Physicochem. Probl. Miner. Process. 53(1), 2017, 121−135

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received March 08, 2016; reviewed, accepted May 15, 2016

INFLUENCE OF POLYVINYLPYRROLIDONE ADSORPTION ON STABILITY OF SILICA AQUEOUS SUSPENSION - EFFECTS OF POLYMER CONCENTRATION AND SOLID CONTENT

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Abstract: The influence of polyvinylpyrrolidone (PVP) adsorption on the silica suspension stability was studied. The effects of silica content, polymer addition and suspension dilution with water were examined. The turbidimetry method was applied to examine stability of the investigated systems as a function of time. It was shown that the suspension without polymer was characterized by the smallest stability, whereas the systems containing PVP (before and after dilution) are successively stable. The specific conformation of PVP chains on the solid surface is responsible for the stabilization–flocculation properties of PVP in the colloidal suspension.

Keywords: *silica suspension stability, polyvinylpyrollidone adsorption, solid content, steric stabilization, zeta potential*

Introduction

The high stability of colloidal suspension is important for many practical applications. However, due to van der Waals attractive forces, the solid particles sisspersed in aqueous medium have a tendency to aggregation. In order to prevent this proccess the modification of the solid surface properties is nessesery. One of the more effective ways to change the surface characteristics in such systems is the use of adsorption phenomena (Nosal-Wiercinska and Grochowski, 2011; Nosal-Wiercinska, 2012;

http://dx.doi.org/10.5277/ppmp170110

Wisniewska et al., 2014; Nosal-Wiercinska et al., 2015). A very good way to obtain the improvement of stability conditions of solid suspension is polymer addition. If polymer chains undergo adsorption on the surfaces of solid particles, the steric repulsion appears (steric stabilization) (Napper, 1983). Increasing concentration of unadsorbed macromolecules can also affect the suspension stability. In such a case depletion stabilization occurs (Semenov, 2008). The stabilization properties of polymers are widely applied in production of paint (i.e. stabilization of titania particles (Liufu et al., 2005; Farrokhpay, 2009, Nowacka et al. 2013), cosmetics (Slivander, 2002; Tadros, 2008), washing agents (detergents) (Mauer, 2004; Grzadka et al., 2015), paper (Roberts, 1996; Pillai and Sharma, 2010), pharmaceutics (controlled drug delivery) (Uhrich et al., 1999; Liechty et al., 2010) as well as in food processing (improvement of taste, smell and consistency) (Ross, 1995; Shahidi et al., 1999).

Polymeric flocculants are also applied in petroleum refining (Jin et al., 2003), mineral processing (Moody, 1992) and textile industry (Hassan et al., 2009). To obtain a desirable stability conditions of the suspension or emulsion in the process of its production, polymer adsorption mechanism at the solid-liquid interface should be known. Therefore, basic research is needed to predict the behaviour of the colloidal system in the presence of the polymer.

On the other hand, many adsorbents (especially porous) find a wide usage in a variety of practical applications. The most important of them are water purification (removal of detergents, polymers, pesticides, bacteria, viruses), purification of air by adsorption of industrial waste gases (SO_x, NO_x) (Nowicki et al., 2013; 2014a; 2014b; 2015), recovery of organic solvents (benzene, toluene, acetone, alcohols, esters), as well as energy storage (adsorption of natural gas, hydrogen and methanol).

Thus, the main aim of this work is to determine the changes in stability of silicon oxide suspension in the presence and absence of nonionic polyvinylpyrrolidone (PVP). The dilution effect with distilled water of the previously prepared systems was also examined. Stability conditions of the suspension under investigations were studied as a function of polymer concentration and silica content. The explanation of polymeric stabilization-flocculation mechanism is undoubtedly the novelty of the present paper. Additionally, the usage of turbidimetry method for determination of suspension stability is original. This technique gives possibility of stability coefficient calculation, which is very helpful for estimation of colloidal system behaviour. The mechanism of polyvinylpyrrolidone adsorption on the silica surface was described in previous papers (Goncharuk et al., 2001; Gun’ko et al., 2004). Additionally, the influence of other adsorbates (i.e. surfactants, dyes) on the silica zeta potential was examined (Jesionowski, 2002; 2005; Jesionowski et al., 2011).

Polyvinylpyrrolidone (PVP), commonly called polyvidone or povidone, is a nonionic polymer. It is soluble in water. For the first time PVP was synthesized by Reppe (Buhler, 2005) and patented in 1939 for one of the acetylene derivatives. Originally PVP was used as an expander of blood plasma and later in various fields such as medicine, pharmacy and cosmetics production.

Silica finds also wide practical usage. This compound is characterized by numerous useful physicochemical properties. These are well-defined surface area and particle size, high purity, high-temperature stability, mechanical strength and chemical inertness. Due to excellent polishing ability, SiO_2 is applied for shaping and smoothing of high-precision semiconductor (Okawa and Watanabe, 2009). This solid is a very good dispersant for preparation of pigments without surfactants (Bondioli et al., 1998; Krysztafkiewicz et al., 2004; Wawrzkiewicz et al., 2015). Additionally, silica is used in water treatment as a destabilizing agent for removing of undesirable components (macromolecular substances, surfactants, inorganic impurities and many others) technologies (Pal et al., 2010; Majewski et al., 2012; Qu et al., 2013; Karnib et al., 2014). Silica gel (xerogel of hydrated silica) is applied as a stationary phase in chromatography, as a drying agent, catalyst and catalyst carrier (Yuan et al., 2007; Li et al., 2013).

Experimental

Characteristics of silica and polymer samples

The samples of silica were produced in the Chuiko Institute of Surface Chemistry, National Academy of Science of Ukraine, Kiev. They were used in the experiments as an adsorbent. The solid specific surface area is 294.6 ± 8.7 m^2/g and the average pore diameter is 10.1 nm. These values were obtained by the low-temperature nitrogen adsorption-desorption method – BET (Micrometritics ASAP 2405 analyzer).

