Influence of solution pH, supporting electrolyte presence and solid content on the stability of aqueous nanosilica suspension

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A B S T R A C T

The effects of solution pH, supporting electrolyte presence and solid content on nanosilica suspension stability were examined. The turbidimetry method was applied to monitor the changes in the system stability in the short (about 2 h) and long (about 18 days) periods of time. The stability coefficients and aggregate diameters were calculated numerically to estimate colloidal system properties. The sodium chloride presence (as a supporting electrolyte) improves the stability conditions of SiO_2 suspension. The greatest effect of solution pH change is observed in the aqueous medium. The most unstable system occurs at pH 10.6 after 18 days.

Introduction

Colloidal silica (particle diameter in the range 1–1000 nm) possesses a wide range of practical applications. It is characterized by numerous useful physicochemical properties which are exploited in many areas of industry, science and environmental protection.

Its excellent polishing ability [1] is used for shaping and smoothing high-precision in semiconductor production and optical lenses preparation. SiO_2 also improves the hardness of decorative coatings, provides them with anti-soiling properties and delivers high pigment dispersion [2,3]. The use of colloidal silica as a dispersant gives opportunity to prepare pigment dispersions without surfactants or other organic compounds. These substances can affect negatively the paint properties, i.e. large vulnerability to weather, occurrence of adverse foaming process, high affinity for dirt and deterioration of adhesion to the substrate. Small charged silica particles undergo adsorption on the pigment molecules, producing long-term stable dispersion, which has great light scattering efficiency (increase of paint hiding power).

Catalysis is a very important application of colloidal SiO_2 [4,5]. This is a component of many catalysts due to its well-defined surface area, particle size, high purity, high-temperature stability, mechanical strength and chemical inertness.

In water treatment technologies, silica is used as a destabilizing agent for removing undesirable components, i.e. macromolecular compounds, surfactants, inorganic impurities and many others [6–9]. It also improves dewatering efficiency of the removed precipitates.

Such huge variety of colloidal silica justifies the basic research on the properties of SiO_2 suspension, especially in the aqueous medium [10–12]. The essential issue for the colloidal system is its stability. It can be affected by many factors, among others: solution pH, type of supporting electrolyte and solid content. The influence of these factors on the colloidal silica stability is the subject of research in the present paper. Short (2 h) and long (18 days) periods of time were taken into consideration. This is very important because of need for a long-term storage of many products containing a dispersed solid. The effect of polymer addition (polyacrylic acid, polyvinyl alcohol, polyethylene glycol) was studied previously [13–16].

When two colloidal particles come close to each other at a distance allowing their interactions, there appear attraction and repulsion forces between them. Stability of the colloidal system depends on the ratio between these two types of forces. All the

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forces acting between the solid particles can be considered as interactions between the electric charges of individual atoms.

Attractive van der Waals forces between the molecules can be manifested in three possible ways, namely by interactions between: permanent dipoles (Keesom forces), dipole - induced dipole (Debye force) and electrically neutral molecules (London dispersion forces). All these forces are short-range type acting at the distances of a few tens of nanometers. In the case of colloidal particles built of 10^6–10^{10} atoms, all possible attractive interactions sum each other, so the interactions between colloidal particles have a much greater range (5–10 nm) in comparison to single atoms. Hamaker [17] developed description of attractive interactions between colloidal particles.

The source of repulsive forces are primarily the ones between the particles endowed with the same sign of the charge. Overlapping of their electrical double layers (edl) results in charge distribution and potential changes around both particles. Repulsive forces have a long range (5–10 nm). For this reason, both repellent and attractive interactions play a fundamental role in stabilization or destabilization of the colloidal systems.

In the present study stability of the aqueous suspension of silica was determined by the use of the turbidimetry method. The specialized software enabled detailed description of processes occurring in the examined sample by calculation of many parameters characterizing the system stability. For this reason, this method has a significant advantage in comparison to other measurement techniques.

Materials and methods

The colloidal silica (synthesized at the Chuiko Institute of Surface Chemistry, Kalush, Ukraine) was used in the study. The adsorbent has the BET surface area equal to $247\,\mathrm{m^2\,g^{-1}}$. It was determined from the low-temperature nitrogen adsorption-desorption isotherm using the ASAP (Accelerated Surface Area and Porosimetry System) 2405 analyzer produced by Micrometritics. Additionally, the size of solid particles was measured using high-resolution scanning electron microscope Quanta 3D FEG (FEI firm). The mean diameter of silica particles was 10 nm.

