Physicochemical Problems of Mineral Processing, 41 (2007), 177-184
Fizykochemiczne Problemy Mineralurgii, 41 (2007), 177-184

Stanisław CHIBOWSKI*, Jan PATKOWSKI*

A RESEARCH ON STABILITY OF SiO_2 IN THE PRESENCE OF POLYETHYLENE OXIDE OF DIFFERENT PURITIES

Received May 10, 2007; reviewed; accepted June 28, 2007

The influence of impurities present in polymer solutions on stability of the suspension of PEO 100 000 with commercial silica was analysed. Stability was measured indirectly, with absorbance measurements of silica and polyethylene oxide suspensions. 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, four different samples of PEO were used: commercial of low quality, commercial of high quality, filtrated and fractionated.

The stability of silica is greatly influenced by the presence of polymer of different purities. Silica without adsorbed polymer is stable in the whole period of analysis. An addition of polymer firstly stabilises the suspension but after some time the suspension is suddenly destabilised. The times of stabilisation and destabilisation of the suspensions are different for polymer samples of different purities. It is greatly dependent on the content of impurities and polydispersity index of a polymer.

Key words: polymers, polyethylene oxide, silica, stability, polydispersity index

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 macromolecules adsorption including food, cosmetic, dyer industries and many technological processes used in environment

---

* Department of Radiochemistry and Chemistry of Colloids, Faculty of Chemistry, UMCS,
pl. Marii Curie-Skłodowskiej 3, 20-031 Lublin, Polska, jpatkows@hermes.umcs.lublin.pl

protection (Fleer et al., 1993; Fleer and Scheutjens, 1993; Markovic, 1996; Pan et al., 2001).

Polymer adsorption also influences the stability of dispersed systems. Low-molecular mass polymers adsorbed onto oxide surface mostly cause strong steric repulsion, i.e. steric stabilisation. This phenomenon is used when stable emulsions and suspensions are required. High-molecular mass polymers cause colloidal systems to flocculate, which is mostly used for utilization of industrial slurries and many other applications. The aspect of stability is the case to study in the presented research.

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 Scheutjen's – Fleer theory application. In order to improve their quality, a filtration process (purification and initial fractionation) as well as fractionation on chromatographic column can be used.

$$-\!\!\left[O - CH_2 - CH_2 \right]\!\!-$$

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 for 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).

The aim of the presented research was to:

- define the influence of polyethylene oxide on stability of silica;
- define the influence of impurities present in polymer material on the process of stabilisation/destabilisation of silica;
- define the influence of concentration of polymer on stability of silica.

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} mole·dm^{-3} NaCl was used. Absorbance was measured with a Specord M42 by Carl Zeiss using a wavelength range from 220 to 400 nm. pH of the measured samples was 6 and the amount of an added oxide equalled a surface of 1.04 m^2. All measurements were carried out at a constant temperature of 25°C.

RESULTS AND DISCUSSION

Commercial polymers, available to purchase, should be of high purities, which is often not fulfilled. This problem can be solved by purification of the polymers on your own. That is why polymers used in the presented research were purified by filtration process or fractionation on chromatographic column.

Table 1. Conductivity of commercial, filtrated and fractionated PEO solutions [μS/cm]

PEO 100 000	Conductivity [μS/cm]
commercial	7.1
filtrated	1.45
fractionated	2.09

Conductivities of water solutions of PEO 100 000 of concentration of 100ppm (commercial, filtrated and fractionated respectively) are presented in Table 1. Presented data clearly show, that commercial polymer solutions are impure in the greatest degree. This fact emerges from not only the variety of ions present in the solution but also its high concentration.

A comparison between conductivities of filtrated and fractionated polymers surprisingly indicate, that solutions of fractionated polymers have higher conductivity compared to filtrated ones. The reason for this fact can be impurities present in chromatographic resins, which were eluted during fractionation process.

Table 2. XRF analysis of researched polymers, content of impurities

	PEO 100 000
commercial	Si 0.9% Ca 0.3% Cu, Zn
filtrate	Si 0.9% Ca 0.3% Cu, Zn
filtrated	Cu, Zn
fractionated	Si 0.2% Cl, K, Cr, Fe, Zn

A XRF analysis of a filtrate, commercial, filtrated and fractionated polymers were additionally conducted. These data, presented in Table 2, are compatible with conductivities of the same solutions (Table 1). According to the expectations, the biggest amount of inorganic impurities is present in commercial polymer solutions. Si content is about 1%, Ca about 0.3%, while Cu and Zn concentration is on the level of ppm, which is the limit of detection for XRF method and cannot be converted into quantity with acceptable accuracy

Both the quality and the quantity of impurities present in the filtrate are comparable with contents of impurities in commercial polymer. It can be concluded that most of inorganic impurities was removed form the solution in the filtration process. Cu and Zn atoms, present in vestigial quantities in filtrated polymer solutions, should not influence its adsorptive and electrokinetical properties.

