

Adsorption and elektrokinetic properties of the system: carboxymethylcellulose/manganese oxide/surfactant

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Abstract The adsorption of carboxymethylcellulose (CMC) in the presence of the surfactants: anionic SDS, nonionic polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100) and their mixtures SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether with different molar ratios (1:1; 1:3 and 3:1) from the electrolyte solutions (NaCl, CaCl₂) on the manganese dioxide surface (MnO₂) was studied. In every measured system the increase of CMC adsorption in the presence of surfactants was observed. This increase was the smallest in the presence of SDS, a bit larger in the presence of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and the largest when the mixtures of SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether were used. Among the measured mixtures, the mixture of SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether with the molar ratio 1:3 caused the largest increase of CMC adsorption amount. These results are a consequence of formation of complexes between the carboxymethylcellulose macromolecules and the surfactant molecules. In order to determine the electrokinetic properties of the system the surface charge density of MnO₂ and the zeta potential measurements were conducted in the presence

of the CMC macromolecules and the surfactants. The obtained data showed that the adsorption of CMC or CMC/surfactants complexes on the manganese dioxide surface strongly influences the structure of the electric double layer MnO₂/electrolyte solution.

Keywords Polysaccharide adsorption · Surfactants · Interfaces · Surface properties

Introduction

Carboxymethyl cellulose or more correctly sodium salt of carboxymethyl ether of cellulose is an anionic polysaccharide produced from cellulose, monochloroacetic acid and sodium hydroxide. Its molecular weight ranges from 10³ to 10⁶. The maximal, theoretical value of its DS—degree of substitution (the average number of carboxymethyl groups per anhydroglucose unit) is 3, but for the commercial samples of CMC it is usually from 0.5 to 1.5 (Khraisheh et al. 2005). DS influences both the solution characteristics and solubility of CMC molecules. Each CMC unit contains –CH₂COO[–] and –OH groups enabling formation of hydrogen bonds. One of the most important advantages of carboxymethyl cellulose is its complete biodegradability. As this feature of the compound is ideal for industrial applications. CMC is used in many branches of industry including: mineral processing,

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medicine, food, cosmetics, textiles and paints (Wang and Somasundaran 2005).

Manganese dioxide occurs in nature as a mineral pyrolusite. Under standard conditions MnO_2 is insoluble and stable in a broad pH range. Manganese dioxide finds application in the production of matches, in glass-making industry for glass decolourization and as a depolarizer in voltaic cells (Trzebiatowski 1979).

The process of polysaccharides' adsorption on the mineral surface is very sophisticated and it is determined by many factors. The most important ones are: character of interactions between the adsorbent and the adsorbate, type of background electrolyte, ionic strength and pH of the solution. Despite many attempts, the mechanism of polysaccharide adsorption on metal oxide surfaces has not been fully explained. The adsorption of polysaccharides on the surface of different minerals has been widely studied with the hydrogen bonding and the hydrophobic interaction as the primary adsorption mechanisms (Steenberg and Harris 1984; Morris et al. 2002). However, according to other scientists (Liu and Laskowski 1989a, b; Liu et al. 2000) the adsorption of polysaccharides results from the acid–base reaction between polymer macromolecules and metal hydroxyl groups present on the mineral surface. What is very interesting, the hydrogen bond between the adsorbent and the adsorbate might be also treated as an acid–base reaction (Fowkes 1989). When the surface of the adsorbent is positively charged (in pHs much lower than pH_{pzc} of this adsorbent) and the polymer is anionic, their interaction might be strong enough to be labelled as a chemical reaction. On the other hand, when the attraction forces between the adsorbent and the adsorbate are weak or if the solid and the polyelectrolyte have the same charge the interaction between them is considered as the hydrogen bonding (Liu and Laskowski 2006). In some cases, the interaction between the anionic polymer and the metal hydroxide sites acts in synergy with the hydrophobicity of the solid surface (Rath and Subramanian 1997).

Shortridge et al. (2000) studied the effect of chemical composition and molecular weight of CMC and modified guar gum reagents on the flotation of talc. They found out that guar was much more effective depressants of talc than the CMC samples when $0.001 \text{ mol dm}^{-3} \text{ KNO}_3$ was used as the background electrolyte. Morris et al. (2002) studied adsorption, elektrokinetic and microflotation properties of CMC at

the talc–water interface as the function of ionic strength and pH. According to their results the amount of CMC adsorption increases with the decrease of pH and the increase of ionic strength. The latter observation was confirmed by Pawlik et al. (2003). They analysed the adsorption and stability of CMC from the electrolyte solution (NaCl, KCl) varying in ionic strength onto illite and dolomite. They also found out that the increase of adsorption accompanying the increase of ionic strength, which is due to the fact that the CMC macromolecules coil in solution to an extent that depends on electrolyte concentration. Wang and Somasundaran (2005) investigated the adsorption of CMC on talc using adsorption, electrophoretic mobility measurements, FTIR, fluorescence spectroscopy, AFM as well as molecular modelling. They noticed that the adsorption of CMC on talc is affected by pH and ionic strength, which indicates the important role of electrostatic force in adsorption. According to these authors, the main driving forces responsible for CMC adsorption on talc are combination of electrostatic interactions and hydrogen bonding rather than hydrophobic force. Khraisheh et al. (2005) studied the effect of molecular weight and concentration on the adsorption of CMC onto talc at different ionic strengths. They concluded that the increasing molecular weight of CMC results in the increase of CMC adsorption on talc. Another conclusion was that the addition of potassium, magnesium and calcium ions to the system increased the tendency of polymer to adsorb on the talc planes. What is more, changing the ionic strength from 10^{-3} to 10^{-2} using the ions results in the increase in the CMC adsorption on talc. Bacchin et al. (2006) investigated the adsorption of CMC of different molecular weights onto talc (adsorption isotherms, adsorption reversibility), its consequences on the particle properties (electrophoretic mobility and surface wetting) and its effect on their dispersion (settling coefficient). They found out that the presence of CMC improves the dispersion of talc by avoiding foam and aggregate formation. Parolis et al. (2008) studied the effect of monovalent and divalent metal cations on the interaction between CMC and talc using adsorption, microflotation and intrinsic viscosity measurements. They noticed that calcium and magnesium ions increased the CMC adsorption onto talc thus promoting the depression of talc by CMC. Their another conclusion was that at the ionic strengths less than 10^{-1} divalent cations caused greater coiling of CMC chains, but at ionic strength

