ADSORPTION AND CO-ADSORPTION OF PEO-PPO-PEO BLOCK COPOLYMERS AND SURFACTANTS AND THEIR INFLUENCE ON ZETA POTENTIAL OF MAGNESITE AND DOLOMITE

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Abstract. The influence of adsorption and co-adsorption of PEO-PPO-PEO triblock copolymers (Pluronics) as well as surfactants on the zeta potential of magnesite and dolomite aqueous suspension are addressed here. Four Pluronics of various molecular weight were used in these studies. They have been mixed with cationic (CTAB) or anionic (SDS) surfactants. The adsorption isotherms of copolymers and copolymer-surfactant mixture onto magnesite and dolomite have been determined. The adsorbed amount of Pluronics increases with the increasing concentration and reaches plateau. An increase in the adsorbed amounts of both cationic and anionic surfactants onto the mineral surfaces (magnesite and dolomite) has been observed in the presence of Pluronic copolymers. A positive nature of zeta potential was observed in the presence of cationic surfactant, except magnesite without or with a low CTAB concentration. However, an attendant copolymer causes a decrease of zeta potential due to the deformation of an electrical double layer, comparing the presence of an individual cationic surfactant. The adsorbed non-ionic Pluronic layer partially screens the surface charge of mineral particles, and thus, reduces the zeta potential. On the other hand, the adsorption of anionic surfactant and copolymer caused a decrease in the negative value of the zeta potential of both investigated minerals due to increased SDS adsorption. The viscosity measurements were also performed to determine the thickness of adsorbed layer.

keywords: Pluronic, adsorption, synergism, zeta potential, dolomite, magnesite, surfactant, SDS, CTAB, polymer layer thickness

1. Introduction

The use of adsorbing copolymer and surfactant to modification of mineral surface and colloidal dispersion behaviour is significant for industrial applications. For instance, the pharmaceutical industry requires an adjustment of the drug surface to the human body environment. Thus, the use of amphiphilic macromolecules adsorbed onto the biodegradable materials is a new way of medicine delivery (Rapoport, 1999; Batrakova and Kabanov, 2008). Pluronics have been applied in both drug and gene

delivery systems (Shar et al., 1999; Govender and Swart, 2008), as a biological protector of bacterial cell and protein adhesion (Kabanov et al., 2002; Wesenberg-Ward et al., 2005). The application of Pluronics can increase the membrane hydrophilicity and fouling-resistance ability (Taylor et al., 2007).

Pluronics are triblock copolymers of polyethylene oxide (PEO) and polypropylene oxide (PPO). The adsorption of Pluronic macromolecules depends on the hydrophobicity of the sorbent surface. In the case of hydrophilic surface, two terminal PEO_n blocks attach to the surface, whereas the adsorption onto the hydrophobic surface is realized by PPO block which anchors to the surface. The conformation of adsorbed Pluronic molecules onto different surfaces depends on the PPO/PEO ratio (Terayama et al., 2001, Kapilashrami et al., 2003). The adsorption layer density of triblock copolymers at the solid-liquid interface is greater than that of diblock ones. Pluronics can adsorb at the surfaces either in a pancake or brush-like configuration. Polymer brushes are usually made of uncharged polymers rather than polyelectrolyte, most often polyethylene oxide (PEO).

Polymer-surfactant interactions were subjected to intensive theoretical and experimental investigations, especially at both the solution-air and solid-solution interfaces (Torn et al., 2003; Greenwood et al., 1995; Ortona et al, 2006; Zhang R. et al., 2007). Mixed adsorption of polymers and surfactants at the solid-liquid interfaces has been studied far less. A majority of these investigations have been focused on the adsorption onto the hydrophobic surfaces. Relatively low quantities of papers concerns the polymer-surfactant adsorption onto hydrophilic surfaces. It was shown, that the adsorption of Pluronic F108 onto silica was extremely sensitive to SDS concentration and ionic strength (Braem et al., 2001).

This paper involves a detailed study of the adsorption of Pluronics and ionic surfactants (cationic and anionic) on magnesite and dolomite. Subsequently, the zeta potential and viscosity of these systems have been analyzed. As will be shown, different behaviour of magnesite and dolomite suspensions suggests different conformations of the Pluronic-surfactant complexes at the mineral-water interface.

