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Research on adsorptive and electrokinetic properties of SiO_2 in the presence of polyethylene oxide of different purities

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Abstract. The influence of impurities present in polymer solutions on adsorptive and electrokinetic properties of PEO 100 000 with commercial silica was analysed. Adsorption was measured with a spectrophotometric method and zeta potential with a zetasizer. A XRF method was used to estimate the quality and quantity of impurities in polyethylene oxide solutions. Impurities left after the polymerisation process, present in polymer solutions can adsorb competitively with macromolecules of the polymer. As a result of that, they block active centres on the surface of the adsorbent thus leaving less surface available for polymer molecules. Purification process is conducted in order to improve the quality of analysed polymer material. Polyethylene oxides used in the presented research were purified by filtration process and fractionation on chromatographic column. Overall, three different samples of PEO were used: commercial of high quality, filtrated and fractionated. Results show that adsorption of polyethylene oxide of high purity is independent on pH of the solution. Adsorption isotherms of fractionated and analytical-grade polymer are sharp, which indicates their low polydispersity ratio. An adsorption amount of analysed polymers is dependent only on the amount of impurities present in polymer material. Zeta potential measurements show, that polyethylene oxide always increases zeta potential of silica.

keywords: polyethylene oxide, polymer adsorption, silica, zeta potential

1. Introduction

Adsorption of macromolecules onto oxides is a very complicated process and it varies significantly from the adsorption of small molecules and ions (i.e. inorganic ions). There are many applications for adsorption of macromolecules including food, cosmetic, dyer industries and many technological processes used in environmental protection (Fleer et al., 1993; Fleer et al., 1993; Markovic,1996; Zhonghua et al. 2001). One very important field at which adsorption of polymers is of great value is mineral processing. An addition of high-molecular weight substances may change a stability of mineral suspensions. This is very often used in separation of various minerals or ores of metals in process of flocculation (Ansari et al., 2007a, b; Xiaodong et al., 2007).

Studies on adsorption of polymers are very important from both scientific and practical point of view (Wind, 1998). Results of such data show relationship between changing factors (pH, molecular weight of polymer, ionic strength, purity of used materials, type of surface used and many more) and results of adsorption experiments. These can be next used for practical applications as ones mentioned above. One of the ways to study an adsorption process is to measure adsorption amount and zeta potential of the system. Both of these parameters give a good approximation what processes are really occurring on the surface, while a polymer is being adsorbed.

Commercial polymers, available to purchase, have a fairly high degree of polydispersity as well a content of inorganic impurities, which are left after the polymerisation process. Those substances cannot be used for a model research on polymer's adsorption onto metal oxides with application of various adsorption theories (e.g. Scheutjens's – Fleer theory). In order to improve their quality a filtration process (purification and initial fractionation) as well as fractionation on chromatographic column can be used.

$$-\!\left[\mathrm{O{-}CH_2{-}CH_2}\right]\!-$$

Fig. 1. Example of PEO monomer

Polyethylene oxide was used as a polymer in the presented research. It is a non-ionic, hydrophilic polymer with a very simple structure (Fig. 1). It has many interesting applications including paper industry (sheet formation aid, paper and paper board filler retention aid), glass fibre sizing, construction industry (slurry transport, board extrusion, polymer cement, painting), binder for ceramics, pickup and ending adhesive for paper rolls, mining industry (removal of silica clays, flocculation of phosphatic slimes), suspension polymerization, cosmetics industry (hair care products, skin care products, toothpaste), electronics industry (binder for battery, fluorescent lamp), pharmaceutical industry (controlled-release preparations) (www.sumitomoseika. co.jp/peo/).

The aim of the presented research was to determine the amount of adsorption of polyethylene oxide on silica, define the influence of impurities present in polymer material on the process of adsorption on silica, obtain the zeta potential of polyethylene oxide on silica, and define the influence of impurities present in polymer material on the zeta potential on silica. The presented research is a second part of extensive measurements on influence of PEO of various degrees of purity on stability of silica (Chibowski et al., 2007).

