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## INFLUENCE OF SOLUTION pH ON STABILITY OF FUMED SILICA–POLYACRYLIC ACID SYSTEMS

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*The influence of polyacrylic acid (PAA) adsorption on fumed silica (SiO<sub>2</sub>) surface on suspension stability has been studied. Changes in the suspension stability were monitored using a Turbiscan Lab<sup>Expert</sup> with a TLab Cooler cooling module at 25°C. PAA is an anionic polymer containing carboxyl groups; therefore all the measurements were carried out at different pH 3, 6 and 9. Analysis of obtained transmission and backscattering curves and Turbiscan Stability Indexes (TSI) allowed determination of the most probable mechanism of the system stability.*

### INTRODUCTION

The conformation of macromolecules adsorbed at a solid-liquid interface influences structure of a polymer adsorption layer on a metal oxide surface. This structure determines the stabilization-flocculation properties of colloidal systems which are very important to control many technological and ecological processes. The interfacial behavior of metal oxide-polymer solution systems is substantial for mineral flotation, dispersion-flocculation of cosmetics, paints, pharmaceuticals, foods, oil recovery, regulation of ploughlands erosion, purification of the industrial and drinking water, etc. [1–3]. Polyelectrolytes, including a polyacrylic acid classified as an anionic polymer, are especially appropriate for these purposes, because the suspension stability in the presence of PAA can be regulated by both steric and electrostatic forces.

The most important factor influencing the adsorption process of polyacrylic acid on a silica surface is the pH value of the solution. An increase in pH causes an increase in the dissociation degree of the carboxyl groups in the PAA chains that leads to changes in the interactions between adsorbent active sites and polymer functional groups. Taking this fact into consideration, the aim of this paper was to determine the pH influence on the silica suspension stability.

Silica was chosen for the study because it is a very popular adsorbent with well defined solid-liquid interface [4]. Silica gels were widely used as a stationary phases in chromatography and as a drying agent, catalyst and catalyst carrier. Moreover, SiO<sub>2</sub> finds a great application in production of glass, cement, and ceramics. Nanosilica (or fumed silica) is widely used in industry and medicine as powder materials or compact solids, polymer fillers, cores in core-polymer shell particles, etc. Nanosilica is a powder material (bulk density  $\rho_b=0.04\text{--}0.13\text{ g/cm}^3$  depending on the specific surface area between 300 and 50 m<sup>2</sup>/g) composed of aggregates (<1  $\mu\text{m}$  in size, mass fractal dimension  $D_{mf}=2.5\text{--}2.6$ ) and agglomerates of aggregates (>1  $\mu\text{m}$  in size,  $D_{mf}=2.2\text{--}2.4$ ).

### MATERIALS AND METHODS

Fumed silica (pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine) studied has the BET surface area of 57 m<sup>2</sup> g<sup>-1</sup> determined from low-temperature nitrogen adsorption-desorption isotherm measured using a Micro-metric ASAP 2405N analyzer.

Polyacrylic acid (PAA, Fluka) was used at the average molecular weights of 2, 100, and 240 kDa.

All measurements were carried out in the presence of NaCl solution (0.01 mol dm<sup>-3</sup>) which was used as the supporting electrolyte. Moreover, the stability experiments were performed at solution pH=3, 6 and 9 at 25°C.

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The stability measurements of the fumed silica suspensions without and with PAA were carried out using a Turbiscan Lab<sup>Expert</sup> with a TLab Cooler cooling module. This apparatus possesses an electroluminescence diode which emits collimated light beam ( $\lambda=880$  nm) passing through the suspension. The apparatus has two synchronized detectors. A transmission detector recorded light passing through a probe under angle of  $0^\circ$  in relation to the incident light direction. The second one is a backscattering detector registering the light scattered under angle of  $135^\circ$ . The obtained data are stored and converted by a computer program. The results are presented in the form of curves, which show the intensities of transmission and scattering as a function of time.

The analyzed suspension in a glass vial (7 cm in length) was placed in a thermostated measurement chamber. The suspension with 0.02 g of oxide in 20 cm<sup>3</sup> of NaCl solution (solid content 0.1%) was sonicated for 1 min. Then the required pH of the solution was adjusted. The suspension was shaken in a water bath for 30 min and the pH was checked. The changes in the suspension stability were monitored for 15 h (single scans were obtained in every 15 min). The probes of the silica suspension with polyacrylic acid were prepared in the similar way. An appropriate volume of the PAA solution, desired the surface coverage  $\theta=1$  ( $C_{PAA}\approx 500$  ppm), was added to the suspension after sonification.

