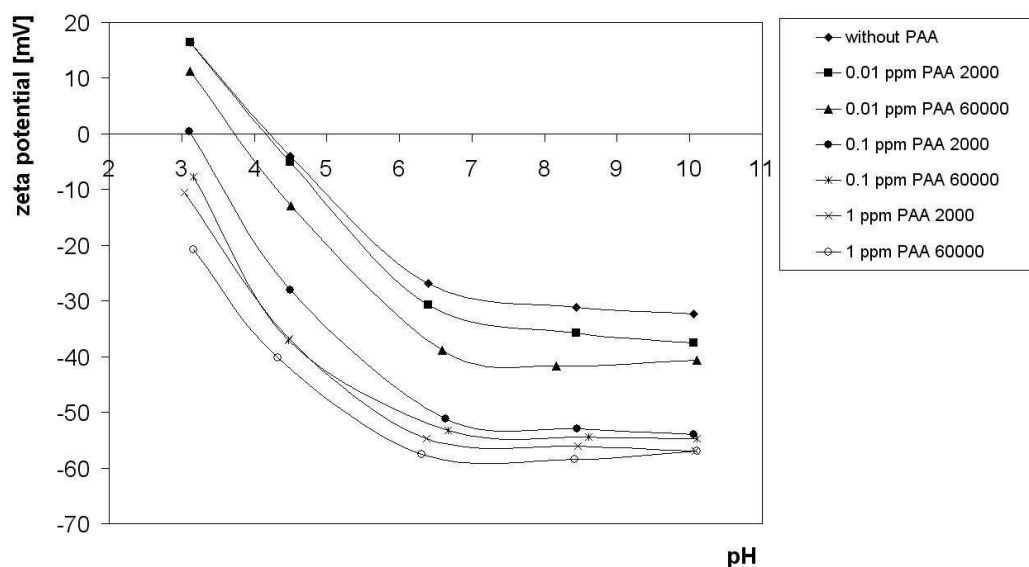


Fig. 4. Manganese dioxide zeta potential as a function of pH in the presence of 0.01M NaCl and PAA

Some conclusions on the influence of kind of electrolyte on the zeta potential of MnO_2 might be drawn from Figure 5. As one can see, when monovalent metal chlorides are used as electrolytes the zeta potential of MnO_2 curves have the similar run and the similar zeta potential values are obtained. This phenomenon is a consequence of the similar character of NaCl and KCl and their equal charge. On the other hand, when CaCl_2 is used as a background electrolyte, higher zeta potential values are obtained in comparison to the zeta potential values decreased in the presence of MgCl_2 . Moreover, in the presence of divalent metal chlorides the obtained zeta potential data are more divergent than rather compact values obtained for the systems: $\text{MnO}_2/\text{PAA}/\text{monovalent metal chlorides}$. It is due to the above mentioned difference between the desorption energies of calcium and magnesium from the metal oxide surface. A competitive adsorption between electrolyte ions and polymer segments may occur in the systems containing calcium cations, but the same process is rare in the systems where magnesium cations are present. That competitive adsorption causes the blockade of the adsorption sites and results in the increase of the zeta potential of MnO_2 in the presence of CaCl_2 .

Moreover, higher zeta potential values are obtained in the presence of divalent metal chlorides in comparison to zeta potential values in the presence of monovalent

chlorides and the smaller differences in the zeta potential of MnO_2 in the presence of polymer and without it in the presence of monovalent metal chlorides are observed. This fact is rather surprising because not only the adsorption of PAA but also the thickness of polyacrylic acid adsorption layer on MnO_2 in the presence of different electrolytes show that polyelectrolyte conformation is spacious in the presence of divalent metal chlorides. For that reason the decrease in elektrokinetic potential was expected in the presence of divalent metal chlorides mainly because of a bigger shift of the slipping plane. The only one explanation of the measured zeta potential increase is more effective screening of negative charge along polymer chains by divalent cations. Furthermore, these cations can interact with metal oxide surface groups and with polymer segments creating bidental complexes type: R-COO-Me-COO-R . This phenomenon is responsible for the second reversal of charge of MnO_2 in the presence of divalent chlorides. This effect is clearly visible at high pH values. Another reason for that is the overcharging of the electric double layer simultaneous with a formation of $-\text{SO}^-\text{Ca}^{2+}$ groups.

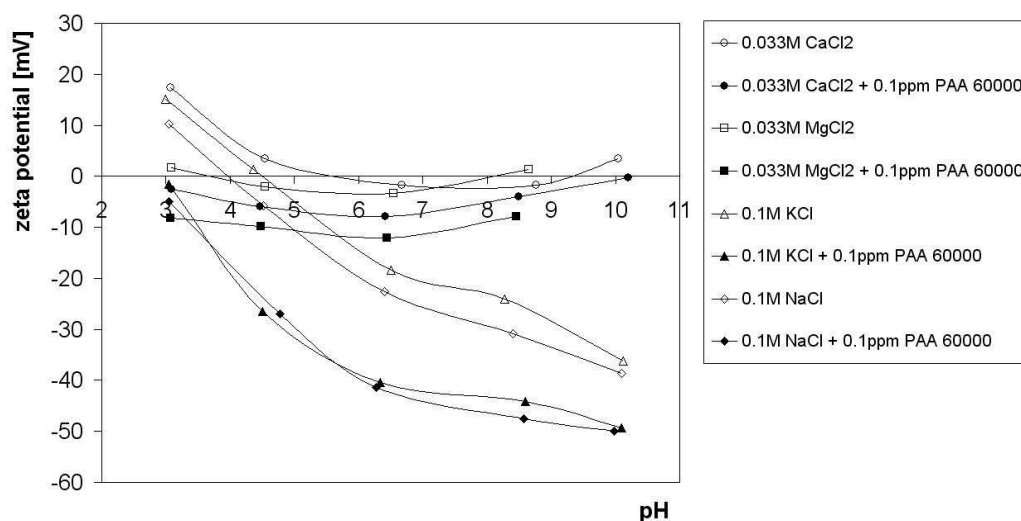


Fig. 5. Manganese dioxide zeta potential as a function of pH in the presence of different electrolytes and PAA 60000