Polyvinylpyrrolidone (PVP), produced by Sigma–Aldrich, was used in the studies as an adsorbate. The polymer was characterized by the weight average molecular weight (M_w) 10 000 Da. It is obtained from the N-vinylpyrrolidon (NVP) by free radical polymerization (Fig. 1).

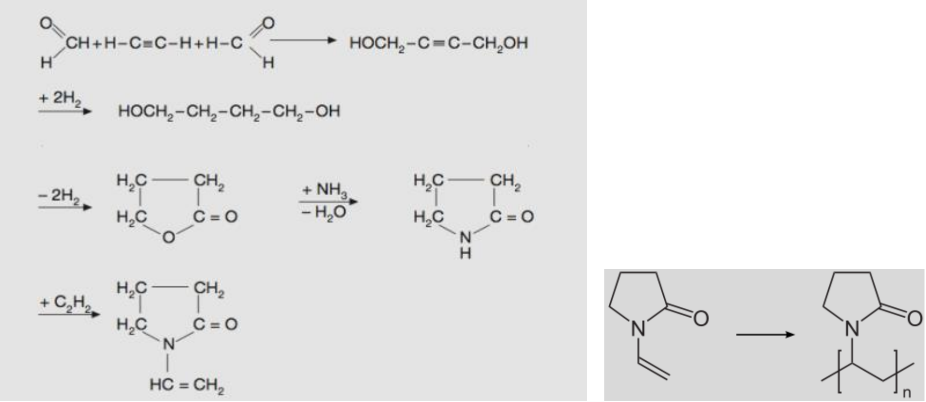

Fig. 1. Reppe's synthesis of N-vinylpyrrolidone (C_6H_9NO)
and its polymerization to polyvinylpyrrolidone

Preparation of silica suspensions without and with polymer

The starting polymer solution was prepared by dissolving 1 g of the polymer in 99 g of distilled water (percentage concentration 1%). For this purpose the PVP solution was kept in the magnetic shaker Magnetic Stirrer type MMG (Polamed) for about 20 min. The basic suspension of silica in water was prepared adding 1.5 g of SiO_2 to 35 cm^3 of distilled water. In this case the solid content was 4.1%. Later this system was put into ultrasounds for 5 min. This basic suspension was used for preparation of three systems characterized by the solid contents: 3.4, 3.1 and 2.3% (by dilution with water).

To obtain a suspension with the polymer of the following solid contents: 3.4, 3.1 and 2.3% (the same as for the system without PVP), 8, 13 and 30 cm^3 of starting polymer solution were mixed with 35 cm^3 of basic silica suspension. Finally all suspensions with the polymer were diluted adding 2 cm^3 of distilled water. All examined systems characteristics and their symbols used in the manuscript are given in Table 1. The pH values of the samples with and without the polymer were measured using the Seven Multi pH-meter (Mettler Toledo). The average pH of the samples in the absence of PVP was 4.5, whereas that of the samples in the presence of the polymer was 5.5.

Table 1. Characterystics of examined silica suspension without and with polyvinylpyrrolidone

Sample symbol	Silica content in suspension (%)	Polymer concentration	Suspension dilution with water
SiO_2_3.4	3.4	-	-
SiO_2_3.4/PVP	3.4	low	-
SiO_2_3.4/PVP/diluted	3.2	low	+
SiO_2_3.1	3.1	-	-
SiO_2_3.1/PVP	3.1	medium	-
SiO_2_3.1/PVP/diluted	2.9	medium	+
SiO_2_2.3	2.3	-	-
SiO_2_2.3/PVP	2.3	high	-
SiO_2_2.1/PVP/diluted	2.1	high	+

Principles of measurements

Stabilities of the investigated systems were measured with Turbiscan Lab^{Expert} with the cooling module TLAb Cooler. This aparatus registers simultaneously light transmission and backscattering on the dispersed solid particles. The reading head was composed of a pulsed near-infrared light source (λ = 850 nm) and the sample information was collected by two synchronized detectors. The transmission detector registered the light, which went through the sample (0 °), whereas the backscattering detector registered the light backscattered by the sample (135 °). The samples were put in a flat-bottom cylindrical glass bottle. This bottle was scanned from the bottom to the top in order to monitor the optical properties of the dispersion (along the height of the sample placed in this bottle). Exactly 20 cm^3 of the examined suspension was introduced into the turbiscan bottle (7 cm long) and then placed in the thermostated measurement chamber. The stability measurements were performed at 37 °C. Changes in the suspension stability were monitored for 15 h (single scans were collected every 15 min). The schematic presentation of light transmission through stable and unstable suspensions is depicted in Fig. 2.

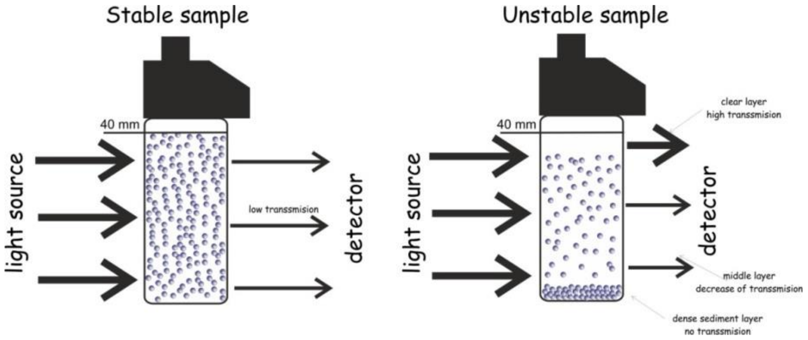

Fig. 2. Schematic representation of measuring bottle containing suspension

The zeta potentials of the silica suspensions in the presence and absence of PVP, as well as the aggregate sizes, were measured with the Zetasizer Nano ZS (Malvern Instruments). This apparatus measures size and microrheology using dynamic light scattering, as well as zeta potential and electrophoretic mobility by means of electrophoretic light scattering.