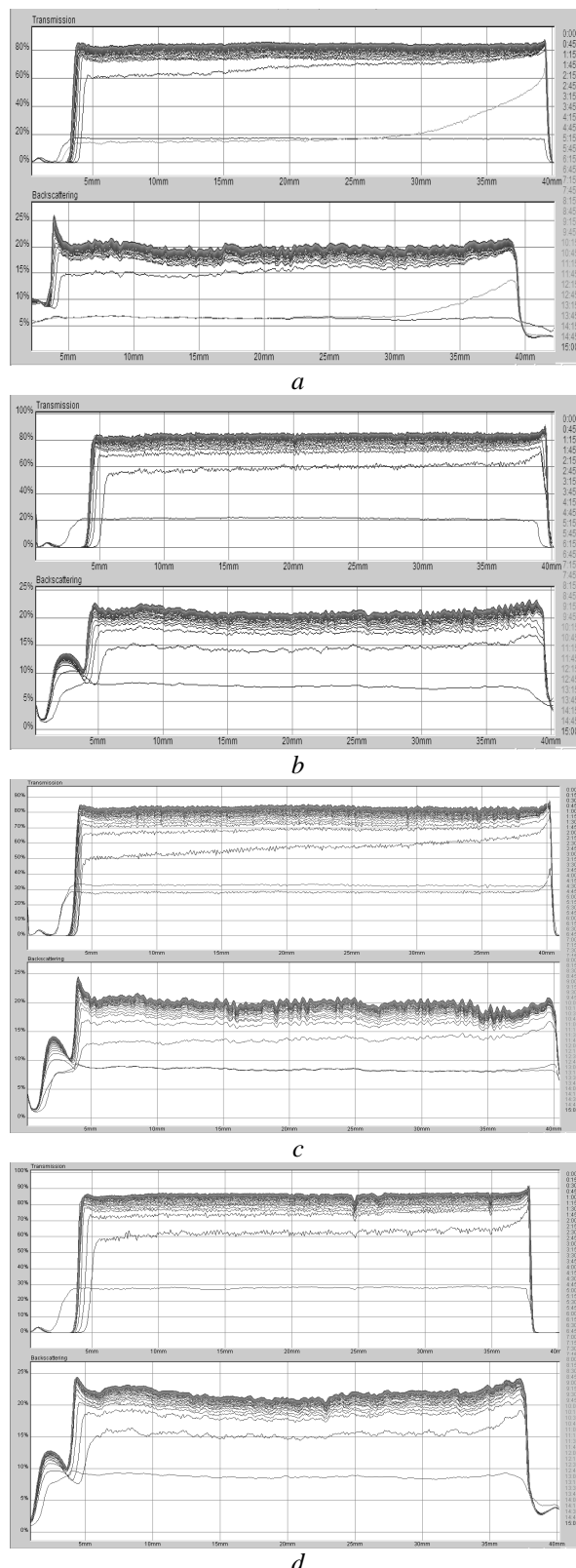
The Turbiscan Stability Indices (TSI) were calculated from the experimental results. The TSI values were obtained using a special computer program from the following equation

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

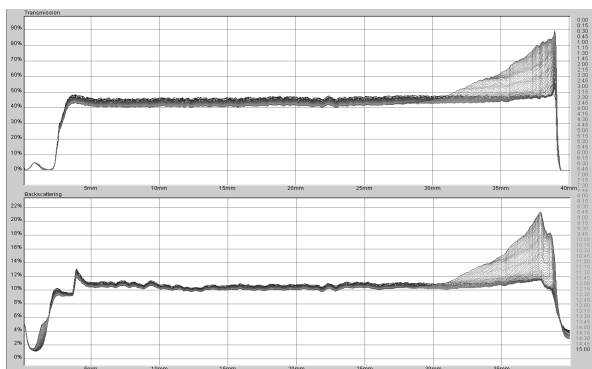
where  $x_i$  is the mean backscattering for each minute of measurement,  $x_{BS}$  is the mean  $x_i$ , and  $n$  is the number of scans. The TSI is a parameter which allows the estimation of the suspension stability. High TSI value indicates that the system is unstable.