The data presented on Figure 6 allows the analysis of the influence of ionic strength on MnO_2 zeta potential. As one can notice, increase of the zeta potential accompanies the increase of salt concentration. This results from the screening effect of negative charge between dissociated PAA carboxylic groups and metal oxide surface by the growing number of background electrolyte cations. Moreover, there are visible differences between the zeta potential curves in the presence of 0.333M MgCl_2

in comparison to the zeta potential curves in the presence of less concentrated electrolytes. These differences result from differences between adsorption of cations and anions (Kosmulski et al. 2007).

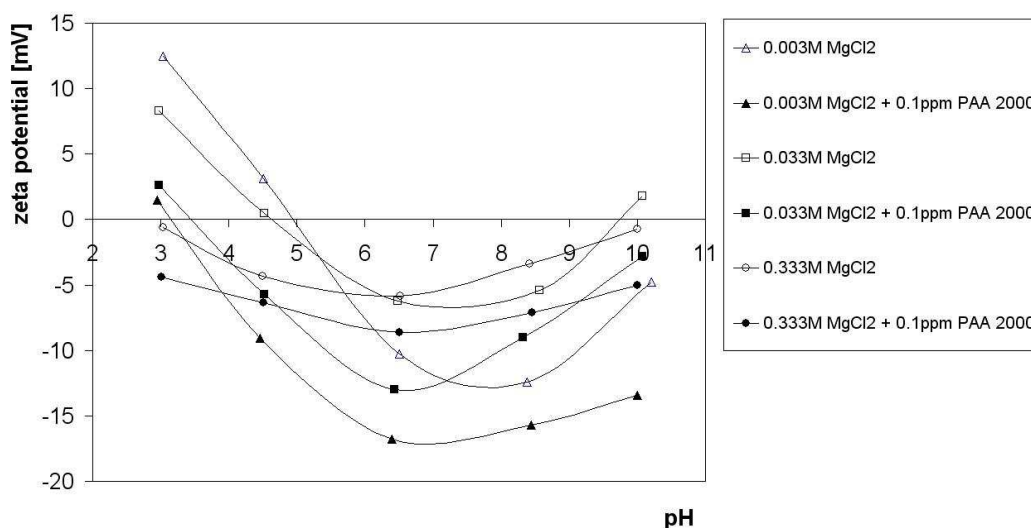


Fig. 6. Manganese dioxide zeta potential as a function of pH for various concentration of KCl in the presence or absence of PAA 2000

CONCLUSIONS

- The highest polyacrylic acid adsorption is observed in the presence of CaCl_2 .
- PAA adsorption on MnO_2 surface is higher for divalent than for monovalent metal chlorides as background electrolytes.
- There are no large differences between the polyacrylic acid adsorption in the presence of NaCl and KCl.
- With the increase of ionic strength the increase of PAA adsorption is observed.
- The presence of divalent cations in the system: PAA/ MnO_2 /electrolyte solution results in the increase of the zeta potential of MnO_2 .
- The increase of electrolyte ionic strength causes the increase of the zeta potential.

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Grządka E., Chibowski S., *Wpływ rodzaju elektrolitu i jego siły jonowej na adsorpcję i właściwości elektrokinetyczne układu: kwas poliakrylowy/ MnO_2 /roztwór elektrolitu.*, Physicochemical Problems of Mineral Processing, 43 (2009), 31–42 (w jęz. ang)

Badano wpływ rodzaju elektrolitu ($NaCl$, KCl , $CaCl_2$ i $MgCl_2$), jego siły jonowej (0.01; 0.1; 1) i pH roztworu (3; 6; 9) na adsorpcję kwasu poliakrylowego (PAA 2 000 i 60 000) na powierzchni ditlenku manganu (MnO_2). Otrzymane wyniki dowodzą, że adsorpcja PAA jest największa w obecności chloru sodu w porównaniu z adsorpcją PAA w obecności innych elektrolitów. Adsorpcja kwasu poliakrylowego wzrasta również wraz ze wzrostem siły jonowej elektrolitu podstawowego lecz maleje ze wzrostem

pH roztworu. Wyniki te pozostają w zgodzie z przewidywaniami teoretycznymi dotyczącymi adsorpcji anionowych polielektrolitów na powierzchni tlenków metali. Mierzono również wpływ rodzaju elektrolitu i siły jonowej na potencjał dzeta w obecności kwasu poliakrylowego. Zostało udowodnione, że potencjał dzeta MnO_2 przyjmuje najwyższe wartości w obecności chlorku wapnia jako elektrolitu podstawowego. Co więcej, wartość ta wzrasta wraz ze wzrostem siły jonowej w każdym z badanych układów.

słowa kluczowe: kwas poliakrylowy, ditlenek manganu, adsorpcja polimerów, konformacja polimerów, potencjał dzeta