higher than 10^{-1} the coiling effect was equivalent between divalent and monovalent cations. However, the CMC adsorption on talc was still greater in the presence of Ca^{2+} and Mg^{2+} suggesting a specific interaction between the mineral surface, the divalent cations and CMC, which did not occur with K^{+} ions.

As one can see, papers analysing the adsorption of CMC on the mineral surface concerning the influence of pH, ionic strength, type of used electrolyte and CMC molecular weight are the most frequent. The obtained results determined also the influence of the above-mentioned factors on the electrokinetic and the rheological properties of the CMC/solid systems as well as their stability and microflotation properties. However, the influence of surfactants on the adsorption and the electrokinetic properties of the system polysaccharide—metal oxide is missing. Because of that the aim of this paper was to analyse the influence of the surfactants: anionic SDS, non-ionic polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100) and their mixtures with the molecular ratios: 1:1; 1:3 and 3:1 on the adsorption of CMC on the MnO_2 surface as well as to analyse the electrokinetic properties (surface charge density, zeta potential) of the carboxymethyl cellulose/manganese dioxide system in the presence of surfactants. Measurements were conducted in 0.01 mol dm^{-3} NaCl and in $0.003 \text{ mol dm}^{-3}$ CaCl_2 which gave the opportunity to compare the impact of background electrolyte on the analysing systems.

It is well known that polymers may interact with the surface active agents (Parida et al. 2006; Nylander et al. 2006; Moudgil and Prakash 1998; Barck and Stenius 1994). The properties of polymer-surfactant complexes are completely different from those of pure solutions of these two substances. There are four adsorption cases between macromolecules of polymer and surfactants molecules:

- only one of these two adsorbates has the affinity for the surface of the solid but they cannot bind to each other
- only one of these two adsorbates has the affinity for the solid surface but they can also bind to each other
- both adsorbates have the affinity for the surface but not for each other
- both adsorbates have the affinity for the surface and for each other

The above mentioned interactions responsible for the adsorption process in which not only a polymer but

also a surfactant is present might be as follows: electrostatic attraction, covalent bonding, hydrogen bonding and non-polar interactions.

Experimental

Materials

MnO_2 produced by POCh Gliwice (Poland) was used as an adsorbent. The BET specific surface area for the sample was found to be $35 \text{ m}^2 \text{ g}^{-1}$. The particle size distribution of MnO_2 sample determined with the use of a Malvern Mastersizer 2000, fell entirely in the range from 1.82 to 22.71 μm , with a volume average size of 6.78 μm . The adsorbent was washed with doubly-distilled water until the conductivity of the supernatant was smaller than $2 \mu\text{S cm}^{-1}$. The XRD measurements confirmed that MnO_2 was free of impurities.

Sodium salt of carboxymethylcellulose was obtained from Sigma–Aldrich. The viscosity average molecular weight measured using a rotary rheometer CVO 50 (Bohlin Instruments) was found to be 22,000. This value was calculated using Mark-Houwink equation (Husband 1998). The degree of substitution was measured using the potentiometric titration. This value was determined at 1.02 ± 0.013 . The example formula of CMC is presented in Table 1.

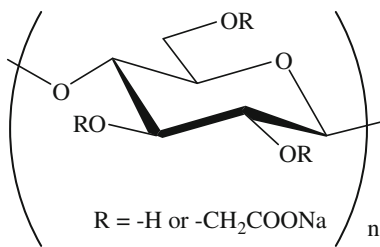
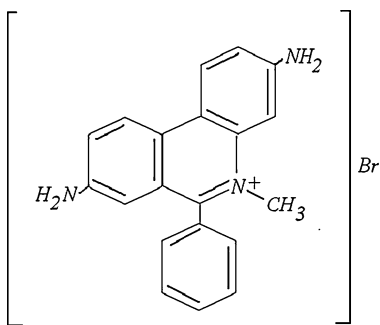
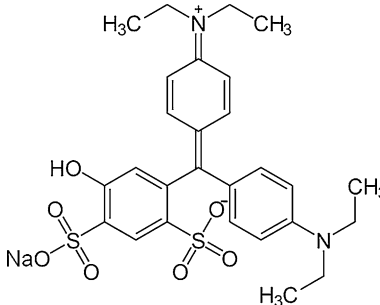
SDS and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100) were purchased from Fluka. The concentrations of used surfactants and their mixture in all measured systems equalled $10^{-4} \text{ mol dm}^{-3}$. Such a value prevents from exceeding of the critical micelle concentration. For SDS the critical micelle concentration is $0.00825 \text{ mol dm}^{-3}$ (Rodriguez-Cruz et al. 2005) whereas for polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether the critical micelle concentration is $0.00029 \text{ mol dm}^{-3}$ (Rharbi and Winnik 2001). NaCl and CaCl_2 both produced by Fluka were used as the supporting electrolytes. The experiments were carried out in doubly-distilled water at room temperature ($\cong 25 \text{ }^\circ\text{C}$).