2. Materials and methods

2.1. Materials

2.1.1. Minerals

A natural dolomite from old quarry Kletno (Lower Silesia, Poland) and magnesite from magnesite mine Grochow (Lower Silesia, Poland) were used as mineral samples. The X-ray diffraction analysis of magnesite showed the sample contains impurities, such as silica and Fe-compounds, while the dolomite is relatively pure. Chemical analysis showed that the magnesite and dolomite contain 88% and 98 % of carbonates, respectively. The mineral samples were ground and classified. The -40 µm fraction was used in the adsorption experiments. The magnesite and dolomite samples had density 2.60 g/cm^2 and 2.77 g/cm^2, respectively. The BET specific surface area was

determined using FlowSorbII 2300 apparatus (Micromeritics) and was found to be 1.92 m^2/g for dolomite and 23.06 m^2/g for magnesite. The particle size distribution measurements were carried out by using a Mastersizer2000 laser diffractometer, equipped with a HydroMu dispersion unit (Malvern Instruments), and showed that the mean particle diameter was about 7.7 and 17.3 μm for magnesite and dolomite, respectively.

2.1.2. Chemicals

Amphiphilic block copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) – Pluronics, with different molar mass and different contents of hydrophilic and hydrophobic segments were obtained as a gift from BASF Corporation. The general information about Pluronics PE 10500 and PE 6800 are presented in Table 1.

Cetyltrimethylammonium bromide (CTAB) $(C_{16}H_{33})N(CH_3)_3Br$ and sodium n-dodecyl sulphate (SDS) were used. They were purchased from Alfa Aesar GmbH & Co and were used without further purification. Tannic acid was obtained from Fluka.

Table 1. Characteristics of applied Pluronics

Pluronic	Structure	Average molecular weight	Molar mass of PO block
PE 3500	$EO_{11}PO_{16}EO_{11}$	1900	950
PE 6400	$EO_{13}PO_{30}EO_{13}$	2900	1750
PE 6800	$EO_{72}PO_{28}EO_{73}$	8000	1750
PE 10500	$EO_{37}PO_{56}EO_{37}$	6500	3250

2.2. Methods

2.2.1. Adsorption experiments

Adsorption isotherms were determined by solution depletion method, where the amount of Pluronics or surfactants adsorbed at the particle surface was determined from the difference between the initial and final concentration. The single component adsorption isotherms were established by mixing 50 cm^3 copolymer or surfactant solution with 0.5 g of the mineral sample. After 24 hours, the dispersed solid was separated using a centrifuge at 2000 rpm for 10 minutes and the supernatants were analyzed. The concentration of Pluronics in the supernatants was measured according to tannic acid method described by Tsurumi et al. (Tsurumi et al., 2006). The reaction between tannic acid and PEO block of Pluronic results in a turbidity of solution. The turbidity was established by measuring the absorbance at 600 nm using Helios Gamma UV–Vis spectrophotometer (Thermo Electron Corporation). The equilibrium concentration of CTAB was detected by a colorimetric method with SDS, while sodium dodecyl sulfate concentration was determined using a two-phase titration method with Hyamine 1622 (Zhang S.J. et al., 2007). Adsorption of surfactant-copolymer mixtures was carried out according to the single surfactant isotherm

determination procedure described above. The mixture of two components were prepared in a flask and combined with a mineral sample immediately.

2.2.2. Zeta potential measurements

Zeta potential values of magnesite and dolomite sample were measured depending on the amount of copolymer and surfactant using ZetaSizer Nano ZS (Malvern Instruments). The zeta potential measurements were carried out at constant ionic strength of 0.1 mM NaCl. The pH of suspensions was the natural value imposed by the minerals and was 8.5 and 10.4 for magnesite and dolomite, respectively. The results were averaged over four independent measurements.

2.2.3. Viscosity measurements

The viscosity measurements of mineral suspensions were conducted using dynamic stress rheometer CVO 50 (Bohlin Instrument). The mineral suspensions for the adsorbed layer thickness measurements were prepared according to the procedure described above in a section 2.2.1. Since dolomite suspensions showed a strong coagulation, the viscosity measurements were carried out only for the magnesite suspensions.

All experiments were carried out at room temperature, i.e. 25ºC.