Impurities content of a fractionated polymer, which was gained by processing a commercial one, is much lower than this observed for the latter. Si content after the fractionation process lowers approximately 4 times. However, other previously absent elements appear: Cl, K, Cr, Fe. The only possible reason for that is the fact of elution of above-mentioned atoms (probably bonded in chemical compounds) from the chromatographic column material. There is a certain probability that these impurities might have an effect on adsorption process and stability of the analysed suspension.

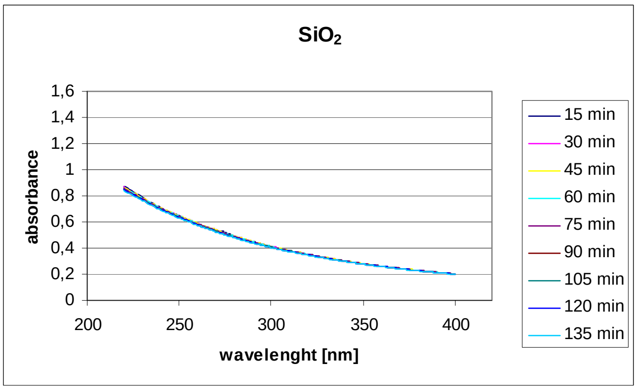

Fig. 2. Absorbance of silica suspension without polymer

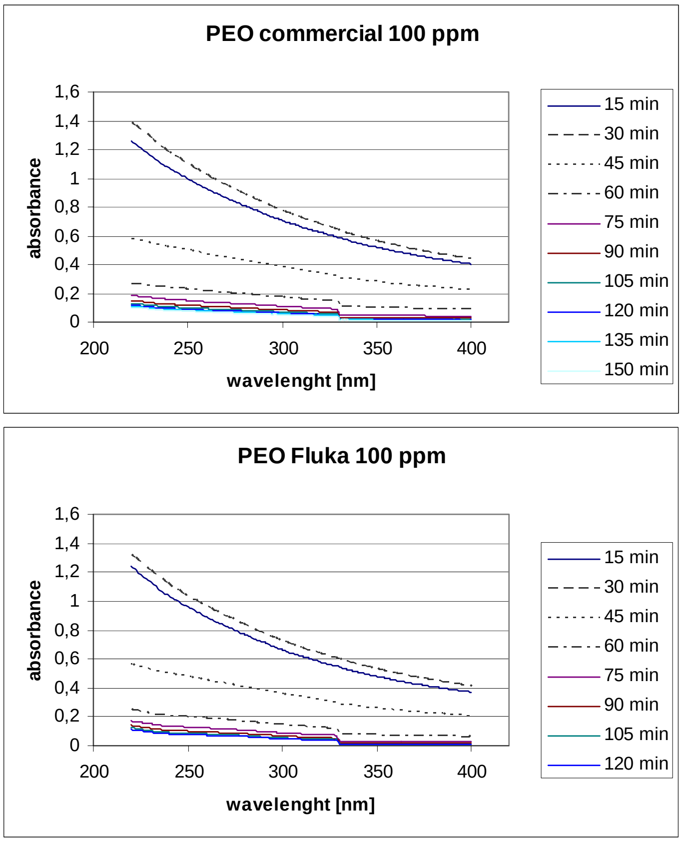

Fig. 3. Absorbance of silica suspension with 100ppm PEO (commercial of low and high quality)

In Figure 2 an absorbance of silica suspension without polymer is presented. The measured range of wavelength is 220-400nm. The change in absorbance of suspension is used as a measure of stability of this suspension. As it can be seen, the absorbance of silica suspension doesn’t change in measured period of time. It can be safely stated that over this period of time (over 2h) measured silica suspension is stable.

On the other hand, in Figures 3 and 4 the absorbance of the same silica suspension is presented but with the addition of polyethylene oxide of different purities. Commercial of low quality, commercial of high quality, fractionated and filtrated polymers are being presented respectively. The first thing that can be seen is a distinct change in absorbance of the suspension over measured time for all four polymers analysed. In all cases, the absorbance of the solution increases in the beginning and then decreases suddenly. The increase in absorbance (increase in stability) is caused by the kinetics of the adsorbing polymer. Concentration of the polymer in the solution decreases and concentration on the interface solution/silica increases until equilibrium is reached. This first stage may be considered as a stabilisation of the suspension with the adsorbing polymer. After the equilibrium is reached, polymer chains adsorbed on separate silica particles start to interact with each other. The result of that interaction is a creation of aggregates. The greater the number of those aggregates, the less stable the suspension is. This second process is seen on absorbance curves as a sudden decrease in absorbance of the analysed solutions.