## RESULTS AND DISCUSSION

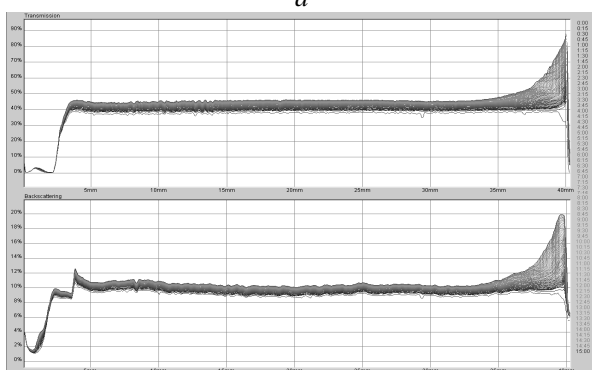
The obtained transmission and backscattering curves for investigated systems are presented in Figures 1–3. Calculated values of TSI were shown in Table 1 and Fig. 4. The analysis of these data suggests that samples are the most unstable at pH 3. The addition of PAA improves insignificantly the SiO<sub>2</sub> suspension stability.



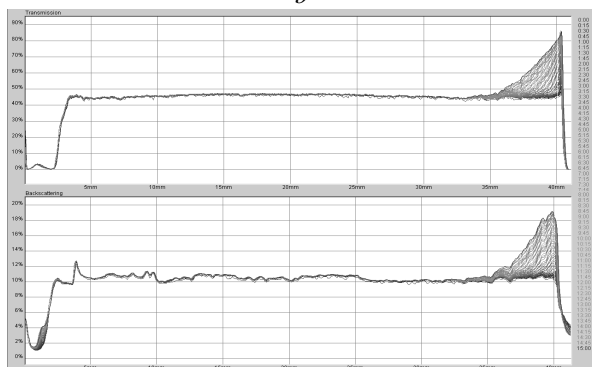
**Fig. 1.** Transmission and backscattering at pH 3 for the systems: a) SiO<sub>2</sub> - NaCl, b) SiO<sub>2</sub> - NaCl - PAA 2 kDa, c) SiO<sub>2</sub> - NaCl - PAA 100 kDa, d) SiO<sub>2</sub> - NaCl - PAA 240 kDa



