Production improvement of aqueous solutions of nanosized silica

P S Baskakov, V V Strokova*, E O Kuzmin
Belgorod State Technological University named after V.G. Shoukhov, 46, Kostyukova street, Belgorod, 308012, Russian Federation

E-mail: vvstroko@gmail.com

Abstract. The article deals with the method for obtaining aqueous solutions of silica nanoparticles based on sol-gel technology, namely, products of hydrolysis of silicon alkoxides and their polycondensation in an alcohol medium. In order to prevent polymorphic changes and dehydration of SiOH-groups, preference was given to low-temperature and vacuum methods. To combat the excessive foaming ability of surfactants and replace the solvent (alcohol with water), a method of distillation was proposed for partial supply of dry steam with air and water. To separate aqueous surfactant solution (tween-80), a method of oil flotation with petroleum ether addition, characterized by its low solubility, both in water and in alcohol, was proposed. The specifications of obtained nanosilica of aqueous solutions can be estimated using optical spectrophotometry, for which the concentration and size coefficients of the Geller Equation for this system were determined. The optimum concentration of SiO2 in the system was also determined when no particles above 100 nm were formed. Methods for the reagents reuse of ethanol, petroleum ether and tween-80 were proposed.

Introduction
During the synthesis of nanosilica by the sol-gel technology, the production of particles is accompanied by hydrolysis of silicon alkoxides and polycondensation in an alcohol medium. This leads to a further increase in alcohol concentration. In turn, when using synthesized nanoscale silica as a modifying component in the cement binder system, low-molecular diphilic organic compounds involved in the synthesis and remaining in the system slow down the process of structure formation of the cement stone and adversely affect the process of its strength.

To stabilize the nanoscale level of silica, a surfactant is added to the reaction mixture. In this study, polyoxyethylene (20) sorbitan monoaleate (TWIN-80) was used as a surfactant stabilizer. Being a non-ionic stabilizer of direct emulsions (HLB = 15–15.6), according to the Bancroft rule, it tends to settle in the hydrophilic medium of synthesized nanosilica. Presumably, this may allow the formation of bulk solvation shells that prevent aggregation on its surface. Unfortunately, this effect negatively affects the ability to hydrate cement minerals, which ultimately reduces the stone strength.

To minimize this effect, many researchers [1–4] apply two-stage thermal effects to spirit solutions of nanosilica with surfactant: drying (105 °C) and calcination (300–600 °C) at different exposure times. This can lead to interrelated morphological and polymorphic changes, which can be explained as a contribution of pressure due to the presence of surface stress and curvature of nanoparticles [5].
In the case of silica, this is manifested in the fact that the observed theoretical predictions of particle size do not agree with the observed experimental results [6]. An example is the study conducted on anatase (titanium dioxide), where the authors [7] had to apply additional pressure to nanocrystalline anatase to compensate for the internal pressure due to the nanoscale [8]. In turn, for silica nanoparticles, their polymorphism can be described as follows:

1. Conventional amorphous forms, consisting of elementary spherical particles of SiO$_2$, smaller than 100 nm in size, the surface of which is formed either from anhydrous SiO$_2$ or from SiOH groups. They are characterized as compressed dense solid particles insoluble in water [9].

2. Hydrated amorphous silica, in the structure of which all or almost all silicon atoms hold one or more hydroxyl groups. They are characterized by limited dissolution in water and strong swelling in an alkaline medium, which significantly increases the viscosity of solutions [10–11].

To preserve hydrated forms on the surface of silica, coagulate hydrocolloid structures and to prevent crystallization of large aggregates, it was decided to use non-thermal methods of cleaning nanosilica solutions from surfactants and alcohols. To do so, a special cleaning regime was selected, the first stage of which implied the replacement of the solvent (alcohol replaced with water) and further flotation separation of surfactants.

The classical method of replacing solvent is based on the separation of solute from the solution by replacing the solvent as a highly dispersed insoluble phase. The macromolecules of dissolved silica, which is in a state of molecular dispersion in ethanol, when they get into conditions of poor solubility (water) when changing the solvent, begin to condense into larger colloidal particles. It is impossible to achieve effective distillation of alcohol without a significant rise in temperature (above the boiling point) and strong shear forces with stirring.

For this purpose, a laboratory setup was assembled to distill ethanol under vacuum followed by condensation (refer with figure 1).