The electrokinetic measurements were performed using the analogous suspension to those which were applied in turbidimetric experiments (aqueous medium, SiO_2 without PVP – pH 4.5; SiO_2 with PVP – pH 5.5).

Results and discussion

Stability of the silica suspension without and with polyvinylpyrrolidone

The sample stability can be estimated and compared using the Turbiscan Stability Index (TSI). This parameter takes into account all single measurements during experiments and the TSI value is obtained from their averaging. All processes taking place in the sample, including sediment and clear layer formation as well as particle settling, were summed up. This coefficient was calculated with the special computer program Turbiscan Easy Soft with the following Equation 1:

$$TSI=\sqrt{\frac{\sum_{i=1}^{n}\left(x_i-x_{BS}\right)^2}{n-1}} \tag{1}$$

where: x_i – average backscattering for each minute of measurement, x_{BS} – average x_1, n – number of scans (repetitions of single measurements during the total time of the experiment).

The TSI values change in the range 0–100. The increase of TSI value indicates the deterioration of suspension stability. The obtained values of TSI for the systems under investigation are presented in Table 2.

Table 2. TSI values of silica suspensions in the absence and presence of PVP (total and for suspension levels at the top and bottom of measuring bottle)

Sample	TSI_{Total}	TSI_{Top}	TSI_{Bottom}
SiO_2_3.4	22.2	26.5	18
SiO_2_3.4/PVP	3.1	8.8	2.1
SiO_2_3.4/PVP/diluted	5.1	6.1	3.9
SiO_2_3.1	18.7	24.7	15.6
SiO_2_3.1/PVP	6.7	8.3	8.1
SiO_2_3.1/PVP/diluted	10.7	18.8	10.3
SiO_2_2.3	9.9	15.9	7.4
SiO_2_2.3/PVP	1.6	2.7	1.7
SiO_2_2.1/PVP/diluted	5.6	10.6	4.0

Figures 3–5 show the transmission curves of the silica suspension in the absence and presence of polymer (PVP) and also that after dilution. The relative position of the transmission curves in different time cycles of the experiment indicates the dynamics of processes occurring in the system under investigation. The level of suspension in the measurement bottle (mm) is along the x axis and the transmitted light intensity (%) is along the y axis. The value of 40 mm in the x axis in these figures is the mark to which the investigated suspension was poured in the measuring bottle.

Table 2 presents the stability parameters (TSI) of the sample at the top and bottom of the measurement bottle and its total value. Overall, comparing all the samples, the addition of PVP and further dilution (Figs. 3–5) improve the stability of silica suspension (TSI values are smaller than those for the system without the polymer).

As follows from Table 2, the silica suspension without the polymer (3.4%) is the most unstable. This is evidenced by the calculated TSI value which is 22.2. Moreover, Fig. 3A shows a large distance between each line. This indicates the low system stability under these conditions. For comparison, the level of light transmission in the first hour of the measurement is 40% and for the last scan it is 65%. The formation of aggregates in the whole sample volume takes place. Transmition increases by 25% in the total time of analysis and the sample is more and more penetrated by light (sedimentation of formed aggregates).