3. Results and discussion

3.1. Adsorption isotherms of copolymers and copolymer-surfactant mixtures on the carbonates mineral surface

The isotherms of Pluronics adsorption onto the hydrophilic surfaces of magnesite and dolomite are presented in Fig. 1 and Fig. 2.
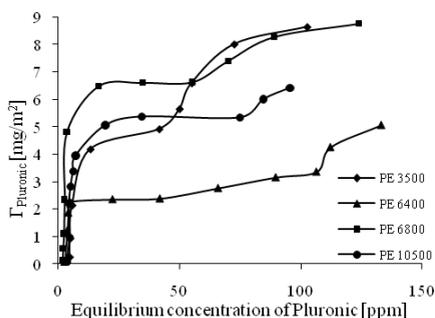

Fig. 1. Adsorption isotherms of Pluronics on magnesite (pH 8.5 and $C_{NaCl}=1\cdot10^{-4}$M)
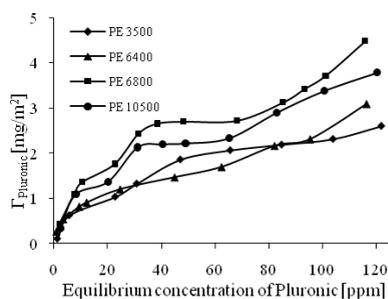
Fig. 2. Adsorption isotherms of Pluronics on dolomite (pH 10.4 and $C_{NaCl}=1\cdot10^{-4}$M)

The results for magnesite mineral showed that the adsorbed amount of investigated copolymer sharply increased up to 6.7, 5.4, 4.7 and 2.3 mg/m^2, reaching the first plateau for PE 6800, PE 10500, PE 3500 and PE 6400, respectively. Further increase

in initial Pluronics concentration led to the formation of the second plateau. This observation corresponds to research of Pluronics adsorption on hydrophilic surfaces reported in literature. Tiberg and co-workers (1991) investigating the adsorption of PE 6200 copolymer onto silica surface concluded that sudden increase of adsorption densities of block copolymers on silica surface at high Pluronic concentration corresponded to the formation of more than one layer on surface. It was also observed that the multilayer can be only formed on the hydrophilic surfaces, where the adsorption occurs by terminal PEO group of copolymer (Paterson et al., 1999). In the case of dolomite mineral, the adsorbed amount of investigated copolymer slowly increased with the concentration and the regions observed for magnesite are barely apparent.

The adsorption of copolymer molecules onto carbonate minerals surface depends on the polymer molecular weight. One can see that the copolymer of PE 6800 exhibited the greatest adsorption affinity to the surface, whereas the worst adsorption was observed in system containing PE 6400 copolymer. Data presented in Table 1 show that PE 6800 copolymer has the highest molecular weight, 8000 g/mol and the largest number of PEO group, whereas PE 6400 is characterised by low molecular weight, 2900 g/mol and the smallest amount of PEO group. This finding is in a good agreement with the results published elsewhere (Dijt et al., 1990; Fleer et al., 1993; Holmberg, 2002; Sakar-Deliormanli, 2007). Higher molecular weight of copolymer (M_w) means higher flexibility of the entire molecule which results in better protection of PPO block and better adsorption of molecules onto hydrophilic surfaces. But if we compare the adsorption behaviour adsorption of PE 3500 and PE 6400, as it is seen in Figure 1, PE 3500 with lower molecular weight (M_w = 1900 g/mol) and higher PEO part showed higher adsorption onto magnesite surface than PE 6400. Very similar results were observed in literature. Sakar-Deliormanli (2007) noticed that copolymer F 68 (Mw = 8400 g/mol, EO = 80%) adsorbed better at silica surface than copolymer F 127 (Mw = 12600 mg/g, EO = 70%). It has been suggested that the larger portion of segments of PEO groups were in macromolecules, the larger amount of copolymer was adsorbed onto silica surface, even if the molecular weight of Pluronic was smaller. It was attributed to the adsorption of block copolymer onto silica surface by hydrogen bonding between the ether oxygen and the silanol groups (Colic et al., 1998; Kawaguchi et al., 2001). In our investigated systems the magnesite sample contained 88% of carbonates and 12% of traces of minerals like talc, silicates and quartz. We can supposed that in our case, Pluronics have not only adsorbed onto silicates and quartz but also onto magnesite surface by complex formation. The mineral dissolution experiments in aqueous medium at pH 9 showed that concentration of Mg^{2+} in suspension was $3.50 \cdot 10^{-4}$M. Magnesium cation may play crucial role in interaction between Pluronic molecules and the carbonate surface. It is well-known that poly(ethylene oxide)-based nonionic polymers are able to bind metal ions from solution and form a "pseudopolycations" which are capable of interacting with negatively charged species. It was also observed that POE chains in surfactant are

