



Comparison of the influence of a kind of electrolyte and its ionic strength on the adsorption and electrokinetic properties of the interface: Polyacrylic acid/MnO₂/electrolyte solution

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ABSTRACT

The influence of a kind of electrolyte and its ionic strength on the adsorption of polyacrylic acid (PAA) 2000 and 60 000 on the surface of manganese dioxide (MnO₂) was measured. As background electrolytes NaCl, KCl, CaCl₂ and MgCl₂ were used. It was proved that PAA adsorption amount is the highest in the presence of CaCl₂ in comparison to PAA adsorption amount in the presence of other electrolytes. Polyacrylic acid adsorption amount increases with the increase of electrolyte ionic strength in all measured systems.

The influence of a kind of electrolyte and its ionic strength on the zeta potential in the presence of polyacrylic acid of different concentrations was also measured. It was observed, that the zeta potential of MnO₂ is higher when CaCl₂ is used as a background electrolyte in comparison to the zeta potential of MnO₂ in the presence of NaCl or KCl. What is more, the zeta potential of MnO₂ increases with the increase of ionic strength for all measured systems.

Potentiometric titrations of MnO₂ suspensions in the presence of polymer and chosen electrolyte prove the large impact of polymer presence on MnO₂ surface charge density. Other factors which also have the influence on the surface charge density are: a kind of used electrolyte and its ionic strength.

Free energies of PAA adsorption in the presence of different electrolytes and ionic strengths were also calculated.

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1. Introduction

Stabilization and destabilization of colloidal dispersions by polymers is an interesting subject for many scientists. Behavior of polymers macromolecules in dispersed solid solutions is a very complicated process, determined by a lot of factors and mechanisms. Researches of the polymer adsorption on solid surfaces are carried out in two aspects: theoretical and practical one [1–4]. The theoretical interest in the adsorption of polymers on the metal oxide/polyelectrolyte solution interface results from the fact that the polymer adsorption is completely different from the adsorption of small particles and ions. The small particles and ions have invariable, defined shape whereas polymer chains may form lots of different conformations in both the bulk phase and the interface. The practical aspect of the polymer adsorption on the solid surface is associated with the polymer usage in the stabilization and flocculation processes. Sterical stabilization of the system is caused by addition of low-molecular weight polymer into the dispersion.

This process can be applied in the production of: drugs [5], cosmetics [6], paints, varnishes and also in the production of paper [7]. On the other hand, high molecular weight polymers adsorbed onto colloid particles cause their flocculation. This process is widely used in utilisation of industrial wastes occurring as water suspensions.

Moreover, many natural systems occurring in nature may be treated as specific colloidal systems with macromolecules of high biological importance adsorbed on the dispersed phase. Examples of such systems are: DNA complexes with specific proteins [8] dispersions of polysaccharides and biopolymers produced by microorganisms and phytoplankton presented in water reservoirs [9,10] as well as aluminosilicates and metal oxides located in sacrificial parts of soil. Also blood and other body fluids may form characteristic suspensions.

Because of that, understanding and faultless explanation of interactions in colloidal systems is extremely important.

The aims of this paper were:

- determination of the influence of a kind of electrolyte and its ionic strength on polyacrylic acid (PAA) adsorption on manganese dioxide (MnO₂) surface,

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Table 1
Contributions to the PAA adsorption mechanism on MnO₂ surface in various pH

	<i>pH=3</i>	<i>pH=6</i>	<i>pH=9</i>
	- nondissociated polymer (Tab. 4-5)	- partly nondissociated polymer (Tab. 4-5)	- fully nondissociated polymer (Tab. 4-5)
	- positively charged surface (MnOH ₂ ⁺ groups) [28]	- negatively charged surface (MnOH and MnO ⁻ groups)	- negatively charged surface (MnO ⁻ and MnOH groups)
	← increase of PAA adsorption →		
<i>Mechanisms of PAA adsorption on MnO₂ surface</i>	nonelectrostatic, specific interactions	nonelectrostatic, specific interactions	nonelectrostatic, specific interactions
	<ul style="list-style-type: none"> • hydrogen bond • complexes between Mn atoms and -COOH groups slight electrostatic interactions	<ul style="list-style-type: none"> • strong creation of complexes • hydrogen bond 	<ul style="list-style-type: none"> • creation of complexes • hydrogen bond

- determination of the influence of a kind of electrolyte and its ionic strength on the surface charge of MnO₂ and the zeta potential of MnO₂ in the presence and absence of PAA.

Polyacrylic acid was used as a polyelectrolyte because of wide range of its practical applications [11]. If its molecular weight is in the range of 5000–20 000 it is used as a dispersant. If its molecular weight is in the range of 300 000–500 000 it is used as a thickener. In the case when PAA molecular weight is higher than 1 000 000 it finds application as a flocculent. Examples of practical applications of polyacrylic acid are: supplement to surfactants, compound used in the production of paper, inhibitor of fur formation, concentrators in cosmetics and components of drugs: artificial tears. There are also some measurements which explain the fact of stability changes of phase colloids in the presence of polyacrylic acid [12].

Manganese dioxide was chosen as an adsorbent. This chemical compound is one of the most stable manganese (IV) compounds. It occurs in nature as a mineral cold battery manganese or pyrolusite. Manganese dioxide forms a few polymorphic modifications (α , β , γ) but none of them has stoichiometric composition [13]. Properties of this adsorbent are strictly depended on conditions of its obtaining, time of its storage and treatment of precipitated deposit. Under standard conditions MnO₂ is insoluble and has amphoteric properties. Manganese dioxide finds applications in the productions of matches, in glass-making industry to decolourization of glass and as a depolarizer in voltaic cells [14].

Very characteristic property of manganese dioxide is its chemical inertness, which allows to use this chemical compound as an adsorbent in many adsorption processes. MnO₂ has also well-

defined interface MnO₂/polyelectrolyte solution as well as stability in broad pH range.

2. Materials and methods

MnO₂ produced by POCh-Gliwice was used as an adsorbent in all measurements. The specific surface area of manganese dioxide, calculated using the BET (Brunauer, Emmet, Teller) method was 38 m² g⁻¹ and the average diameter of this oxide particles equalled 280 nm. MnO₂ average pores diameter, also calculated using BET method, equalled 46 Å. Before the measurements MnO₂ was washed with doubly distilled water until the conductivity of the supernatant smaller than 2 μ S cm⁻¹. After that the supernatant was analyzed using atomic absorption spectrometry. All impurities enclosed in the supernatant were below the range of sensitivity of atomic spectrophotometer.

NaCl, KCl, MgCl₂ as well as CaCl₂ were used as background electrolytes. Polyacrylic acid (molecular weights: 2000 and 60 000) produced by Aldrich was used as a polyelectrolyte.

The adsorption of PAA (I [mg m⁻²]) in the concentration range from 30 ppm to 200 ppm on the MnO₂ surface was carried out using the static method [15,16] 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 h. 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 that was the reaction between polyacrylic acid and

Table 2
Contributions to the PAA adsorption mechanism on MnO₂ surface in various NaCl ionic strengths

	<i>0.01M NaCl</i>	<i>0.1M NaCl</i>	<i>1M NaCl</i>
	← increase of PAA adsorption →		
<i>Mechanisms of PAA adsorption on MnO₂ surface</i>	low screening effect between the adsorbent and the adsorbate	medium screening effect between the adsorbent and the adsorbate	the highest screening effect between the adsorbent and the adsorbate

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