Methods

Adsorption measurements

0.2 g of manganese dioxide was added to 10 mL of solution prepared from the polymer stock solution

Table 1 Names and structures of organic chemical compounds used in the measurements

Name	Chemical name	Chemical structure
CMC	Carboxymethylcellulose	 <p>R = -H or -CH₂COONa</p>
SDS	Sodium dodecylsulfate	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_2\text{Na}^+$
Triton X-100	t-Octylphenoxy-poly-ethoxyethanol	$\text{C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{-}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ <p><i>n</i> ~ 9.5</p>
Dimidium bromide	3,8-Diamino-5-methyl-6-phenylphenanthridinium bromide	 <p>Br⁻</p>
Patent blue	[4-(Alpha-(4-diethylaminophenyl)-5-hydroxy-2,4-disulfophenyl-methylidene)2,5-cyclohexadien-1-ylidene] diethylammonium hydroxide, sodium salt	

(CMC), electrolyte (NaCl or CaCl₂), doubly-distilled water and surfactant (SDS, TX-100 or their mixture with the molar ratios 1:1; 1:3 and 3:1). Next pH was adjusted to the desired value using 0.1 mol dm⁻³ HCl and 0.1 mol dm⁻³ NaOH. Seven different initial concentrations of CMC were used (25–300 ppm). The suspension was shaken for 20 h, to achieve

the adsorption–desorption equilibrium, using a thermostated stirrer. To determine the CMC adsorption amount, the calorimetric method described by Dubois et al. was used (Dubois et al. 1956). 0.05 mL 80% phenol and 5 mL 98% sulfuric acid were added to 2 mL of supernatant obtained after centrifugation with a speed of 14,000 rpm using a high speed

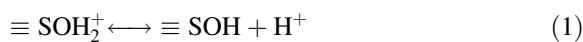
centrifuge (310b Mechanika Precyzyjna). Time of centrifugation equalled 15 min. After 30 min of colour development, the absorbance was measured at a wavelength of 490 nm using a spectrophotometer (Specord M42, Carl Zeiss) with the computer programme M500. All measurements were done as triplicates. In this paper the average values are reported. The amount of CMC adsorption on the MnO₂ surface was calculated from a calibration curve according to the concentration difference before and after the adsorption tests.

SDS concentration was analysed by a variation of Zerbe et al. method (Zerbe et al. 2000). One litre of indicator solution was prepared by dissolving 0.16 g of dimidium bromide and 0.04 g of patent blue in doubly-distilled water in the presence of 40 mL of 1.25 M sulphuric acid. Next, in a separation funnel, 0.5 mL of sample solution was mixed with 39.5 mL pure water, followed by the addition of 10 mL of indicator solution and 20 mL of chloroform. The obtained mixture was vigorously shaken for 1 min and allowed for phase separation. The spectrophotometric measurement of chloroform solution at 526 nm was performed, using pure chloroform as a reference. The SDS concentration in the measured solutions was calculated from a calibration curve. All measurements were done as triplicates and the average values are reported. The measurement error in the analyses was from 3 to 8%.

The polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether concentration was determined directly by UV absorbance at a wavelength 278 nm with doubly-distilled water as the reference (Collen et al. 2002). All measurements were done as triplicates and the average values are reported. The measurement error in the analyses was from 1 to 5%.

Potentiometric titration

The surface charge on the metal oxide is formed as a result of reactions between the surface hydroxyl groups and the electrolyte ions. In aqueous solutions hydrogen/hydroxide ions as well as ions of background electrolyte are the most important in the surface charge formation process. Hydrogen ions influence the surface charge through the acid–base reactions of surface hydroxyl groups:



In classic theories of the electric double layer, background electrolyte ions are assumed to adsorb non-specifically, but in modern models these ions undergo also the specific adsorption.

A comparison between a titration curve of electrolyte and a titration curve of the metal oxide suspension, both of the same ionic strength is used to determine the surface charge density of metal oxide. The surface charge density is calculated from the dependence between the volume of acid/base added to the suspension in order to obtain the desired pH value:

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

where ΔV —dependence between the volume of acid/base added to the suspension in order to obtain the desired pH value, c —molar concentration of acid/base, F —Faraday constant ($9.648 \times 10^4 \text{ C mol}^{-1}$), m —mass of metal oxide, S —specific surface area of metal oxide.

MnO₂ surface charge density in the presence and absence of CMC and surfactant (SDS, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and their mixtures with the molecular ratios: 1:1; 1:3 and 3:1) was determined using the potentiometric titration method. The NaCl concentration was 0.01 mol dm⁻³ whereas CaCl₂ concentration equalled 0.003 mol dm⁻³. Such concentrations of the salts give demanded ionic strength of the solutions ($I = 0.01$) for both electrolytes. The solution volume was 50 mL. A thermostated, Teflon vessel with a shaker, an automatic burette (Dosimat 665, Methrom) and a pH-meter were the parts of the measurement set. The process was controlled by a computer. The density of MnO₂ surface charge was determined using the “Miar_t” programme written by W. Janusz. The surface charge density measurements were done as triplicates for every measured system. The results were obtained with the measurement error lower than 4%.

Zeta potential measurements

0.05 g of manganese dioxide was added to the supporting electrolyte solution (NaCl or CaCl₂) with or without CMC and surfactants (SDS, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and

their mixtures with the molecular ratios: 1:1; 1:3 and 3:1). The volume of the solution was 500 mL. The obtained suspensions were ultrasonicated for 10 min. Then pH was adjusted and the electrophoretic mobility was measured using a zetameter (Zetasizer 3000, Malvern Instruments) and then the zeta potential (ζ) was calculated from the Smoluchowski equation. The zeta potential measurements were done as triplicates and the results were obtained with the measurement error from 2 to 7%. In the paper the average values are reported.