2. Experimental

SiO_2, used as an adsorbent was obtained from Aldrich. Silica was washed with doubly distilled water until conductivity of supernatant decreased down to 2 μS/cm.

Specific surface of SiO_2 measured by a BET method was 261.7 m^2/g. Average size of silica molecules was 157 nm with polydispersity ratio 0.252, which was estimated using Zetasizer 3000 by Malvern Instruments. Similar results for the radius of silica particles were obtained using electron microscopy.

Applied commercial polymers PEO 100 000 and PEO 108 000 were produced by Aldrich and Fluka respectively. Commercial as well as filtrated and fractionated polymers were used. The aim of a filtration process was to remove both inorganic impurities and macromolecules which molecular weights were much lower than those of the examined polymers. The process was carried out in an ultrafiltrating cell TCF-10 by Amicon. A XM-30 membrane (blocking macromolecules of molecular weight greater than 30 000) was applied for a PEO 100 000. Apart from purification an initial fractionation was also a result of this process because of separation of macromolecules of masses lower than 30 000 from the final solution. A fractionation of the polymers was carried out on a chromatographic column filled with Sephacryl S-300 HR gel by Amersham Biosciences.

A background electrolyte 10^{-2} $mol \cdot dm^{-3}$ NaCl was used. Absorbance was measured with a Specord M42 by Carl Zeiss using a wavelength of 500 nm. pH of the measured samples was 3, 6 or 9 and the amount of an added oxide equalled a surface of 10.5 m^2. All measurements were carried out in a constant temperature of 25°C.

2.1. Measurements of adsorption of PEO onto SiO_2

In order to measure adsorption amount of polyethylene oxide, 15 portions of commercial SiO_2 of 0.04 g each, was carefully measured. The amounts of SiO_2 were chosen, taking into account a surface area of the adsorbent. Next, they were placed in 15 Erlenmeyer flasks of 25ml volume, containing 2.5ml of 10^{-1}M NaCl each. PEO was added to Erlenmeyer flasks in sufficient amounts, so that final concentrations were as follows: 10, 50, 100, 150, 200 (ppm). Adsorption process was carried out in pH 3, 6, and 9, set by addition of small amounts of HCl and NaOH. The value of pH was set initially and controlled throughout the entire adsorption process. Flasks were shaken for 24 hours on mechanical shaker in temperature 25°C. After that time, solutions were centrifuged and 2 ml of supernatant was taken from each sample and transferred to 15 test-tubes. Next 8 ml of tannic acid was added to each test tube and left for 60 minutes in dark place. After that time an absorbance measurement was conducted on a UV-VIS spectrophotometer.

With a help of a calibration curve, values of unknown concentration of PEO were obtained from measured absorbance values. By simple subtracting of equilibrium from initial concentration of PEO, it was possible to calculate a concentration of adsorbed PEO. From this value, an amount of adsorbed PEO was calculated.

2.2. Zeta potential measurements

A 500 cm^3 sample of 10^{-2}M NaCl along with a polymer of a certain concentration (10, 50, 100 ppm) was transferred to a beaker. 0.05g of SiO_2 was added to prepared solution. A resulting suspension was ultrasonificated for 3 minutes. Such a solution was introduced into five 100ml Erlenmeyer flasks, where a constant value of pH was set (3, 5, 7, 9, 11). Prior to the measurement, a measuring system was flushed with measured solution. Next, 10 ml of a solution was introduced into zetasizer to measure zeta potential. Measurements were taken in 25°C. From obtained data a dependence of ζ=f(pH) was created.

3. Results and discussion

3.1. Adsorption measurements

Figures 2, 3 and 4 present adsorption isotherms of filtrated, fractionated PEO of molecular weight 100 000 and high-analytical grade (Fluka) PEO of molecular weight 108 000 onto SiO_2, with background electrolyte NaCl 10^{-2}M, respectively. Presented experimental data indicate, that pH of the solution does not influence the adsorption amount of PEO onto SiO_2. The cause for such a behaviour is a character of adsorbing polymer. PEO, by nature, is a non-ionic polymer, which does not possess functional groups in its chain that are dissociable. Thus, their character does not change upon changes of pH and its properties are not pH-dependent. In such a way, the only possible explanation of adsorption of PEO onto SiO_2 is a hydrogen bonding between hydrogen atom in –OH groups in silica and highly electronegative oxygen atom in PEO chain (Bjelopavlic et al. 2000).