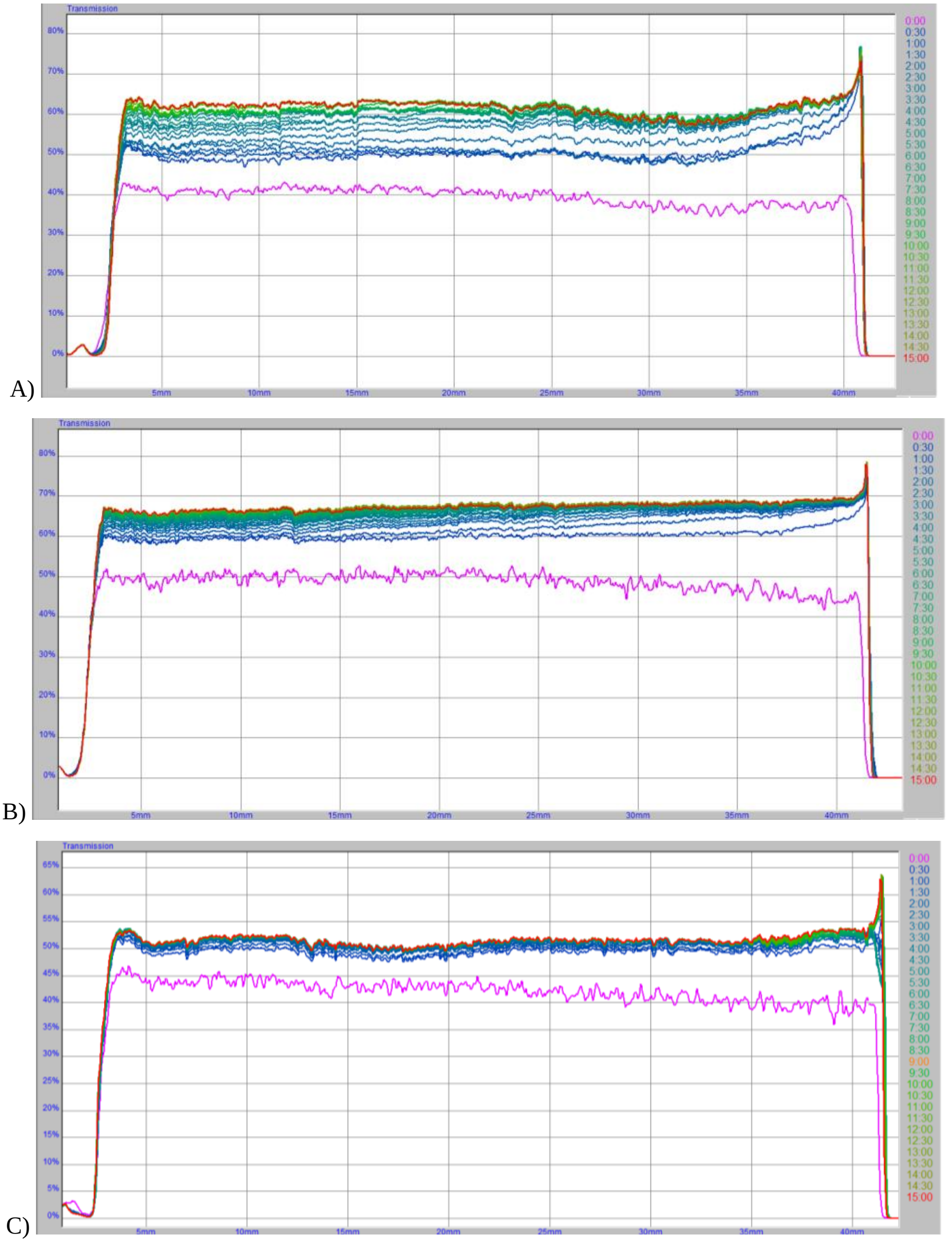

Fig. 3. Transmission curves for silica suspensions without polymer:
A) SiO_2_3.4; B) SiO_2_3.1; C) SiO_2_2.3

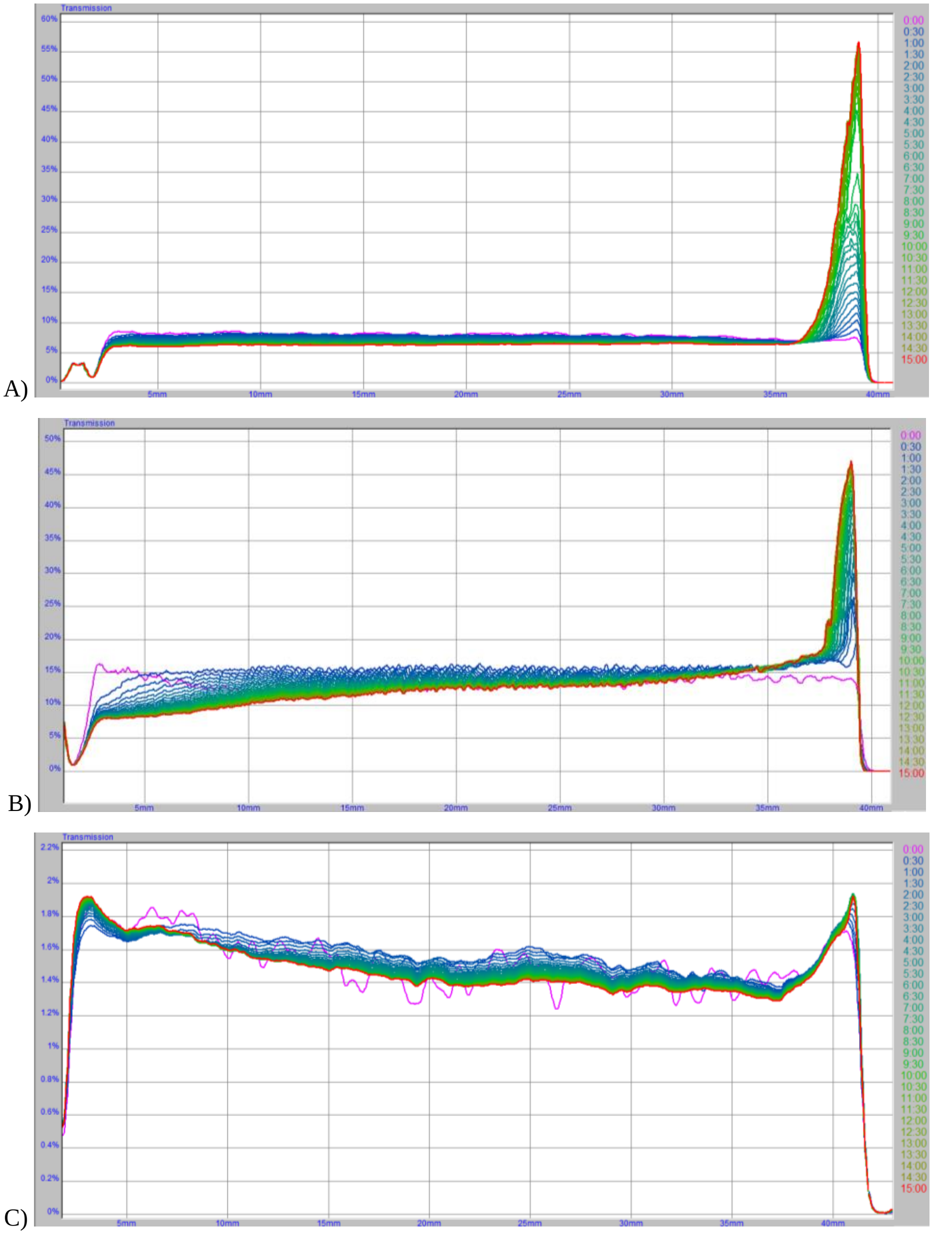

Fig. 4. Transmission curves for silica suspensions with polymer:
A) SiO_2_3.4/PVP; B) SiO_2_3.1/PVP; C) SiO_2_2.3/PVP