adsorbed to minerals surface through hydrogen bonding between oxygen atoms in POE chains and water molecules in the hydration layers of exchangeable cations such calcium and magnesium (Deng et al., 2006).

The results of cationic surfactant adsorption onto the magnesite and dolomite surface are presented in Fig. 3 and Fig. 4, respectively. The presence of copolymer caused greater adsorption of surfactant from mixed solution than from individual one. It can result from the synergistic interaction between block copolymer and cationic surfactant. In such system, cationic surfactant molecules anchor to the hydrophobic parts of copolymer molecules as it is schematically presented in Fig. 5. The surfactant molecules act as a bridge between the mineral surface and hydrophobic part of copolymer. This scheme was created based on the data published by Torn and co-workers (2003), which regard the structure of PVD-SDBS complexes. In the case of magnesite, the synergistic effect is significant for both investigated copolymers, which concentration in the mixture was 120 ppm. For PE 6800 and PE 10500 the plateau amount of CTAB was 8 and 12 mg/m^2, respectively. For the latter one, the value reached is twice as for an individual surfactant. Similar results were observed for dolomite sample, where the plateau value of CTAB in the presence of copolymer PE 6800 and PE 10500 was twice and three times greater than for an individual surfactant, respectively. It was observed that the presence of copolymer PE 10500 was more influencing on the adsorption of cationic surfactant than copolymer PE 6800. It can be explained by longer hydrophobic part in PE 10500 molecule to which the surfactants molecules or aggregates can be attached as it was shown in Fig. 5.
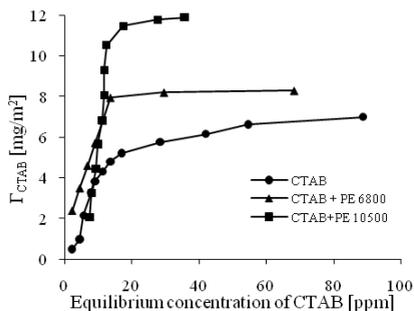

Fig. 3. Cationic surfactant adsorption on magnesite from mixed solutions (Pluronic concentration - 120 ppm, pH 8.5, $C_{NaCl} = 1 \cdot 10^{-4}$ M)
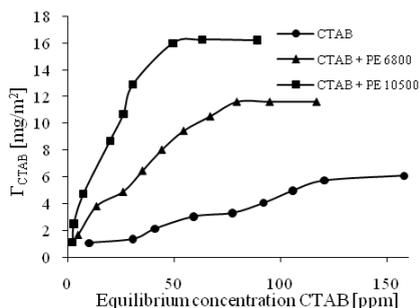
Fig. 4. Cationic surfactant adsorption on dolomite from mixed solutions (Pluronic concentration - 120 ppm, pH 10.4, $C_{NaCl} = 1 \cdot 10^{-4}$ M)

The adsorption isotherms of Pluronics onto carbonates minerals in the presence of cationic surfactant are shown in Figs. 6 and 7. The obtained data revealed that PE 6800 and PE 10500 molecules have greater affinity to both investigated mineral surfaces in the presence of CTAB, which initial concentration was 120 ppm. The plateau value of PE 6800 and PE 10500 in mixed system, was 9 and 11 mg/g^2 for magnesite and 10 and 18 mg/g^2, respectively. Earlier studies presented by Ivanova et