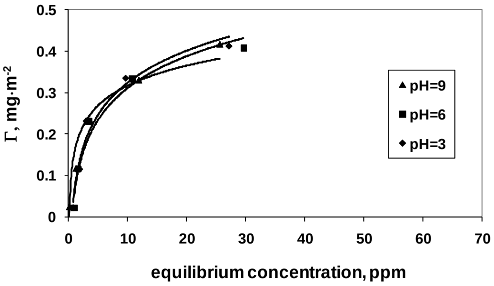

Fig. 2. Adsorption isotherms of filtrated PEO 100 000 onto SiO_2

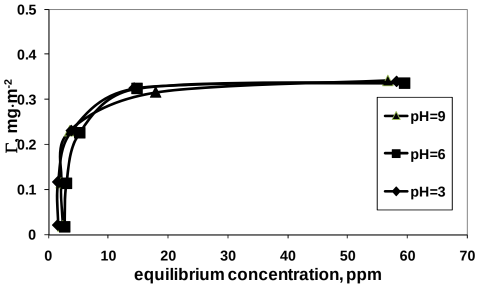

Fig. 3. Adsorption isotherms of fractionated PEO 100 000 onto SiO_2

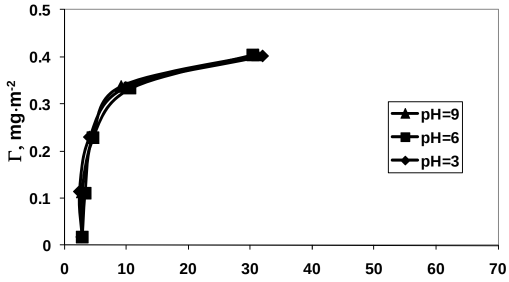

Fig. 4. Adsorption isotherms of analytical-grade PEO 108 000 onto SiO_2

Comparison of experimental data brings the result that adsorption amount for fractionated PEO is the lowest compared to the other two. Maximum surface coverage in this case is 0.33 mg·m^{-2}, while for filtrated polymer is gives a value of 0.4 mg·m^{-2} and analytical grade PEO 0.41 mg·m^{-2}. Such a result can be easily explained by presence of impurities in analysed samples (Table 1 and Table 2).

Table 1. Measured conductivities (μS·cm^{-1}) of water solutions of PEO 100 000, concentration of polymer 100 ppm

degree of purification	conductivity (μS·cm^{-1})
filtrated	1.45
fractionated	2.09
analytical-grade	1.53

Table 2. Amount of impurities (wt percentage) in analysed samples

degree of purification	amount of impurities (wt %) in PEO 100 000
commercial (non-purified)	Si 0.9, Ca 0.3, Cu, Zn on ppm level
filtrated	Si 0.2, Cu, Zn on ppm level
fractionated	Cl, K, Cr, Fe, Zn on ppm level

The diversity and type of ions being impurities in fractionated sample is higher compared to the commercial non-purified one. This is probably a result of elution of inorganic ions from the material of chromatographic column, that the process of fractionation was carried out on. Presence of inorganic ions in solutions of polyelectrolytes can cause distinct changes in adsorption amount of a polymer on the surface of a solid. These additional ions can cause either an increase or a decrease of adsorption amount. This is dependent on type of inorganic ions, nature of polymer and a type of surface groups. For instance, when an inorganic ion is bonded more strongly to the surface than a polymer segment, a competitive adsorption between the two will result in greater adsorption of an inorganic ion. Thus it will decrease an adsorption of the polymer. On the other hand, when an ion is less strongly adsorbed to the surface of the solid than a polymer, it will not significantly influence the adsorption amount of the polymer. It might, though, influence a time required to reach equilibrium between polymer in the solution and polymer adsorbed on the surface, due to interference between inorganic ions and polymer segments.