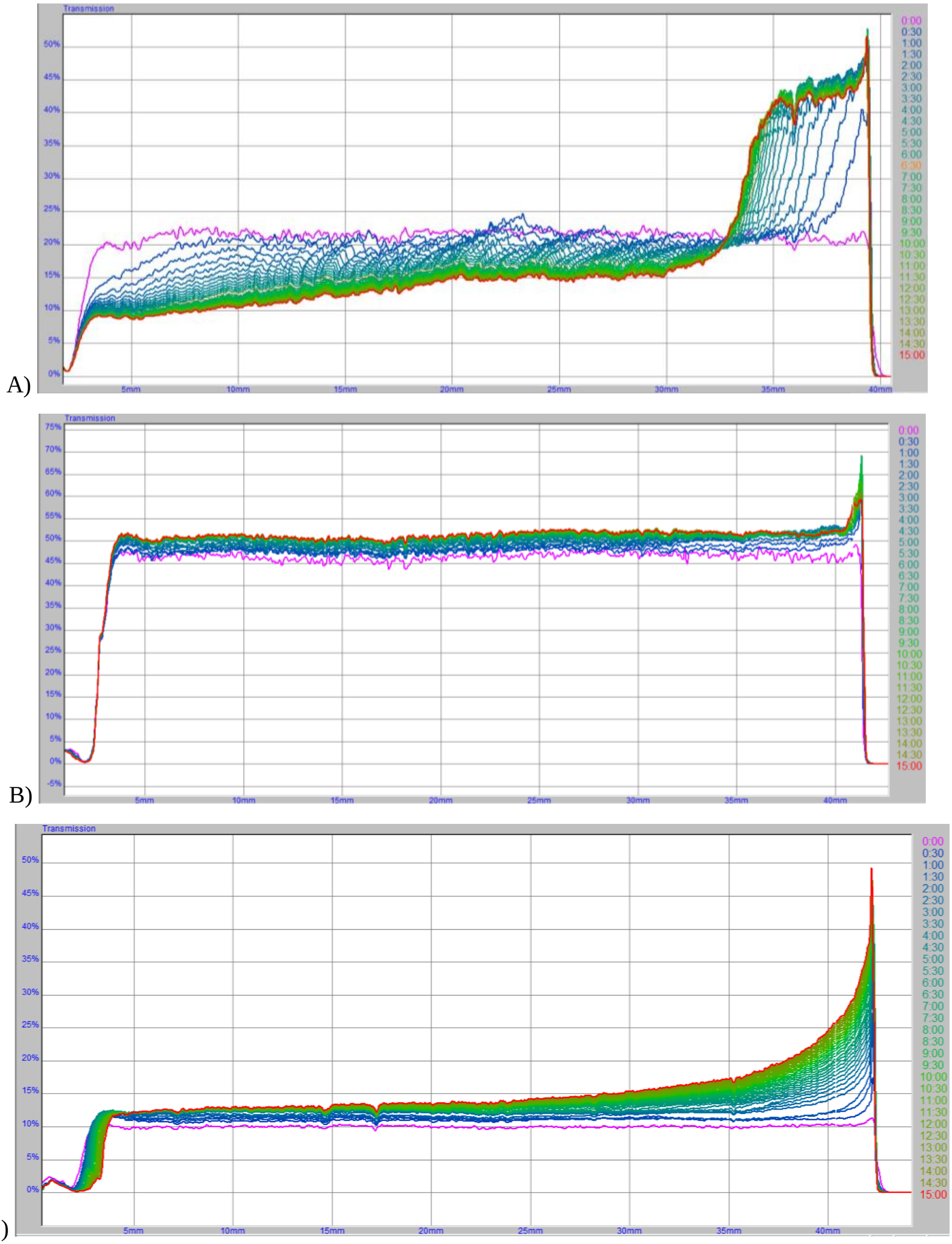

Fig. 5. Transmission curves for silica suspensions with polymer after dilution:
A) SiO_2_3.2/PVP/diluted; B) SiO_2_2.9/PVP/diluted; C) SiO_2_2.1/PVP/diluted

After the PVP addition the same silica suspension (3.4%) behaves in a complety different way (Fig. 4A). Under these conditions stability of the system is considerably improved. The manifestations of its high stability are lower value of TSI coefficient

(3.1) and low values of transmission signal (it is between 7–10% almost along the whole length of the measuring bottle). At the top of the suspension the clarification process is observed. This is demonstrated by the presence of transmission peak whose width provides information about the thickness of clear layer (transmission increases from 5% to 55% at the top suspension level). The clear layer thickness is about 2 mm.

The stability conditions of this suspension after its dilution get slightly worse (TSI increase to 5.1). As can be seen in Fig. 5A, the transmission signal oscillates between 9–25%. In addition, the formation of little aggregates takes place and clarification proccess at the top layer occurs.

Generally the main phenomenon that takes place in the system without the polymer (Figs. 3A–C) is slight destabilization. This effect is the most visible for the sample with the highest silica content. The transmission signal obtained for the silica sample without the polymer containing 3.1% of the solid varies in the range 46-67% (Fig. 3B). This is confirmed by the TSI value equal to 18.7 (the second as regards the least stable suspension of all examined systems). Comparison with the samples of silica containing polymer and the diluted system (Figs. 4B and 5B) leads to the conclusion that the addition of polyvinylpyrrolidone enhances their stability (TSI = 6.7 and 10.7, respectively). Nevertheless, the observed improvement of stability conditions is not as effective as for the systems with the highest solid content (Figs. 3A, 4A and 5A). Analyzing Fig. 4B one can note that the relative position of transmission curves at the bottom of the sample (2–10 mm) indicates that transmission decreases more gradually in the total time of experiment. The reason for this can be connection of small agregates into larger structures. Moreover, amplification of the transmission signal at the top of the bottle means that the clarification process is present in the system. After the addition of distilled water to the SiO_2-PVP suspension (Fig. 5B), its stability deteriorates (TSI increases to 10.7). The transmission signal is in the range 45-52% due to the most effective sedimentation of particle aggregates with the polymer in diluted system compared to the more concentrated one.