al. (2001), and Sastry and Hoffmann (2004) showed that hydrophobic part of CTAB monomers at concentration below cmc adsorb at PPO segments making it more hydrophilic because of the hydrophilic part of surfactants molecules exposed to solution. A greater adsorption of PE 10500 than PE 6800 at magnesite and dolomite surface can result from longer hydrophobic domain in molecule of PE 10500. The longer this domain was in molecules, the greater adsorption of CTAB at this segment occurred and the better affinity of copolymer-cationic surfactant mixture was observed.
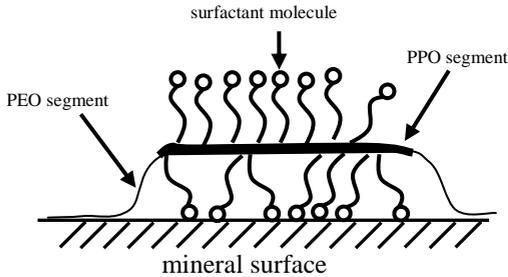
Fig. 5. Schematic diagram of Pluronic-surfactant system onto hydrophilic surface

The effect of Pluronics addition on anionic surfactant adsorption from the polymer-surfactant mixture is shown in Fig. 8 and 9. In this case, the similar behaviour was observed as for cationic surfactant. However, the plateau value of surfactant was lower in comparison to cationic one due to the mechanism of SDS adsorption onto carbonates minerals, described by Celik et al. (1998).

Figures 10 and 11 present the adsorption isotherms of Pluronics onto carbonates minerals in the presence of anionic surfactant. The obtained amounts of adsorbed PE 6800 and PE 10500 molecules were much greater in the presence of SDS for both investigated minerals. These results were similar to data obtained in the system containing CTAB, described above.
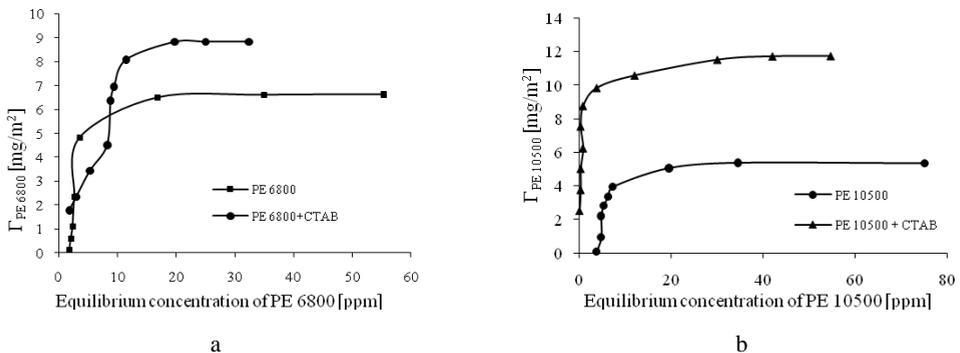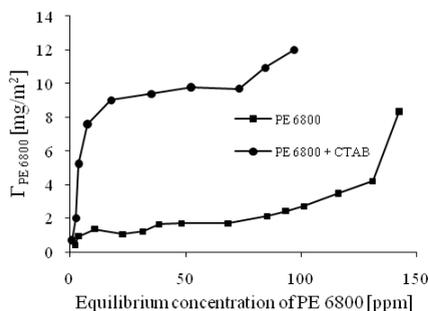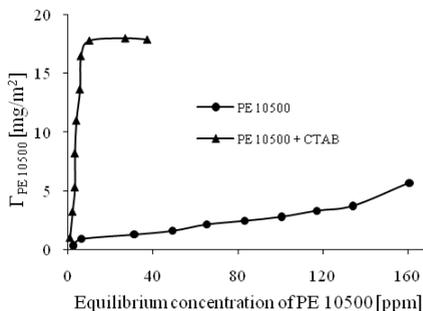

a   b

Fig. 6. Adsorption isotherms of Pluronic PE 6800 (a) and PE 10500 (b) on magnesite from mixed solution (CTAB concentration - 120 ppm, $C_{NaCl}=1\cdot10^{-4}$M, pH 8.5)

a   b

Fig. 7. Adsorption isotherms of Pluronic PE 6800 (a) and PE 10500 (b) on dolomite from mixed solution
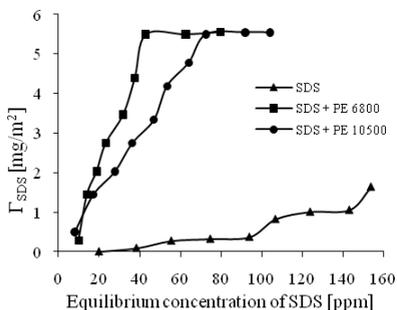(CTAB concentration - 120 ppm, $C_{NaCl}=1\cdot10^{-4}$M, pH 10.4)