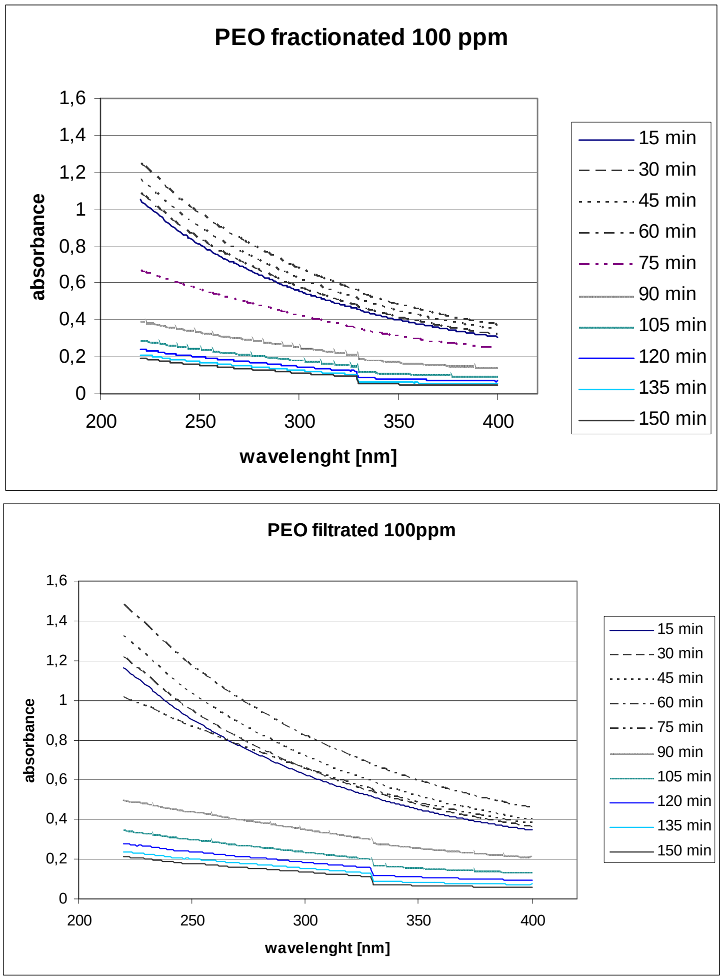

Fig. 4. Absorbance of silica suspension with 100ppm PEO (fractionated and filtrated)

If one compares the rate of establishing of equilibrium, for commercial polymers (both of low and high quality) absorbance increases after 15 and 30 minutes from the start, after that it starts to fall down. For purified polymers (both filtrated and fractionated) absorbance increases up for twice as long (to 60 minutes) and then starts to fall down. This difference in time the absorbance increases is the result of longer establishing of the adsorption equilibrium for purified PEO on SiO_2. As there are less impurities in purified polymers, the only molecules that try to adsorb on the surface are the macromolecules of the polymers. Those, being quite large and slow moving, compete together for adsorption sites on silica. The result of that is an increase in time needed to achieve an equilibrium between solution and interface. For commercial polymers the time is shorter, because there are some impurities left after the polymerisation process. Those impurities, being mostly inorganic, are quite fast-moving and adsorb quickly on the silica surface. The result of this is a faster achievement of equilibrium between solution and interface between polymer and impurities molecules.