Intrinsic viscosity measurements

Intrinsic viscosity measurements were carried out using a rheometer (CVO 50, Bohlin Instruments). The CMC samples were dissolved in the electrolyte (0.01 mol dm^{-3} NaCl) and allowed to stand overnight for complete hydration. Then they were diluted to the required concentration and surfactants were added. Typically five concentrations were measured to yield the regression line of the reduced viscosity versus concentration from which intrinsic viscosity was extracted by extrapolation to zero concentration. The polymer concentration range over which these measurements were made was $0.1\text{--}5 \text{ g dm}^{-3}$.

Results and discussion

In order to estimate the time needed to achieve the adsorption–desorption equilibrium, preliminary kinetic experiments were conducted before the adsorption measurements. Figure 1 presents the adsorption kinetics of CMC on the MnO_2 surface in the presence of 0.01 mol dm^{-3} NaCl. As can be seen from the presented data, the adsorption equilibrium in the presence of 0.01 mol dm^{-3} NaCl is reached almost immediately. This result is in agreement with the literature reports according to which the CMC adsorption on the metal oxide surface reaches a steady value even after 30 min (Khraisheh et al. 2005). For the systems where not only electrolyte (0.01 mol dm^{-3} NaCl) but also surfactant ($10^{-4} \text{ mol dm}^{-3}$ SDS or $10^{-4} \text{ mol dm}^{-3}$ polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) were present the adsorption amount changes during the first 500 min and reaches a constant value after this time. The case is different when the surfactant mixtures (SDS/polyethylene glycol

p-(1,1,3,3-tetramethylbutyl)-phenyl ether with the molar ratios: 1:1; 1:3 and 3:1) are added to the adsorption system. Then the adsorption equilibrium is reached after 1,100 min. This fact results from a large number of possible reconformations in the systems where not only polymer but also two surfactants are present. Different dependences are observed in the systems where CaCl_2 is used as a background electrolyte (Fig. 2). As can be seen from the presented data, the adsorption amount of CMC on MnO_2 increases in every measured system during the first 1,100 min and then reaches the constant value. The reason is the fact that these above-mentioned reconformations result from the interactions between the calcium cations, CMC macromolecules and surfactant molecules along with the interactions with the solid surface. One should bear in mind that possibility of these reconformations in the above-mentioned adsorption systems is higher in the presence of divalent cations. Considering kinetic experiments 1,440 min (24 h) was chosen to be the conditioning time in all adsorption measurements. In fact, this time could be shorter for the systems with NaCl but the author decided to provide the identical parameters of the adsorption processes in all measured systems.

Figures 3, 4 present the adsorption isotherms of CMC on the MnO_2 surface in the presence of surfactant (SDS, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and their mixtures SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether with the molar ratios: 1:1; 1:3, 3:1). The data presented in Fig. 3 were obtained in the presence of NaCl as the background electrolyte, whereas the data presented in Fig. 4 in the presence of CaCl_2 . Concentrations of these electrolytes were chosen to obtain the same values of ionic strength. In general, mechanism of polysaccharides adsorption is a consequence of

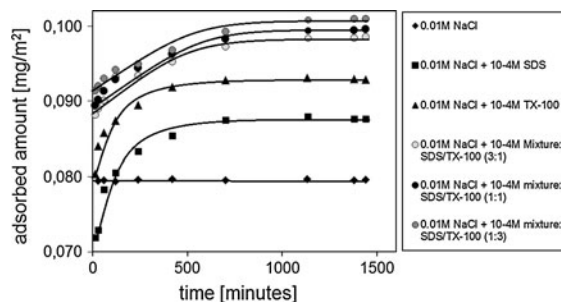


Fig. 1 Kinetics of CMC adsorption (100 ppm) in the system: CMC/ MnO_2 /0.01M NaCl/surfactant

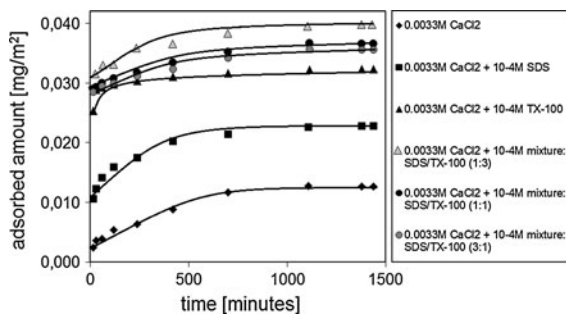


Fig. 2 Kinetics of CMC adsorption (100 ppm) in the system: CMC/MnO₂/0.003M CaCl₂/surfactant

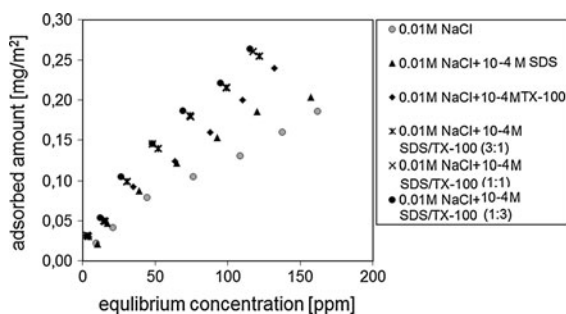


Fig. 3 Adsorption isotherms of CMC on MnO₂ surface in the presence and absence of surfactants in 0.01M NaCl, pH=7