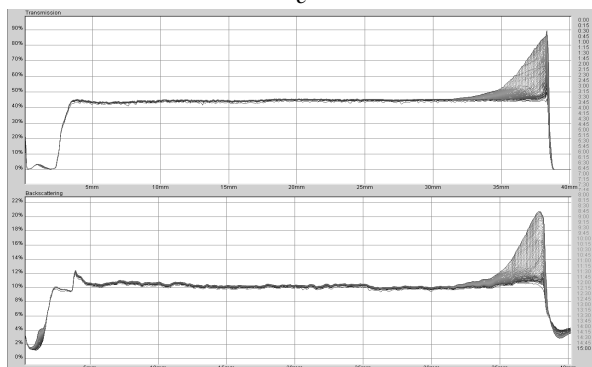
*a*



*b*

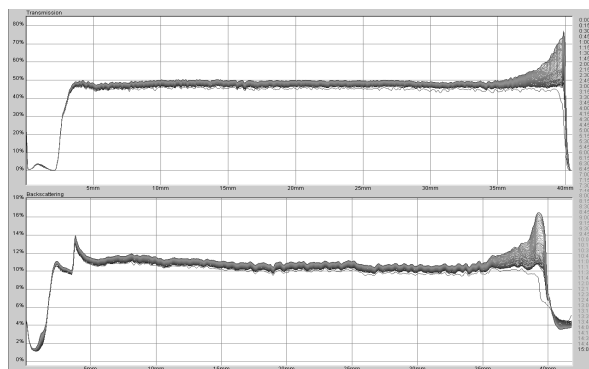


*c*

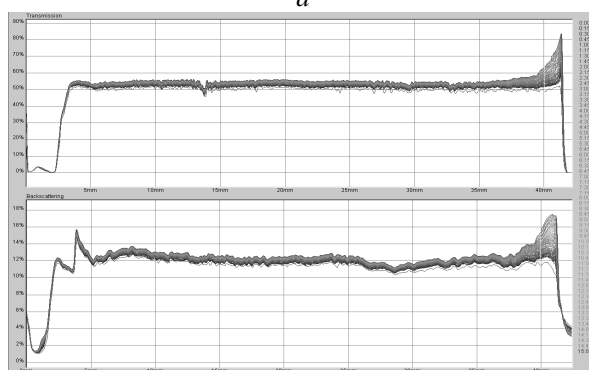


*d*

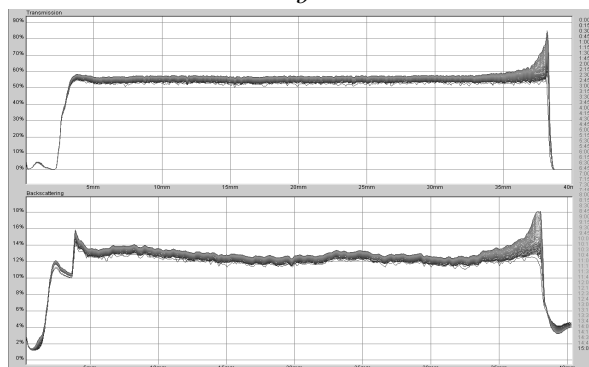
**Fig. 2.** Transmission and backscattering at pH 6 for the systems: *a*)  $\text{SiO}_2$  - NaCl, *b*)  $\text{SiO}_2$  - NaCl - PAA 2 kDa, *c*)  $\text{SiO}_2$  - NaCl - PAA 100 kDa, *d*)  $\text{SiO}_2$  - NaCl - PAA 240 kDa



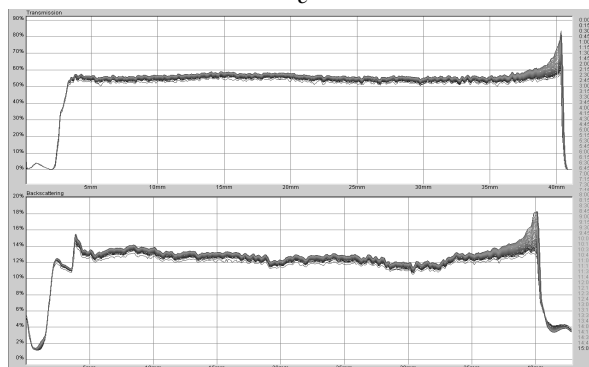
*a*



*b*



*c*

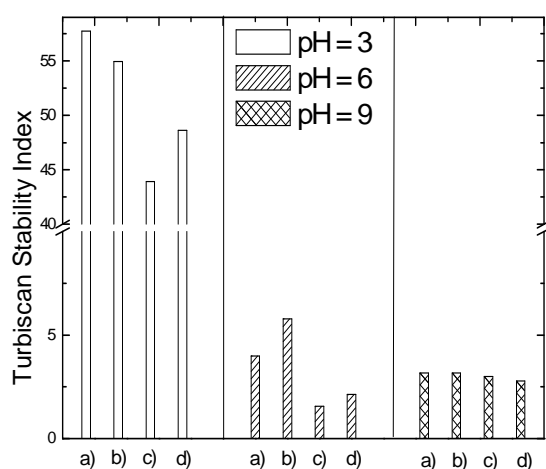


*d*

**Fig. 3.** Transmission and backscattering at pH 9 for the systems: *a*)  $\text{SiO}_2$  - NaCl, *b*)  $\text{SiO}_2$  - NaCl - PAA 2 kDa, *c*)  $\text{SiO}_2$  - NaCl - PAA 100 kDa, *d*)  $\text{SiO}_2$  - NaCl - PAA 240 kDa

**Table 1.** TSI values for SiO<sub>2</sub> - PAA systems at different pH values

System	TSI		
	pH 3	pH 6	pH 9
SiO <sub>2</sub>	57.75	4.00	3.17
SiO <sub>2</sub> -PAA 2 000	54.95	5.79	3.17
SiO <sub>2</sub> -PAA 100 000	43.94	1.56	3.00
SiO <sub>2</sub> -PAA 240 000	48.62	2.14	2.79



**Fig. 4.** TSI values at different pH for the systems:  
 a) SiO<sub>2</sub> - NaCl,  
 b) SiO<sub>2</sub> - NaCl - PAA 2 kDa,  
 c) SiO<sub>2</sub> - NaCl - PAA 100 kDa,  
 d) SiO<sub>2</sub> - NaCl - PAA 240 kDa

Completely different situation takes place at pH 6 and 9 where the suspensions are successively stable and addition of polymer minimally influences their stability.

To explain observed features of the systems stability, it is necessary to analyze the ionization degree of PAA carboxylic groups and the SiO<sub>2</sub> surface charge density with increasing pH value. The increase in pH causes dissociation of the polyacrylic acid groups. Their dissociation degree ( $\alpha_d$ ) at pH 3 equals to 0.03. At pH 4.5 ( $pK_{PAA}=4.5$  [5])  $\alpha_d=0.5$  and at pH 7.5 practically all the PAA macromolecules are fully ionized ( $\alpha_d=0.999$ ).