The analysis of the turbidimetric curves obtained for the SiO_2-PVP system containing the smallest solid content (Fig. 4C) indicates that transmission reaches the lowest level (changing in the range 1.4–1.6%) of all examined suspensions. The TSI is equal to 1.6, which confirms very high stability of the system. Good evidence for this fact is the absence of transmission peak at the top level – the clarification process does not occur.

After dilution of this highly stable suspension, the minimal deterioration of its stability takes place (Fig. 5C). The clarification process appears at the top of suspension. Additionally, the transmission increases to about 10% and the stability coefficient value is 5.6.

Mechanism of silica suspension stabilization in the presence of polyvinylpyrolidone

The explanation of stabilization and destabilization properties of the investigated systems needs defining the conformation of polymer chains in the bulk solution and adsorbed on the solid surface.

The point of zero charge (pzc) of silica surface occurs at pH about 3 (Wiśniewska, 2010; 2012a; 2012b). It means that at pH > pH_{pzc} the solid surface is negatively charged. The pH values of the examined suspension were in the range 4.5–5.5. Thus, under such pH conditions, the silica surface has a slight negative charge. The nonionic PVP adsorption on the SiO_2 surface proceeds through hydrogen bridges, formed between the silanol groups of the solid (≡Si–OH) and oxygen atoms in the PVP functional groups.

The analysis of TSI values obtained for the silica systems without the polymer indicates that the system stability increases with the decrease of the solid content in the suspension (Table 2). The SiO_2 system containing 3.4% of the solid is characterized by the lowest stability of all examined systems (TSI_{Total} = 22.2). In such a case the silica particles dispersed in the water medium repel slightly due to their small negative surface charge (electrostatic effect). Nevertheless, the highest solid content in the suspension facilities collisions of colloidal particles and aggregates formation. With the decrease of the solid content, these collisions become less probable. It results in the TSI values decrease and visible improvement of system stability (TSI_{Total} = 18.7 and 9.9 for SiO_2_3.1 and SiO_2_2.3 suspensions, respectively). The evidence for this is the smallest aggregate sizes (Table 3) obtained for the SiO_2_2.3 system (196.3 nm) in comparison to those with a higher solid content (about 280 nm).

Table 3. Size and zeta potential values of the silica in the absence and the presence of PVP

Sample	Aggregate size (nm)	Zeta potential (mV)
SiO_2_3.4	280	-7.2
SiO_2_3.4/PVP	296	-9.36
SiO_2_3.4/PVP/diluted	474	-9.8
SiO_2_3.1	285	-10.4
SiO_2_3.1/PVP	348	-17.7
SiO_2_3.1/PVP/diluted	456	-18.3
SiO_2_2.3	196	-6.13
SiO_2_2.3/PVP	381	-9.79
SiO_2_2.1/PVP/diluted	456	-18.3

The PVP addition to the silica suspension causes significant increase of its stability (for all examined solid contents). The presence of polymeric layers around the solid particles results in the appearance of steric forces. They significantly limit the particle contacts and prevent them from joining in larger structures, leading to steric stabilization of the suspension. Moreover, the evidence for the steric layer formation is decrease of the zeta potential of solid particles in the polymer presence compared to the systems without PVP (Table 3). This is due to the shift of slipping plane from the solid surface as a result of polymer adsorption.

In the case of system containing 3.4% of SiO_2 and simultaneosly the lowest polymer concentration, the adsorbed PVP chains assume flat conformation on the solid surface. The surface area accesible to not very numerous macromolecules is large. The polymeric segments form mainly train structures on the solid surface.The schematic presentation of stability mechanism for this system is given in Fig. 6A.

The steric stabilization in the silica suspension containing 3.1% of SiO_2 and medium polyvinylpyrrolidone concentration is a result of more extended conformation of adsorbed chains (Fig. 6B). This is provided by a smaller surface area accesible to more numerous PVP macromolecules. In this case, tail and loop structures occurs in the polymeric adsorption layer.

The most stable system of all examined ones is that characterized by the lowest silica content (2.3%) and the highest PVP concentration. Besides the steric stabilization caused by the adsorbed chains with significantly extended conformation, the depletion forces can appear (Fig. 6C). Depletion stabilization is caused by not adsorbed macromolecules located in the solution. Their presence leads additionally to obtaining a highly stable SiO_2 suspension containing the polymer.

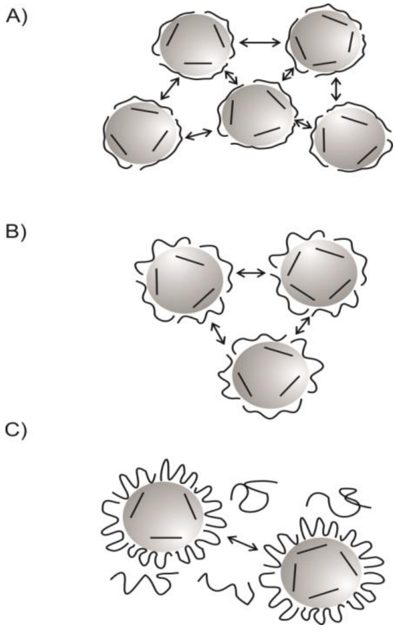

Fig 6. Schematic presentation of stabilization mechanisms of silica suspension in the presence of PVP: A) SiO_2_3.4/PVP; B) SiO_2_3.1/PVP; C) SiO_2_2.3/PVP

The analysis of the data concerning the dilution effect of silica suspensions containing polyvinylpyrrolidone indicates that the addition of water makes the system stability slightly worse. Additionally, the zeta potential values are smaller in comparison to the systems before dilution. The increase of negative values of zeta potential indicates a higher shift of slipping plane from the solid particle surface. Such behaviour corresponds with formation of thicker adsorption layers by polymer macromolecules. The water molecules (added to the system during its dilution) interact with the outer part of the PVP adsorption layer, causing some development of the polymer chains located there. In this case single polymer bridges can be formed between the SiO_2 particles covered with the macromolecular compound. The increase of aggregate sizes is also the evidence of such behaviour.