In the analysed case specifically adsorbed inorganic ions cause a blockage of active sites on the surface of an oxide. While a competitive adsorption between polymer segments and inorganic ions take place, this limits a number of active sites available to polymer molecules which results in a decrease of adsorption amount.

An analysis of a shape of adsorption isotherm can help to estimate the degree of polydispersity of adsorbed polymer. More rounded isotherms are a result of an adsorption of a more polydisperse macromolecular substance. So, the system where adsorption of filtrated polymer is analysed (Fig. 2) is characterized with a significant rounding of adsorption isotherm and a lack of *plateau*. Rounding of an isotherm is caused by a gradual increase of the amount of adsorbed polymer with its increasing concentration. It is caused by a fact that smaller molecules are adsorbed in the first place (because of their faster movements). After that they are being gradually desorbed from the surface by high-molecular weight molecules, which are adsorbed more strongly by a surface (but move slower due to their size). The amount of molecules of high molecular weight increases with increasing concentration of a solution. Therefore, the greater a polydispersity of a polymer, the greater a rounding of an isotherm is.

So-called ‘sharp’ isotherms with a distinct *plateau*, are a result of an adsorption process of low polydispersed polymers. In such a case, a surface of oxide is very quickly coated with molecules of similar of even identical molecular weight. A desorption process does not take place or its significance is negligible. Such a shape is observed for fractionated PEO (Fig. 3) and analytical-grade PEO (Fig. 4). From these data comes a conclusion that a fractionation process helps to gain substances with a very low polydispersity, or low spread of molecular weights.

Results obtained with fractionated polymer can be used for a quantitative research on the process of adsorption and can be compared with theoretical results, that comply with present theories which concern adsorption in polymer systems.

3.2. Zeta potential measurements

Figures 5, 6 and 7 present a dependence of zeta potential on pH for filtrated, fractionated PEO 100 000 and analytical-grade PEO 108 000, concentrations 10, 50 and 100ppm onto SiO_2, background electrolyte $NaCl\cdot10^{-2}M$, respectively. It can be stated that for all presented systems, zeta potential does not change for pure silica and silica with polymer in pH range from 3 to 5. One can also state, that above pH 5 an addition of polymer always causes an increase of zeta potential of silica in all presented systems compared to silica without a polymer. A value of zeta potential is always negative and because of that fact, the pH_{IEP} is never observed in analysed pH range. When individual systems are more closely analysed, some differences start to appear though.

In a case of filtered PEO (Fig. 5) an increasing concentration of polymer increases a zeta potential of a system. The greater the concentration of PEO, the less negative the value of zeta potential is. A change of zeta potential by adsorbing polymer can be explained with three phenomena: 1) an introduction of ionised functional groups into electrical double layer, 2) a desorption of counterions from compact layer of electrical double layer by adsorbing polymer chains, 3) a shift of slipping plane of electrical double layer. In presented systems, the first phenomenon cannot take place, due to a lack of functional groups in polymer chain that are capable of dissociation. As the shift of slipping plane moves it away from the surface of a solid, therefore always decreases an absolute value of a zeta potential of a system. In presented results an addition of polymer always increases zeta potential, but since all values are negative, this means an decrease of an absolute value of a zeta potential. Therefore, desorption of counterions and a shift of slipping plane are two phenomena responsible for observed changes.