Fig. 8. Anionic surfactant adsorption isotherms
onto magnesite from mixed solution from
Pluronic-SDS solutions (Pluronic concentration -
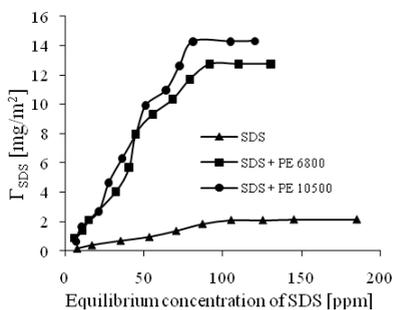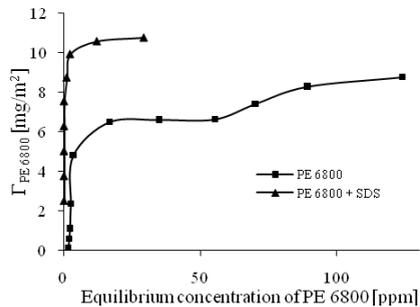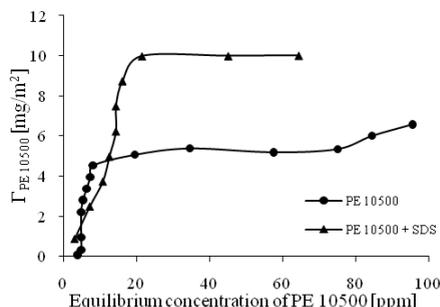120ppm, $C_{NaCl}=1\cdot10^{-4}$M, pH 8.5)

Fig. 9. Anionic surfactant adsorption isotherms onto
dolomite from mixed solution from Pluronic-SDS
solutions (Pluronic concentration - 120ppm,
$C_{NaCl}=1\cdot10^{-4}$M, pH 10.4)

a   b

Fig. 10. Adsorption isotherms of Pluronic PE 6800 (a) and PE 10500 (b) on magnesite from the mixed
solution (SDS concentration - 120 ppm, $C_{NaCl}=1\cdot10^{-4}$M, pH 8.5)

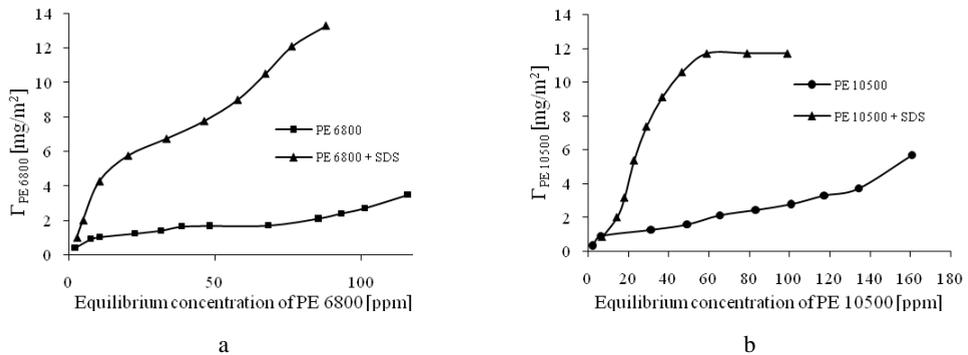Fig. 11. Adsorption isotherms of Pluronic PE 6800 (a) and PE 10500 (b) on dolomite from the mixed solution (SDS concentration - 120 ppm, $C_{NaCl}=1\cdot10^{-4}M$, pH 10.4)

3.2. Influence of the presence of copolymer, surfactant and the complex of copolymer-surfactant on the zeta potential of carbonate minerals