Conclusions

The influence of nonionic polyvinylpyrrolidone (PVP) adsorption on the stabilization-destabilization properties of the silica aqueous suspension was studied. The turbidimetric data and the calculated values of Turbiscan Stability Indexes (TSI) indicate that the addition of PVP causes improvement of SiO_2 stability. The mechanism of this stabilization is steric. The polymeric adsorption layer covering solid particles assures their effective repulsion. The most stable system was obtained in the case of the lowest solid content in the suspension and the highest PVP concentration. Besides the steric forces, the depletion ones appear under such conditions. The dilution of the SiO_2-PVP systems with water leads to slight deterioration of the system stability. The water molecules (located in the outer part of PVP adsorption layer) cause development of polymer chain. This facilitates formation of single polymer bridges between the SiO_2 particles covered with PVP.

Acknowledgements

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n^{o}PIRSES-GA-2013-612484. We acknowledge the ERASMUS program for the financial support of Salvador Perez's visit at Maria Curie Skłodowska University.

References

BONDIOLI F., FERRARI A.M., LEONELLI C., MANFREDINI T., 1998, *Syntheses of Fe_2O_3/silica red inorganic inclusion pigments for ceramic applications*. Mat. Res. Bull. 33, 723-729.

BUHLER V., 2005, *Polyvinylpyrrolidone excipients for pharmaceuticals,* Springer-Verlag, Germany.

FARROKHPAY S., 2009, *A review of polymeric dispersant stabilisation of titania pigment*. Adv. Colloid Interf. Sci. 151, 24-32.

GONCHARUK E.V., PAKHOVCHISHIN S.V., ZARKO V.I., GUN'KO V.M., 2001, *Properties of aqueous suspensions of highly dispersed silica in the presence of polyvinylpyrrolidone*. Colloid J. 63, 283-289.

GRZADKA E., WISNIEWSKA M., GUN’KO V., ZARKO V., 2015, *Adsorption, elektrokinetic and stabilizing properties of the guar gum/surfactant/alumina system*. J. Surfac. Det. 18, 445-453.

GUN'KO V.M., VORONIN E.F., ZARKO V.I., GONCHARUK E.V., TUROV V.V., PAKHOVCHISHIN S.V., PAKHLOV E.M., GUZENKO N.V., LEBODA R., SKUBISZEWSKA-ZIĘBA J., JANUSZ W., CHIBOWSKI S., CHIBOWSKI E., CHUIKO A.A., 2004, *Interaction of poly(vinyl pyrrolidone) with fumed silica in dry and wet powders and aqueous suspensions*. Colloids Surf. A. 233, 63-78.

HASSAN A., ARIFFIN M., LI T.P., ZAINON N.Z., 2009, *Coagulation and flocculation treatment of wastewater in textile industry using chitosan*. J. Chem. Nat. Res. Eng. 4, 43-53.

JESIONOWSKI T., 2002, *Effect of surfactants on the size and morphology of the silica particles prepared by an emulsion technique*. J. Mat. Sci. 37, 5275-5281.

JESIONOWSKI T., 2005, *Characterisation of pigments obtained by adsorption of C.I. Basic Blue 9 and C.I. Acid Orange 52 dyes onto silica particles precipitated via the emulsion route*. Dyes Pigm. 67, 81-92.

JESIONOWSKI T., PRZYBYLSKA A., KURC B., CIESIELCZYK F., 2011, *The preparation of pigment composites by adsorption of C.I. Mordant Red 11 and 9-aminoacridine on both unmodified and aminosilane-grafted silica supports*. Dyes Pigm. 88, 116-124.

JIN Z., ZHANG Y.F., CHEN X.P., GAO H.S., 2003, *Application of organic polymeric flocculants in centrifugal dewatering of oil refinery sludge*. J. Env. Sci. (China) 15, 510-513.

KARNIB M., KABBANI A., HOLAIL H., OLAMA Z., 2014, *Heavy metals removal using activated carbon, silica and silica activated carbon composite*. Energy Proc. 50, 113-120.

KRYSZTAFKIEWICZ A., BINKOWSKI S., DEC A., 2004, *Application of silica-based pigments in water-borne acrylic paints and in solvent-borne acrylic paints*. Dyes Pigm. 60, 233-242.

LI X., YANG Y., YANG O., 2013, *Organo-functionalized silica hollow nanospheres: Synthesis and catalytic application*. J. Mater. Chem. 1, 1525-1535.

LIECHTY W.B., KRYSCIO D.R., SLAUGHTER B.V., PEPPAS N.A., 2010, *Polymers for drug delivery systems*. Ann. Rev. Chem. Biomolec. Eng. 1, 149-173.

LIUFU S., XIAO H., LI Y., 2005, *Adsorption of poly(acrylic acid) onto the surface of titanium dioxide and the colloidal stability of aqueous suspension*. J. Colloid Interf. Sci. 281, 155-163.

MAJEWSKI P., LUONG J., STRETTON K., 2012, *The application of surface engineered silica for the treatment of sugar containing wastewater*. Water Sci. Tech. 65, 46-52.