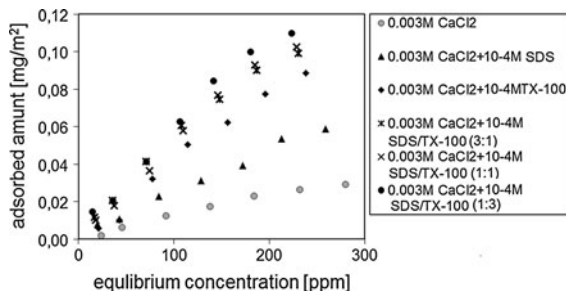


Fig. 4 Adsorption isotherms of CMC on MnO₂ surface in the presence and absence of surfactants in 0.003M CaCl₂, pH=7

hydrophobic and (or) electrostatic interactions. Hydrogen bonding and hydrophobic interaction seem to be the most “popular” adsorption mechanisms (Steenberg and Harris 1984; Morris et al. 2002). However, according to the other scientists (Liu and Laskowski 1989a, b) the adsorption of polysaccharides results from the acid–base reaction the between polymer macromolecules and the metal hydroxyl groups from the solid surface. It is known that in the absence of surfactants, the carboxylic and hydroxyl groups of CMC interact with the metallic species on the mineral

surface (Bicak et al. 2007). However, the carboxyl groups interact with various forms of metallic ionic species whereas the hydroxyl groups interact mostly with the metal hydroxyl species which is an acid–base interaction (Laskowski and Liu 1999; Liu et al. 2000). The schematic representation of one of possible interactions between the surface groups of MnO₂ and the active groups of CMC is shown in Table 2.

It is completely different when the surface active agent is added to the system. There is much evidence in the world literature that polysaccharides form complexes with surfactants. Bain et al. (2010) studied the CMC and DTAB (dodecyltrimethylammonium bromide) complexes as well as those of CMC and CTAB (hexadecyltrimethylammonium bromide) using light scattering and zeta potential measurements. Liu et al. (2010) pointed out to existence of a complex between sodium carboxymethylcellulose and C12mimBr (1-dodecyl-3-methylimidazolium bromide) using the isothermal titration microcalorimetry, turbidimetric titration and surface tension measurements. Terada et al. (2004) measured the effect of SDS (sodium dodecyl sulphate) on the adsorption behaviour of hydroxyethyl cellulose and hydrophobically modified cationic cellulose. They also concluded that there are formed complexes between above mentioned polysaccharides and the SDS molecules. Samoshina et al. (2005) also found out the existence of the SDS and amphiphilic polyelectrolytes complexes. As one can see in Figs. 3, 4, the amount of carboxymethylcellulose adsorption is always higher in the presence of surfactants or their mixtures. The increase of the adsorption is the smallest in the presence of anionic SDS, larger in the presence of non-ionic polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and the largest in the presence of the surfactant SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixtures. Among the above-mentioned mixtures the greatest increase in the amount of CMC adsorption on MnO₂ is observed when the SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture with the molar ratio 1:3 is added to the adsorption system. The increase of CMC adsorption in the presence of the surface active agents results from formation of the CMC macromolecules and the surfactants molecules complexes. In the adsorption system: SDS/CMC/MnO₂ these complexes are definitely non-electrostatic. Unfortunately the nature of these complexes has not been fully understood due to complications connected with the fact that in the

Table 2 Hydrogen bonds interactions between the surface active groups of MnO₂ and the adsorbates particles (CMC and surfactants)

Types of surface groups MnO ₂	Possible hydrogen bonds interactions between CMC groups and surfactants (SDS; TX-100) particles		
	CMC	Triton X-100	SDS
Mn-O-H			
Mn-O ⁻			
Mn-O-H+			

presence of the surface active agent in the adsorption system the interactions like: polymer-surface, surfactant-surface and polymer-surfactant complex-surface have to be considered. One of possible mechanisms of these complexes are hydrogen bonds (Table 3). The additional role in the polymer-surfactant interactions might be played by hydrophobic interactions between the CMC and SDS molecules. In the presence of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether higher increase in the adsorption amount of CMC is observed. The reason for that is nonionic character of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether. This surfactant does not dissociate and does not form any charge, but has large capability of formation of complexes (Zeng and Osseo-Asare 2004). As CMC adsorption amount in the presence of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether is larger than in the presence of SDS, it means that the complexes between CMC and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether are created more effectively than those between CMC and SDS due to the electrostatic repulsion between the anionic CMC and the negatively charged SDS which lowers the possibility of complex formation. As follows from the analysis of the obtained data the adsorption amount of CMC is the lowest in the

presence of surfactants mixture SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether with the molar ratio 3:1, a bit higher in the presence of the SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture with the molar ratio 1:1 and the highest when the SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture with the molar ratio 1:3 is used. As it is known, mixtures of anionic and nonionic surfactants exhibit a synergetic effect (Wang and Kwak 1999; Soriyan et al. 2009; Reif and Somasundaran 1999), resulting in the increase of adsorptive, foaming and rewetting properties of surfactant mixtures in comparison to pure surfactant solutions. This effect is clearly visible in the adsorption system under consideration. Moreover, the comparison of the results obtained for three different molar ratios of SDS and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether allows to draw a conclusion which of these two surfactants is more effective to increase the polymer adsorption amount. The SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture with the molar ratio 1:3 is responsible for the highest increase of the CMC adsorption amount, which means that polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether interacts with CMC macromolecules more willingly than SDS. This observation is in agreement

Table 3 Hydrogen bonds interactions between CMC macromolecules and surfactant particles