Previous investigations indicated that  $pH_{pzc}$  of silica is equal to approximately 3 [6]. It means that the SiO<sub>2</sub> surface is negatively charged in the whole pH range studied from 3 to 9; however, the surface charge density ( $\sigma_0$ )

is small at pH < 7. In such a situation, the electrostatic repulsion between the solid surface and PAA chains appears. Its strength increases with increasing pH. This results in more and more stretched conformation of the negatively charged macromolecules on the negatively charged adsorbent surface. For this reason the pH increase causes a decrease in the polymer adsorption [6]. However, the PAA adsorption on the silica surface occurs in the whole range of pH, even at the highest values of pH. It proved that different non-electrostatic forces had to be responsible of the PAA adsorption on the SiO<sub>2</sub> surface. Otherwise, the adsorption of negatively charged polymer chains on the negatively charged solid surface should not take place. The energy of these interactions [6] corresponds to the energy of strong hydrogen bonds (40-50 kJ/mol). These bonds can be formed between both neutral ( $\equiv SiOH$ ) or charged ( $\equiv SiO^-$ ,  $\equiv SiOH_2^+$ ) silanol groups of adsorbent and dissociated or neutral groups of the polymer.

At pH 3 without the polymer, the silica suspension is characterized by much lower stability (TSI=57.75) as compared to that at pH 6 and 9 (TSI=4.00 and 3.17, respectively). This is caused by lowering  $\sigma_0$  value, as well as diffusion layer charges, with decreasing pH close to the point of zero charge [6]. The repulsive interactions between solid particles are weak and not able to provide the system stability; therefore, the coagulation takes place. The addition of PAA insignificantly improves the dispersion stability. At such pH, the PAA chains are practically non-dissociated. The adsorbed macromolecules form more coiled structures at the silica surface. Such coils adsorbed on a particle can interact with the macromolecules adsorbed on other particles or with bare particles. As a result, large flocs composed of solid particles covered with a densely packed polymer layer are formed in the suspension. Thus, a decrease in the silica suspension stability in the presence of PAA can be due to bridging interactions PAA-silica and PAA-PAA leading to flocculation of the system.

Completely different situation is observed at pH 6 and 9. The systems both in the absence and in the presence of polymer are stable. The high stability of silica suspension without PAA is caused by electrostatic interactions between negatively charged solid particles.

The adsorption of polyacrylic acid weakly affects the SiO<sub>2</sub> suspension stability. Under these conditions, the polymer chains are completely dissociated that results in strong electrostatic repulsion between polymer-coated particles. This effect is additionally strengthened by intermolecular repulsive interactions of dissociated carboxylic groups in non-adsorbed polymer chains in the solution. As a result, both steric and electrostatic effects are responsible of high suspension stability in the presence of the polymer. Thus, at pH 6 and 9 electrosteric stabilization of the SiO<sub>2</sub> – PAA suspension occurs.

#### ACKNOWLEDGEMENT

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### Вплив рН розчину на стабільність систем високодисперсний кремнезем – поліакрилова кислота

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*Вивчено вплив адсорбції поліакрилової кислоти (ПАК) на поверхні високодисперсного кремнезему (SiO<sub>2</sub>) на стабільність суспензії. Зміни стабільності суспензії спостерігались за допомогою приладу Turbiscan Lab<sup>Expert</sup> із охолоджуючим модулем TLab Cooler при 25°C. ПАК є аніонним полімером, що містить карбоксильні групи, тому всі вимірювання проводились при різних рН (3, 6 та 9). Аналіз одержаних кривих перенесення та зворотнього розсіювання, а також індексів стабільності (Turbiscan Stability Indexes (TSI)) дозволив визначити найбільш вірогідний механізм стабілізації вивчених систем.*

### Влияние рН раствора на стабильность систем високодисперсний кремнезем – поліакрилова кислота

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*Изучено влияние адсорбции полиакриловой кислоты (ПАА) на поверхности высокодисперсного кремнезема (SiO<sub>2</sub>) на стабильность суспензии. Изменения стабильности суспензии наблюдались с помощью прибора Turbiscan Lab<sup>Expert</sup> с охлаждающим модулем TLab Cooler при 25°C. ПАА является анионным полимером, содержащим карбоксильные группы, поэтому все измерения проводились при различных рН (3, 6 и 9). Анализ полученных кривых переноса и обратного рассеяния, а также индексов стабильности (Turbiscan Stability Indexes (TSI)) позволил определить наиболее вероятный механизм стабилизации изученных систем.*