MAUER K.H., 2004, *Detergent proteases*. Cur. Opinion Biotech. 15, 330-334.

MOODY G., 1992, *The use of polyacrylamides in mineral processing*. Mining. Eng. 5, 479-492.

NAPPER D.H., 1983, *Polymeric stabilization of colloidal dispersions*. Academic Press, London.

NOSAL-WIERCINSKA A., 2012, *Adsorption of cystine at mercury/ aqueous solution of chlorate (VII) interface in solutions of different water activity*. Cent. Eur. J. Chem. 10, 1290-1300.

NOSAL-WIERCINSKA A., GROCHOWSKI M., 2011, *Adsorption of thiourea and its methyl derivatives from chlorate(VII) with varied water activity*. Coll. Czech. Chem. Comm. 76, 265-275.

NOSAL-WIERCIŃSKA A., GROCHOWSKI M., WISNIEWSKA M., TYSZCZUK-ROTKO K., SKRZYPEK S., BRYCHT M., GUZIEJEWSKI D., 2015, *The influence of protonation on the electroreduction of Bi(III) ions in chlorates (VII) solutions of different water activity*. Electrocatal. 6, 315-321.

NOWACKA M., SIWINSKA-STEFANSKA K., JESIONOWSKI T., 2013, *Structural characterisation of titania or silane-grafted* TiO_2*-*SiO_2 *oxide composite and influence of ionic strength or electrolyte type on their electrokinetic properties,* Colloid Polym. Sci. 291, 603–612.

NOWICKI P., KAZMIERCZAK J., SAWICKA K., PIETRZAK R., 2015, *Nitrogen-enriched activated carbons prepared by the activation of coniferous tree sawdust and their application in the removal of nitrogen dioxide*. Int. J. Envir. Sci. Tech. 12, 2233-2244.

NOWICKI P., KUSZYNSKA I., PRZEPIORSKI J., PIETRZAK R., 2013, *The effect of chemical activation method on properties of activated carbons obtained from pine cones*. Centr. Eur. J. Chem. 11, 78-83.

NOWICKI P., SKIBISZEWSKA P., PIETRZAK R., 2014a, *Hydrogen sulphide removal on carbonaceous adsorbents prepared from coffee industry waste materials*. Chem. Eng. J. 248, 208-215.

NOWICKI P., SUPŁAT M., PRZEPIORSKI J., PIETRZAK R., 2014b, *NO_2 removal on adsorbents obtained by pyrolysis and physical activation of corrugated cardboard*, Chem. Eng. J. 10, 195-196.

OKAWA S. WATANABE K., 2009, *Chemical mechanical polishing of titanium with colloidal silica containing hydrogen peroxide-mirror polishing and surface properties.* Dent. Mater. J. 28, 68-74.

PAL A., ADAK A., KONER S., 2010, *Cationic surfactant adsorption on silica gel and its application for wastewater treatment*. Des. Water Treat. 22, 1-8.

PILLAI C.K.S., SHARMA C.P., 2010, *Absorbable polymeric surgical sutures: chemistry, production, properties, biodegradability and performance*. J. Biomat. Appl. 25, 291-366.

QU X., ALVAREZ P.J.J., LI Q., 2013, *Applications of nanotechnology in water and wastewater treatment*. Water Res. 47, 3931-3946.

ROBERTS J.C., 1996, *Paper chemistry*. Chapman & Hall, London.

ROSS Y., 1995, *Characterization of food polymers using state diagrams*, J. Food Eng. 24, 339-360.

SEMENOV A.N., 2008, *Theory of colloid stabilization in semidilute polymer solutions*. Macromol. 41, 2243-2249.

SHAHIDI F., ARACHCHI J.K.V., YEON Y.J., 1999, *Food application of chitin and chitosans*. Trends Food Sci. Tech. 10, 37-51.

SLIVANDER M., 2002, *Steric stabilization of liposomes - A review*. Prog. Colloid Polym. Sci. 120, 35-40.

TADROS T.F., 2008, *Colloid aspects of cosmetic formulations with practicular reference to polymeric surfactants*, Colloid Interf. Sci. Series. Vol. 4: Colloids in Cosmetics and Personal Care, Wiley-VCH.

UHRICH K.E., CANNIZZARO S.M., LANGER R.S., SHAKESHEFF K.M., 1999, *Polymeric systems for controlled drug release*. Chem. Rev. 99, 3181-3198.

WAWRZKIEWICZ M., WIŚNIEWSKA M., GUN'KO V.M., ZARKO V.I., 2015, *Adsorptive removal of acid, reactive and direct dyes from aqueous solutions and wastewater using mixed silica-alumina oxide.* Powder Tech. 278, 306-315.

WISNIEWSKA M., 2010, *Temperature effect on adsorption properties of silica – polyacrylic acid interface*. J. Therm. Anal. Cal. 101, 753-760.

WISNIEWSKA M., 2012a, *Temperature effects on the adsorption polyvinyl alcohol on silica*. Centr. Eur. J. Chem. 10, 1236-1244.

WISNIEWSKA M., 2012b, *The temperature effect on the adsorption mechanism of polyacrylamide on the silica surface and its stability.* Appl. Surf. Sci. 258, 3094-3101.

WISNIEWSKA M., URBAN T., NOSAL-WIERCIŃSKA A., ZARKO V.I., GUN'KO V.M., 2014, *Comparison of stability properties of poly(acrylic acid) adsorbed on the surface of silica, alumina and mixed silica-alumina nanoparticles – application of turbidimetry method*. Cent. Eur. J. Chem. 12, 476-479.

YUAN G., LOUIS C., DELANNOY L., KEAN M.A., 2007, *Silica- and titania-supported Ni–Au: application in catalytic hydrodechlorination*. J. Catal. 247, 256–268.