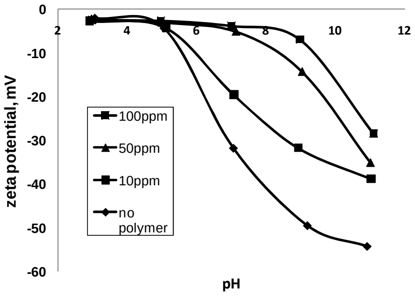

Fig. 5. Zeta potential of PEO 100 000 filtrated onto SiO_2

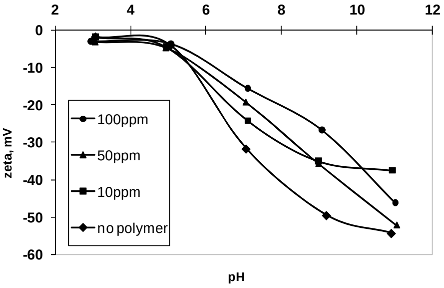

Fig. 6. Zeta potential of PEO 100 000 fractionated onto SiO_2

In a presented system, negatively charged surface of silica, attracts positively charged cations form a solution. In this specific case, cations being $Na^+_{(aq)}$ ions, which come from dissociation of a background electrolyte – NaCl and $Cu^{2+}_{(aq)}$, $Zn^{2+}_{(aq)}$ present as impurities. Competitive adsorption between previously mentioned cations and polymer molecules of the smallest concentration (10 ppm) results in desorption of cations by the latter. It seems that a hydrogen bond interaction between a surface groups and functional groups of PEO are stronger that electrostatic attraction between negatively charged silica and positively charged sodium ions. In such a case positively charged counterions move outward the surface into a solution and are placed near a slipping plane of electrical double layer. This is observed as an increase of a zeta potential of analysed system. Now, with increasing concentration of polyethylene oxide (50 and 100 ppm), more polymer molecules are adsorbed on a surface of silica. This only approves a proposed mechanism of changes, since increasing number of polymer segments account for greater overall strength of hydrogen bond compared to electrostatic attraction between surface and counterions. As a result of that, more counterions are desorbed from the surface. The zeta potential therefore, increases gradually with increasing concentration of polymer, what can be clearly observed in Fig. 5.

Additionally, adsorbing polymer shifts a slipping plane away from the surface, thus it decreases an absolute value of a zeta potential. For low concentrations of a polymer conformations that lie flat on the surface are preferred (e.g trains). This does not shift a slipping plane significantly, and does not influence a zeta potential. With increasing concentration of a polymer, more spatial conformations are preferred (e.g loops and tails). Those type of conformations affect a shift of slipping plane in greater degree. This is observed for polymer concentrations of 50 and 100ppm. The greatest differences can be seen at pH=9. If conformations are more spatial, it means that slipping plane will be further shifted. This of course accounts for the greatest decrease in the absolute value of zeta potential.

To sum up, both phenomena affect a change of zeta potential. But for small polymer concentrations (10 ppm) a change of position of counterions is the most significant and for higher concentrations of polymer (50 and 100 ppm) both a change of position of counterions and a shift of slipping plane affect observed changes.

A system with fractionated PEO 100 000 adsorbing on silica is presented in Fig. 6. For pH range 3-5, the changes in zeta potential are negligible, so it can be clearly stated that in this pH range, a polymer does not influence zeta potential of this system. For pH range 5-11, for all used concentrations, an increase of value of zeta potential is observed. Once again, similarly to a system presented on Fig. 5, the two mechanisms responsible for observed changes are a change of position of positively charged counterions in electrical double layer and a shift of slipping plane away from the surface. Adsorbing polymer molecules desorb previously adsorbed positive cations from the surface, which are then shifted to diffuse part of edl. Those adsorbing polymer molecules also slightly shift a slipping plane towards bulk solution. These two facts add together and are observed as an increase of a zeta potential of a system.

What is interesting though, is a comparison of plots in Figs 5 and 6. For a system with filtrated PEO (Fig. 5), changes of zeta potential with increasing concentration of polymer are much greater, compared to a system with a fractionated polymer (Fig. 6). This might indicate that a fractionated polymer is being adsorbed with much flatter conformation (mostly conformations where polymer segments are directly bonded to the surface). Such a conformation does not provide an additional factor that shifts a slipping plane away from the surface of silica and does not decrease an absolute value of a zeta potential. In spite of data from purification of presented polymers (Table 1, Table 2), where there are more impurities present in fractionated polymer compared to filtrated, those additional impurities does not seem to interfere with adsorbing polymer molecules. PEO segments have a greater tendency for adsorption to the surface than those inorganic ions and thus create a more flat conformation on the surface of silica. This accounts for smaller increase of zeta potential for a fractionated polymer compared with filtrated.