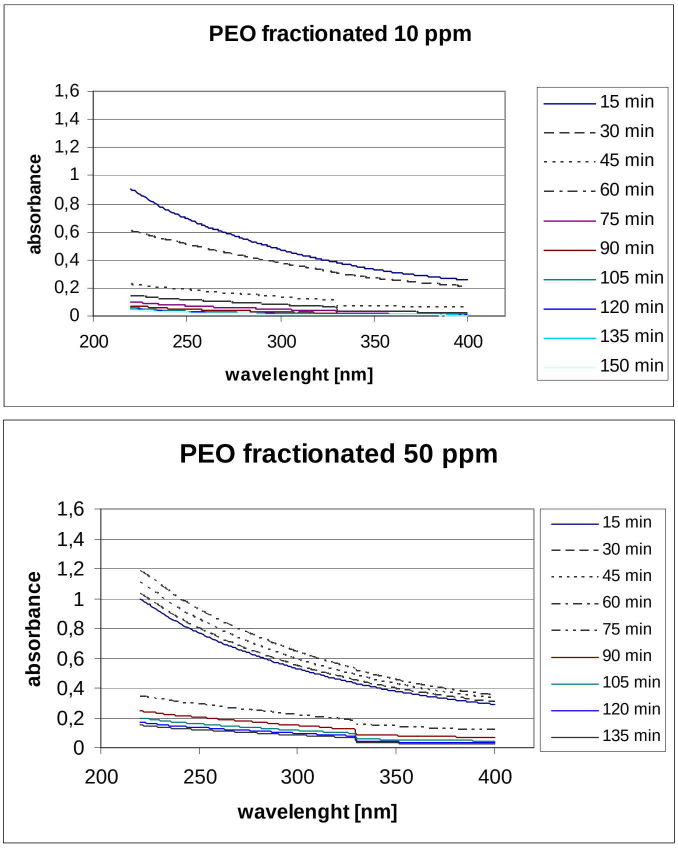

Fig. 5 Absorbance of silica suspension with fractionated PEO (10 and 50ppm)

In Figure 5, a comparison of absorbance of silica suspension with fractionated PEO of different concentrations (10 and 50ppm) is presented. For sample with lower concentration of the polymer an instant decrease in absorbance is observed. This is the result of a very rapid reaching of equilibrium for this system. If the concentration of a polymer is low, there are not so many molecules to adsorb and compete for adsorption sites so the result is almost immediate adsorption equilibrium. Just after that, a flocculation takes place and suspension starts to destabilise (absorption of the solution decreases).

CONCLUSIONS

1. The stability of silica is greatly influenced by the presence of polyethylene oxide.
2. Silica without adsorbed polymer is stable over the time of at least two hours.
3. An addition of polymer firstly stabilises the suspension but after some time the suspension is suddenly destabilised. The times of stabilisation and destabilisation of the suspensions are different for polymer samples of different purities. It is greatly dependent on the content of impurities and polydispersity index of a polymer.
4. Stability of silica is dependent on concentration of polyethylene oxide used. The greater the concentration of the polymer, the longer time is needed to establish adsorption equilibrium, so the more stable the suspension is.

REFERENCES

FLEER G.J., COHEN STUART M.A., SCHEUTJENS J.M.H.M., COSGROVE T., VINCENT B., 1993 *Polymers at Interfaces,* Chapman & Hall, London.

FLEER G.J., SCHEUTJENS J.M.H.M., in: B. Dobias (Ed.), 1993, *Coagulation and Flocculation; Theory and Applications,* Chapter 5, Marcel Dekker, New York.

MARKOVIC B., 1996, *Adsorption of Polyacrilic Acid on Alumina and Silicon Carbide*, Doctoral Thesis, University of Zagreb, Croatia.

PAN Z., CAMPELL A., SOMASUNDORAN P., 2001, Colloids and Surfaces, 191,(1) 71 – 78.

http://www.sumitomoseika.co.jp/peo/

Chibowski S., Patkowski J., *Badanie stabilności SiO_2 w obecności tlenku polietylenu o różnym stopniu czystości,* Physicochemical Problems of Mineral Processing, 41 (2007) 177-184 (w jęz. ang.).

Badano wpływ zanieczyszczeń występujących w roztworach polimerów na stabilność suspensji komercyjnej krzemionki w obecności PEO 100 000. Stabilność suspensji mierzono pośrednio, poprzez określanie wielkości absorbancji badanej suspensji krzemionki i tlenku polietylenu. Ilość oraz jakość zanieczyszczeń obecnych w roztworach polimerów określono przy pomocy badania metodą XRF. Zanieczyszczenia obecne w roztworach polimerów będące pozostałością po procesie polimeryzacji, mogą adsorbować się konkurencyjnie z makrocząsteczkami polimeru. W wyniku tego, blokują miejsca adsorpcyjne na powierzchni adsorbentu pozostawiając mniejszą ilość miejsca dostępnego dla makrocząsteczek polimeru. Proces oczyszczania polimeru został przeprowadzony w celu poprawy jakości analizowanego polimeru. Tlenek polietylenu użyty w przedstawianych badaniach został oczyszczony w procesie filtrowania na membranach oraz frakcjonowania na kolumnie chromatograficznej. Użyto czterech próbek polimeru o różnym stopniu czystości i polidyspersyjności: komercyjny o niskiej jakości, komercyjny o wysokiej jakości, filtrowany oraz frakcjonowany. Obecność zanieczyszczeń w materiale polimeru w zdecydowany sposób wpływa na stabilność układu krzemionka/roztwór polimeru. Krzemionka bez dodatku polimeru jest stabilna w całym badanym zakresie czasu. Dodatek polimeru początkowo stabilizuje suspensję, która po pewnym czasie jest dość gwałtownie destabilizowana. Czas stabilizacji oraz destabilizacji suspensji jest różny dla próbek polimeru o różnej czystości. Dowodzi to faktu, że stabilność takiego układu wyraźnie zależy od zawartości zanieczyszczeń jak również od stopnia polidyspersyjności polimeru.