Types of active groups of CMC	Possible hydrogen bonds interactions with surfactants (SDS; TX-100) particles	
$-\bar{O}H$	$-\bar{O}H \cdots \bar{I}O(CH_2CH_2O)_n-C_8H_{17}$	$-\bar{O}H \cdots \bar{O}S(=O)(=O)CH_2(CH_2)_{10}CH_3$
	$-\bar{O}H \cdots H\bar{O}(CH_2CH_2O)_n-C_8H_{17}$	$-\bar{O}H \cdots \bar{O}S(=O)(=O)CH_2(CH_2)_{10}CH_3$
$-\text{CH}_2\text{C}(=\bar{O})\bar{O}^-$	$-\text{CH}_2\text{C}(=\bar{O})\bar{O}^- \cdots H\bar{O}(CH_2CH_2O)_n-C_8H_{17}$	
	$-\text{CH}_2\text{C}(=\bar{O})\bar{O}^- \cdots H\bar{O}(CH_2CH_2O)_n-C_8H_{17}$	

with the adsorption data obtained in the presence of pure surfactant solutions.

Moreover, it is known that kind of solvent influences the adsorption process. Firstly, because a polymer expands in good solvents and contracts in the poor ones. A result of that is a larger surface area occupied by polymer macromolecules in good solvents and smaller in poor ones. In consequence a larger adsorption amount is obtained from poor solvents. Marra et al. (1983) suggested that the adsorption of polystyrene sulfonate increases around the theta point (4.2 M NaCl). The dimensionless Huggins coefficient k is often used in order to analyse the polymer–solvent interaction. This magnitude might be estimated by intrinsic viscosity measurements (Pawlik et al. 2003). The intrinsic viscosity $[\eta]$ is a measure of the inherent ability of a polymer to increase viscosity of a solution. According to Huggins (1942):

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c \rightarrow 0} + k \left(\frac{\eta_{sp}}{c}\right)_{c \rightarrow 0}^2 c \quad (4)$$

Since η_{sp}/c at $c \rightarrow 0$ is the intrinsic viscosity $[\eta]$:

$$\eta_{red} = [\eta] + k[\eta]^2 c \quad (5)$$

where η_{red} is the reduced viscosity, $[\eta]$ is the intrinsic viscosity, k is the dimensionless Huggins coefficient, and c is the concentration of the polymer (g/dm^3). A plot of $\eta_{red} = f(c)$ should be a straight line with the intercept equal to $[\eta]$ and the slope equal to $k[\eta]^2$. From that k and $[\eta]$ are calculated.

The coefficient k can be used to characterize the polymer–solvent interactions because it is very sensitive to the formation of molecular aggregates. Its physical meaning is as follows: (a) value of k is higher in a poor solvent than in a good one; (b) its value varies from 0.5 to 0.7 under the theta conditions (Sakai 1968).

Figure 5 presents the dependence between the reduced viscosity of CMC in the absence and presence of surfactants and their mixtures versus polymer concentration. The Huggins coefficient k and $[\eta]$ were calculated using the data from Fig. 5. Table 4 presents the values of coefficient k and intrinsic viscosities $[\eta]$ in solutions of 0.01 mol dm^{-3} NaCl in the presence of surfactants and their mixtures. The obtained data of k coefficient are in agreement with the adsorption data. As one can see, the larger adsorption amount the higher k coefficient. Its value is the highest in the systems where mixtures of surfactants are present. It means that such systems are the poorest solvents for CMC macromolecules. What is more none of the systems used can be treated as theta solvent of the analysed polymer.

The adsorption data of CMC at the MnO_2 surface obtained in the presence of NaCl (Fig. 3) and CaCl_2 (Fig. 4) show that the amount of CMC adsorption on manganese dioxide is always higher when NaCl is used as a background electrolyte in comparison to CaCl_2 . The most important reason responsible for the decrease of CMC adsorption amount in the presence of CaCl_2 are complexation reactions between Ca^{2+} ions and CMC molecules. They may proceed between

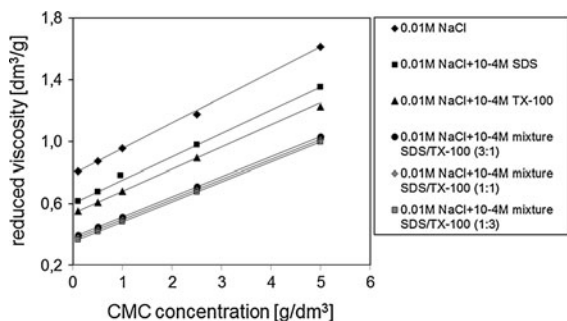


Fig. 5 Reduced viscosity versus CMC concentration in the presence and absence of surfactants and their mixtures

Ca^{2+} ions and two different chains of CMC or between Ca^{2+} ions and the functional groups of CMC belonging to the same macromolecule. If the second interaction takes place, the decrease in the CMC adsorption amount in the presence of CaCl_2 is observed. The formation of intramolecular complexes between Ca^{2+} and CMC was confirmed by the NMR technique (Matsumoto and Ito 1990).

A research on the surfactant adsorption versus the initial concentration of CMC was carried out in order to prepare a comprehensive analysis of the measured systems. Fig. 6 presents the dependence between the amount of surfactant adsorption on MnO_2 versus the initial concentration of CMC. Measurements were conducted in 0.01 mol dm^{-3} NaCl, at $\text{pH} = 6$. As one can see the amount of surfactants adsorption does not depend on the CMC initial concentration. Moreover, the amount of SDS adsorption is the lowest, the adsorption of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether is higher and the adsorption of surfactants mixture SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether is the highest. These surfactants probably do not adsorb directly at the surface of MnO_2 , but they form complexes with CMC macromolecules and such aggregates are adsorbed.