Natural magnesite particles had a negative zeta potential at natural pH of suspension which was 8.5, whereas the natural pH of dolomite suspension was equal 10.4. The isoelectric point of dolomite was in the vicinity of this pH.
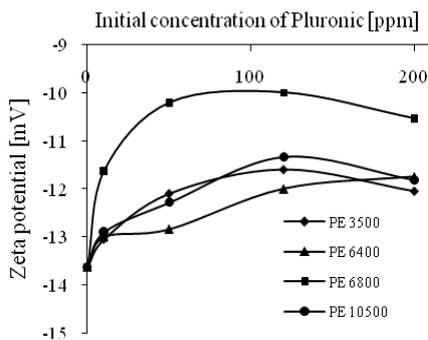

Fig. 12. Zeta potential of magnesite in the presence of Pluronics as a function of copolymer concentration ($C_{NaCl}= 1\cdot10^{-4}$ M, pH 8.5)
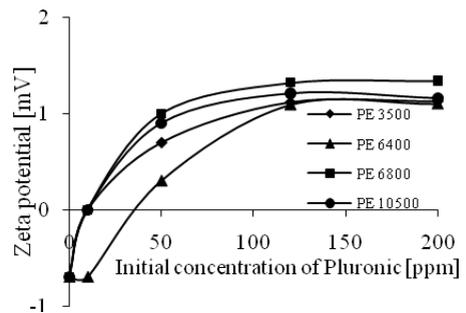
Fig. 13. Zeta potential of dolomite in the presence of Pluronics as a function of copolymer concentration ($C_{NaCl}= 1\cdot10^{-4}$ M, pH 10.4)

Figures 12 and 13 show that the adsorption of nonionic copolymers (Pluronic) onto investigated minerals slightly changes the zeta potential value of carbonate mineral particles due to a shift in the place of slipping plane (Vincent, 1974; M'Pandou and Stiffert, 1987). Experimental data revealed (Fig. 14 and Fig. 15) that the zeta potential value of these particles in the presence of cationic surfactant (CTAB) and Pluronic-CTAB mixture was more positive. It may be explained by the structure of complex

Pluronic-CTAB formed in such solution, which is presented in Fig. 5. The cationic surfactant can be adsorbed at hydrophobic part of expanded Pluronic molecules, shifting the zeta potential value to more positive. However, an attendant copolymer causes a decrease of zeta potential due to the deformation of an electrical double layer, comparing the presence of an individual cationic surfactant. It may be attributed to the screening effect of Pluronic molecules (Liu and Xiao, 2008). In the presence of anionic surfactant the value of zeta potential of investigated minerals was more negative due to the presence of negatively charged surfactant molecules (Fig. 16 and Fig. 17). On the other hand, the co-adsorption of anionic surfactant and copolymer caused a decrease in the negative value of the zeta potential due to increased SDS adsorption. A special configuration of surfactant molecules in Pluronic-surfactant complex (Fig. 5) leads to higher negative zeta potential.
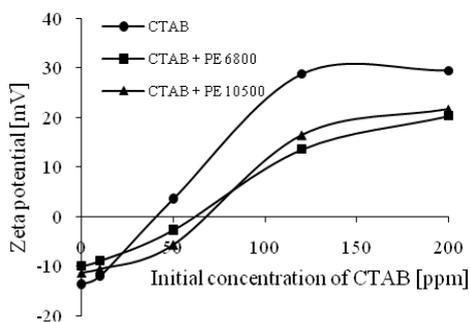

Fig. 14. Zeta potential of magnesite in Pluronic-CTAB mixed solution as a function of cationic surfactant concentration (Pluronic concentration – 120 ppm, $C_{NaCl}= 1·10^{-4}$ M, pH 8.5)
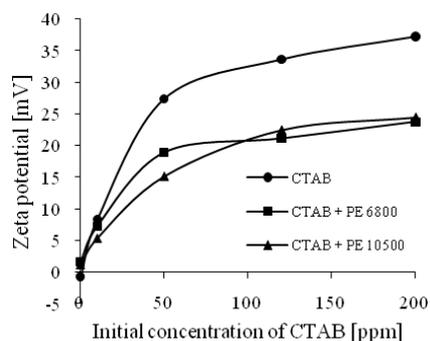

Fig. 15. Zeta potential of dolomite in Pluronic-CTAB mixed solution as a function of cationic surfactant concentration (Pluronic concentration – 120 ppm, $C_{NaCl}= 1·10^{-4}$ M, pH 10.4)