The last of the analysed systems – PEO 108 000 (analytical grade) on silica is presented in Fig. 7. Once again, for all measured concentrations, zeta potential is almost the same for pH range 3-5, so it can be stated that a polymer does not influence zeta potential for this specific pH range. For pH range 5-11, it is always increased by adsorbing polymer compared to pure silica, no matter which concentration was used. As in previous cases, the reason for such behaviour is a change of position of counterions in compact part of electrical double layer and a shift of slipping plane. Polymer molecules are more preferentially adsorbed by the surface that cations, therefore the latter is desorbed from the surface. This results in increase of zeta potential of the analysed system.

The difference compared to filtrated PEO (Fig. 5) and fractionated PEO (Fig. 6) is that observed increase is almost independent of concentration of polymer used. This might suggest that it does not matter which concentration of the polymer is used (10, 50 or 100ppm) – the amount of counterions that is removed from the compact layer of edl is almost the same. Indeed this is no surprise for an adsorption of polymer of such a high quality like analytical grade PEO. Used polymer sample has a very low polydispersity ratio, which means that this sample contains mostly molecules of almost the same mass. As a result of that, those molecules immediately adsorb on the surface with maximum possible amount, even when relatively small concentration of polymer is used (Fig. 4). Surface of the solid becomes saturated with polymer segments and increasing concentration does not significantly change the amount of segments directly bonded to the surface of silica. As a result of that number of counterions that are removed almost does not change and minute changes of zeta potential are observed.

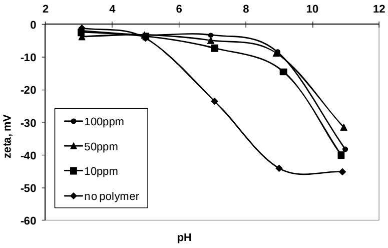

Fig. 7. Zeta potential of PEO 108 000 onto SiO_2

What is more, conformations created by PEO in all used concentrations are very similar. Analysed sample of PEO, having mostly molecules of the same molecular weight, create similar conformations, regardless of concentration. This shifts a slipping plane in every analysed concentration almost the same and that is why no significant differences between zeta potential of polymer with various concentrations are observed.

Thus, one can safely state that zeta potential in presented system almost does not change with changing concentration of polyethylene oxide.

4. Conclusions

1. Adsorption of polyethylene oxide of high purity (PEO 100 000 filtrated and fractionated as well as analytical-grade PEO 108 000) is independent on pH of the solution. It is a result of a lack of dissociable groups in its chain.
2. Adsorption isotherms of fractionated and analytical-grade polymer are sharp, which indicates their low polydispersity ratio.
3. Adsorption amount is dependent on the amount of impurities present in polymer material. The lower the amount of impurities, the higher the

adsorption is (greater number of accessible active sites for polymer molecules on surface of an oxide).

4. Polyethylene oxide always increases zeta potential of silica. For analytical-grade polymers this increase is independent on the concentration of the polymer used. For polymers, where some amount of impurities is present, the increase depends on the concentration of the polymer.

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Zbadano wpływ zanieczyszczeń obecnych w materiale polimeru na adsorpcyjne i elektrokinetyczne właściwości PEO 100 000 na komercyjnej krzemionce. Adsorpcję badano przy pomocy metody spektrofotometrycznej, potencjał zeta przy pomocy zetasizera. Metodą XRF ustalono stężenie oraz jakość zanieczyszczeń w badanych roztworach polimerów.Przeprowadzone badania wskazują, że adsorpcja tlenku polietylenu o wysokiej czystości jest niezależna od pH roztworu. Izotermy adsorpcji PEO frakcjonowanego oraz o wysokiej czystości są ostre, co wskazuje na ich niski stopień polidyspersyjności. Ilość zaadsorbowanego polimeru jest zależna tylko od ilości zanieczyszczeń obecnych w materiale polimeru. Pomiary potencjału zeta wskazują, że obecność tlenku polietylenu zawsze zwiększa potencjał zeta krzemionki.

słowa kluczowe: tlenek polietylenu, adsorpcja polimerów, krzemionka, potencjał dzeta