Table 4 Values of the Huggins coefficient k and intrinsic viscosities $[\eta]$ in 0.01 mol dm^{-3} NaCl in the presence of surfactants and their mixtures

Solvent	$[\eta]$ (g dm^{-3})	$k(\eta)^2$	Huggins coefficient, k
0.01 M NaCl	0.7918	0.1643	0.26
0.01 M NaCl/10-4M SDS	0.6004	0.1503	0.42
0.01 M NaCl/10-4M TX-100	0.5375	0.1424	0.49
0.01 M NaCl/10-4M SDS/TX-100 (3:1)	0.3837	0.1297	0.88
0.01 M NaCl/10-4M SDS/TX-100 (1:1)	0.3685	0.1286	0.95
0.01 M NaCl/10-4M SDS/TX-100 (1:3)	0.3541	0.1288	1.03

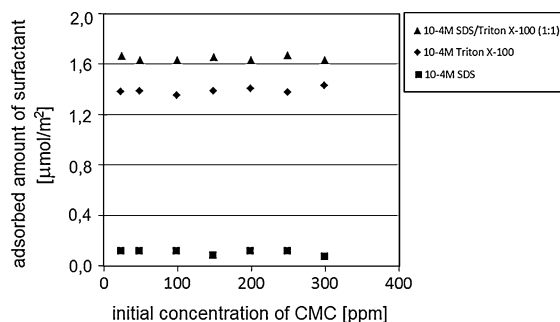


Fig. 6 Dependence between the amount of surfactant adsorption on the MnO_2 surface versus initial concentration of CMC, 0.01 M NaCl , $\text{pH} = 6$

In order to analyse the metal oxide/polysaccharide/surfactant interface the surface charge density measurements together with the zeta potential measurements were conducted. Figures 7, 8 show the influence of pH , CMC and the surfactants (SDS, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether or their mixtures) on the surface charge of MnO_2 . Analysis of the obtained data shows that the surface charge of MnO_2 strongly depends on pH of the solution. It is known that the point of zero charge for manganese dioxide is around 4 (Chibowski et al. 2008). It means that at $\text{pH} < 4$ the solid surface is positively charged because of high concentration of MnOH_2^+ groups but at $\text{pH} > \text{pH}_{\text{pzc}}$ the oxide surface has a negative charge coming from the increasing concentration of MnO^- groups. Moreover, the presence of anionic CMC and the all measured surfactants causes the decrease of the surface charge of MnO_2 in all measured pH range. What is more, the shift of the point of zero charge to lower pH values is observed. This fact can be explained by the presence of the negatively charged groups from the CMC and SDS molecules or from the polysaccharide/surfactant complexes: CMC/SDS, CMC/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether, CMC/SDS/polyethylene glycol

p-(1,1,3,3-tetramethylbutyl)-phenyl ether. These negative groups are not linked with the surface but present in the compact part of the electric double layer (Chibowski et al. 2004, 2010). Another observation is that there is no significant difference between the surface charge density of MnO₂ in the presence of different surfactants. This observation is the evidence that the compact part of the electric double layer is closely packed with CMC molecules that there is no effect of the presence of different kinds of surfactants (ionic or nonionic) on the value of the surface charge density of manganese dioxide. What is more, the above presented results are very similar in both measured electrolytes NaCl (Fig. 7) and CaCl₂ (Fig. 8). Of course the surface charge density of MnO₂ in the presence of CaCl₂ is different from the values obtained in NaCl solution. The reason for that is adsorption of calcium, sodium cations and chloride anions at the surface of manganese dioxide.

Figures 9 and 10 present the influence of carboxymethylcellulose, surfactants (SDS, polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) and their mixtures (molar ratios: 1:1; 1:3; 3:1) on the zeta potential of manganese dioxide. The obtained results indicate that the presence of CMC and surfactants causes the decrease of the zeta potential as well as a shift of isoelectric point (pH_{iep}) from MnO₂ towards lower pH values (pH_{iep} for MnO₂ ≈ 4 (Chibowski et al. 2008)). The last fact is the evidence that carboxymethylcellulose adsorption has a specific, nonelectrostatic character (Chibowski et al. 2005). The zeta potential values of MnO₂ are the highest in pure electrolyte solution (0.01 mol dm⁻³ NaCl—Fig. 9) (0.003 mol dm⁻³ CaCl₂—Fig. 10), a bit lower in the presence of CMC solution, next in the presence of the CMC/

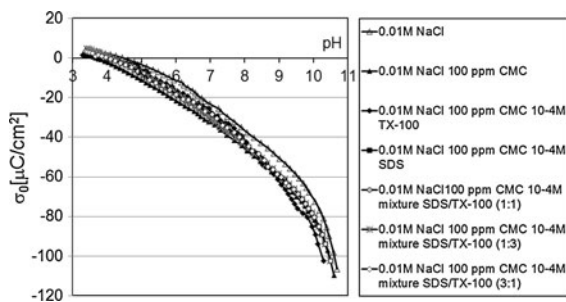


Fig. 7 Influence of CMC and surfactants (SDS, TX-100 and their mixtures SDS/TX-100 with molar ratios: 1:1; 1:3; 3:1) on the surface charge density of MnO₂ in the presence of 0.01M NaCl