The series of solid suspensions in water and in sodium chloride (used as a supporting electrolyte) of the concentrations $1 \times 10^{-2}\,\mathrm{mole\,dm^{-3}}$ was prepared. Moreover, the stability experiments were performed at $25\,^\circ\mathrm{C}$ at five values of the solution pH ranging from 2.9 to 10.6. The suspension pH was adjusted using the pH-meter PHM 240 (Radiometer) with the accuracy ± 0.1. The HCl and NaOH solutions of the concentration $1 \times 10^{-1}\,\mathrm{mole\,dm^{-3}}$ were applied for this purpose.

The solid content in water suspension was 3%, whereas the systems with NaCl contained 3 and 13% of silica. Stability of the examined samples was monitored at specific intervals for 18 days. The stability parameters were calculated for the two specified times: 2 h and 18 days.

Stability measurements of the colloidal silica suspensions were carried out with Turbiscan Lab$^{\text{Expert}}$ with the cooling module TLAb Cooler (France). The collimated light beam ($\lambda = 880$ nm), passing through the investigated suspension, was emitted by the electroluminescence diode. Two synchronized detectors registered light passing through the probe and scattered by the solid particles. The first one (transmission detector) recorded light at the angle 0° in relation to the incident light direction, whereas the other one registered the light scattered at the angle 135°. The obtained data were stored and converted by computer programmes (TLab EXPERT 1.13 and Turbiscan Easy Soft).

The results were presented as curves (so-called scans) showing the intensities of transmission and backscattering as a function of the suspension level in the measurement vial for different times of experiment. The analyzed suspension in a glass vial (70 mm in length) was placed in a thermostated measurement chamber. The examined suspension was poured in this vial to 40 mm. The changes in the suspension stability were monitored for 18 days (single scans were collected every specified time intervals: 2 h, 23.5 h, 1d 23 h, 2d 23 h, 3d 23 h, 6d 23 h, 9d 23 h, 11d 23 h, 14d 23 h, 18d 3 h).

The transmission and backscattering data enable calculation of the stability coefficient TSI (Turbiscan Stability Index) and the diameter of aggregates (using Stokes law [18]). These parameters were obtained from the dependencies:

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

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

$$V(\phi,d) = \frac{\left|\rho_p - \rho_c\right|gd^2}{18v\rho_c} \cdot \frac{[1-\phi]}{\left[1 + \frac{4.6\phi}{(1-\phi)^3}\right]} \tag{2}$$

where v, particles migration velocity; ρ_c, continuous phase density; ρ_p, particle density; d, particle mean diameter; v, continuous phase dynamic viscosity; ϕ, volume fraction of dispersed solid.

The density and viscosity of continuous phases were measured using Density Meter and Rheometer, both produced by Anton Paar (United Kingdom).

The TSI values change in the range from 0 (high stability) to 100 (high unstability). The higher the TSI value is, the more unstable the system is.

Results and discussion

Schematic presentation of light transmission through stable and unstable suspension is placed in Fig. 1. As can be seen for stable sample, the light transmission through suspension is very low or even equal to zero. In the case of unstable system, the light transmission is high in the top clear layer and no transmission occurs in the dense sediment layer. In the middle layer of examined suspension the intermediate transmission is detected.

Figs. 2 and 3 present the exemplary transmission curves of the 3% SiO$_2$–NaCl system at pH 8.4 and 10.6, respectively. Along the x-axis is the level of suspension in the measurement vial – the value 40 mm is the mark to which the investigated suspension was poured in this vial. On the other hand, the transmitted light intensity (%) is along the y-axis. Each figure contains 11 color-coded scans, changing from blue ($T = 0$) through light blue (T about 2 h), to red (T about 18 days).

As can be seen in Fig. 1, the silica suspension in the supporting electrolyte at pH 8.4 is characterized by very high stability. It is evidenced by the extremely low transmission equal to 0%, practically in the whole range of measuring vial height. All scans perfectly overlap – the suspension is very stable in the whole examined period of time (after 18 h).

On the contrary, the same suspension at pH 10.6 shows certain unstability. The transmission reaches the 45% level. Moreover, the sediment layer of about 2.5 mm on the vial bottom was formed (low transmission in the range 0–6%). The thickness of sediment is equal to the width of the first peak. The individual scans are clearly spaced from each other. The first two obtained for $T = 0$ and T about 2 h (marked in blue and light blue, respectively) correspond to a very stable system. As time passes, stability conditions deteriorate