Fig. 16. Zeta potential of magnesite in Pluronic-SDS mixed solution as a function of anionic surfactant concentration (Pluronic concentration – 120 ppm, $C_{NaCl}= 1·10^{-4}$ M, pH 8.5)

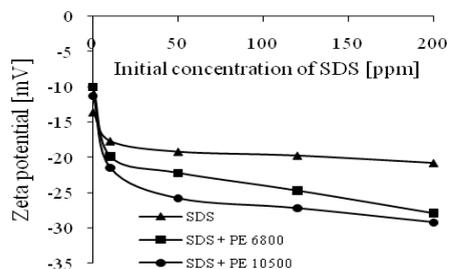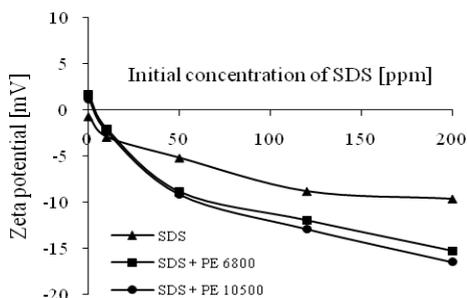

Fig. 17. Zeta potential of dolomite in Pluronic-SDS mixed solution as a function of anionic surfactant concentration (Pluronic concentration – 120 ppm, $C_{NaCl}= 1·10^{-4}$ M, pH 10.4)

3.3. The thickness of adsorbed layer of copolymer and copolymer-surfactant complex onto carbonate minerals

The zeta potential values for dolomite particles without reagents were within the range of -1.0 to +1.5 mV. Mineral suspensions with such a low zeta potential tend to coagulate. For this reason, the viscosity measurements were performed only for the magnesite suspensions, which was stable at the natural pH (pH=8.5).

The adsorbed layer thickness can be calculated from an elastic module data (Greenwood-Ward et al., 1995; Postmus et al., 2007). The adsorbed layer is correlated with the effective volume fraction (φ_{eff}). This relation can be described by following equation:

$$\Phi_{\mathrm{eff}} = \varphi(1+\delta/a)^3$$

where: δ is the thickness of adsorbed layer and a is the particle radius.

The adsorbed layer thickness was calculated using this equation. The results are shown in Table 2. These results were obtained for magnesite suspension in the presence of single Pluronic and Pluronic-surfactant mixture.

Table 2. Thickness of Pluronic and Pluronic–surfactant layers on the magnesite surface obtained from viscosity measurements

Layer	δ (nm)
Pluronic 6800	2.0
Pluronic 10500	2.3
Pluronic 6800-CTAB	3.7
Pluronic 10500-CTAB	3.9
Pluronic 6800-SDS	3.4
Pluronic15000-SDS	3.7

The thickness of copolymer layer was about 2.0 and 2.3 nm for PE 6800 and PE 10500, respectively. It is due to longer hydrophobic loops of PE 10500 expanded from the mineral surface comparing PE 6800. As can be seen from these data, the adsorption of Pluronic-ionic surfactant complex caused an increase in the adsorbed layer thickness. Attendant ionic surfactant molecules at the copolymer chain may impose loose conformation of the chain due to electrostatic repulsion between surfactants heads. Slightly thicker layers formed in the presence of CTAB may be explained by greater hydrophilic moiety of the cationic surfactant.

4. Conclusions

Amount of Pluronic adsorbed on the dolomite and magnesite surfaces depends on the PEO/PPO ratio. When adsorption occurred in mixed system, an increase of Pluronic and surfactant adsorbed amounts was observed. It suggests the existence of a synergistic effect between Pluronic and surfactant adsorbed on minerals surfaces. Adsorption of Pluronic-anionic surfactant complex onto the mineral surface causes an

increase in negative values of zeta potential in comparison with adsorption of the single surfactant. The observed change in zeta potential of both magnesite and dolomite particles as a result of adsorption of the nonionic polymer (Pluronic) and cationic surfactant can be explained by the Pluronic molecules screening effect. Under natural pH condition the dolomite suspensions were strongly coagulated (pH=10.4) and the thickness of adsorbed layers has not been analyzed for this mineral. From viscosity measurement results for the magnesite suspensions, the conclusion can be drawn that the adsorbed copolymer layer thickness increases in the presence of ionic surfactant.

Acknowledgments

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