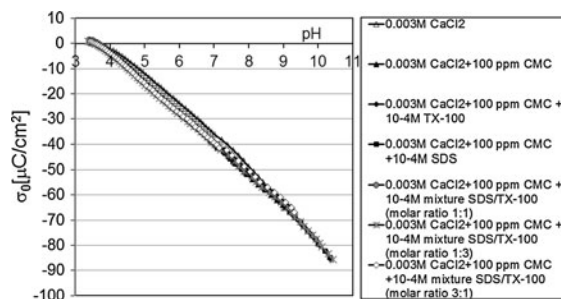


Fig. 8 Influence of CMC and surfactants (SDS, TX-100 and their mixtures SDS/TX-100 with molar ratios: 1:1; 1:3; 3:1) on the surface charge density of MnO₂ in the presence of 0.003M CaCl₂

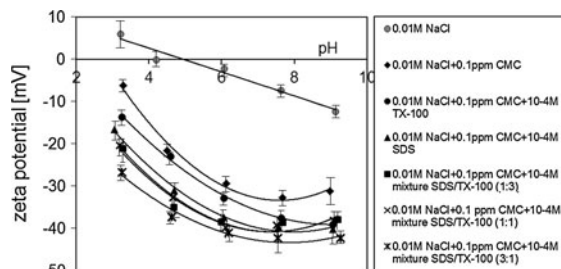


Fig. 9 Influence of CMC and surfactants (SDS, TX-100 and their mixtures SDS/TX-100 with molar ratios: 1:1; 1:3; 3:1) on the zeta potential of MnO₂ in the presence of 0.01M NaCl

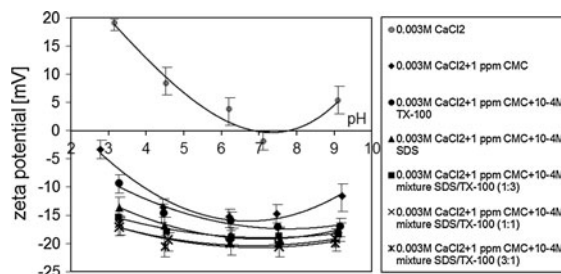


Fig. 10 Influence of CMC and surfactants (SDS, TX-100 and their mixtures SDS/TX-100 with molar ratios: 1:1; 1:3; 3:1) on the zeta potential of MnO₂ in the presence of 0.003M CaCl₂

polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture, much lower in the presence of the CMC/SDS mixture and the lowest when besides CMC, the surfactant (SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether) mixtures are present in the adsorption system. Of three measured adsorption mixtures the obtained values of the zeta potential do not differ a lot, but the highest zeta potential values were obtained in the presence of the SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether mixture with

the molar ratio 1:3. There are two factors which have the influence on the decrease of the zeta potential. The first one is the shift of the slipping plane towards the bulk solution, coming from the adsorption of polysaccharide or the polysaccharide/surfactant complex. The second one is the presence of negatively charged groups originating from the diffused part of the electric double layer (Chibowski et al. 2000). The smallest decrease in the zeta potential is observed in the system: CMC/MnO₂. This decrease results from the presence of negatively charged carboxylic groups from the CMC macromolecules. A bit higher decrease in the presence of CMC and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether is a consequence of complexes formation between the surfactant molecules and the polysaccharide macromolecules as well as the negative charge from the dissociation with the CMC macromolecules. Larger decrease of the zeta potential is observed in the system: CMC/SDS/MnO₂. The explanation of this phenomenon might be found in the presence of negatively charged groups originating from CMC and SDS as well as a shift of the slipping plane towards the bulk solution by the CMC/SDS complexes adsorbed at the surface of manganese dioxide. The largest decrease of the zeta potential of MnO₂ in the presence of CMC and the surfactant mixtures of SDS and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether is observed. As was written above, these mixtures exhibit a strong synergetic effect (Şakar-Deliormanlı 2007) which results for example in the increase of the adsorption amount of polysaccharide (Figs. 3, 4). Of the measured surfactant mixtures the obtained zeta potential values were quite similar. These data suggest that the adsorption layer in the presence of surfactant mixture is the most expanded towards the bulk phase. The comparison between the zeta potential of MnO₂ in the presence of 0.01 mol dm⁻³ NaCl (Fig. 9) and 0.003 mol dm⁻³ CaCl₂ (Fig. 10) shows that the values of the zeta potential of MnO₂ obtained in the presence of calcium chloride are higher than in the presence of sodium chloride which is typical of these electrolytes but the obtained dependences are very similar.

Conclusions

In every measured system the increase of CMC adsorption on the MnO₂ surface in the presence of surfactants was observed. This increase was the

smallest in the presence of anionic SDS, a bit larger in the presence of non-ionic polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and the largest when the mixtures of SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether were used. Of the measured mixtures, the SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether one with the molar ratio 1:3 caused the largest increase of the CMC adsorption amount, the lowest increase of adsorption was observed in the presence of the mixture with the molar ratio 3:1 SDS/polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether respectively which is due to formation of complexes between the CMC macromolecules and the surfactant molecules. These complexes are created more effectively between non-ionic polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether and anionic CMC than between negatively charged SDS and CMC. Moreover, the presence of anionic CMC and the all measured surfactants causes the decrease of the surface charge of MnO₂ and the shift of the point of zero charge to lower pH values. This fact results from the presence of the negatively charged groups from the CMC and SDS molecules or from the polysaccharide/surfactant complexes. Another observation is that there is no significant difference between the surface charge density of MnO₂ in the presence of different surfactants. This is the evidence that the compact part of the electric double layer is closely packed with CMC molecules. Furthermore, the presence of CMC and surfactants causes also the decrease of the zeta potential as well as a shift of isoelectric point (pH_{iep}) from MnO₂ towards lower pH values. There are two factors responsible for that: the shift of the slipping plane towards the bulk solution, coming from the adsorption of polysaccharide or the polysaccharide/surfactant complex and the presence of negatively charged groups in the diffused part of the electric double layer.

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