![Figure 1](image-url)  
**Figure 1.** A device for distillation under vacuum: 1 - reactor with an alcohol solvent of surfactants and nanosilica; 2 - Claisen nozzle; 3 - capillary; 4 - clamp for adjusting the air leaks and capillary; 5 - sealing rubber; 6 - tap to the vacuum system trap; 7 - prolong; 8 - receiving vessel.

The residual alcohol content in the solution was determined by the amount of condensate (by weight) in the flask and its concentration (refractometric analysis). The distillation had been carried out for 3 hours at a temperature of 60 °C and under a vacuum pressure of 1 kPa (refer with figure 2). A replacement solvent (water) was introduced with the air.
By reducing the alcohol concentration below 10% of the initial concentration (120-minute distillation), an intense foaming occurs due to the content of surfactant in the composition/mixture. The formed resistant foam is captured by the evacuated outlet with a cooler, as a result of which silica nanoparticles in a significant amount (up to 0.01% by mass) also enter the condensate. To solve these problems, it was decided to use a distillation method with direct dry steam supply with partial entrapping of air instead of the distillation method (refer with fig. 3). The temperature was reduced to 60 °C and was sustained mainly due to the heat transfer of steam.

This system made it possible to significantly reduce foaming, reduce foam trapping, and decrease the concentration of water in the alcohol condensate, which made it possible to use it again.

As a result, an aqueous solution was obtained with a concentration of nanosilica from 0.1 to 0.5%, containing 5–10% surfactant, defined as mass residues after final drying and roasting. The surfactant stabilizer used is characterized by the complex nature of surface activity (refer with Figure 4).

The surface tension of surfactant aqueous solutions was determined using a Kruss K100 processor tensiometer using the Wilhelmy plate method. The surface tension is calculated as a ratio of force expended when lifting the plate damped in the solution to the product of the length of the damped surface and the contact angle.
Figure 4. Effect of surfactant concentration in aqueous solution on surface tension (σ) and Gibbs surface adsorption

The surfactant surface adsorption curve in all cases shows several inflection points (maxima and minima), which may indicate compression of the adsorption layer, formation of folds, and polymolecular layers. This represents not so much a quantitative interest as a qualitative one expressed in the concentrations at which a change occurs in the orientation of the molecules in the interfacial layer. Since the Gibbs surface adsorption is an excess concentration, in the areas of concentration from 25 to 75 g/l, from 175 to 210 g/l and above 300 g/l, surfactants dissolve mainly in volume, binding and thickening water. The effectiveness of the aqueous solution thickening was estimated by the Huggins equation (1) according to the rotational viscometer data (Rheotest RN 4.1) when measuring the shear stress in the direction of increasing the shear rate from 0 to 160 s⁻¹.

\[
\frac{\ln \eta_r}{c} = [\eta] + \left( k' - \frac{1}{2} \right) [\eta]^2 c + \cdots
\]  

where, \( \frac{\ln \eta_r}{c} = \ln(\eta/\eta_0) \) is viscosity ratio; 
\( k' \) is Huggins parameter.

To simplify the approximation of viscosity versus concentration curves in a linear form \( y = ax+b \) (Fig. 5 a), it was decided to determine constant coefficients and variables in the following manner:

\[
y = \ln \eta_r/c; \ x = c/10; \ a = (k' - 0.5) [\eta]^2; \ b = [\eta].
\]

On the basis of the obtained data, it is possible to determine the Huggins coefficient \( k' = a/b^2 + 0.5 \). After the approximation and finding the coefficients \( [\eta] \) and \( k' \), the curve of function (2) was constructed, based on the previous equation (1):

\[
\eta = \eta_0 e^{(1-0.5)(k' - 0.5) [\eta]^2 c^2}.
\]

which allowed us to compare the experimental and model data (refer with fig. 5 b).

A negative characteristic viscosity ([\eta] = - 0.033) suggests a plasticizing effect at low molecular weights and concentrations. At the same time, the macromolecule itself appears as a globular formation, which is characterized by a value of the Huggins coefficient greater than 0.5 (\( k' = 2.42 \)).

For the removal of surfactants, it was decided to use the oil flotation method based on the different wettability of nanocarbon particles, solvent and surfactants. In connection with the established values of viscosity, Gibbs adsorption and reference HLB values, the optimum oil volume was determined.
with the close HLB value (10–12). The petroleum ether (refer with Table 1), which has an extremely low solubility in water and in ethanol, is relatively safe and has a low cost as such oil.

![Figure 5. The results of approximation (a) of viscosity dependence on the concentration of (b) surfactants](image)

**Table 1.** Specifications of petroleum ether grade 40/70.

| Indicator                          | Analysis result |
|-----------------------------------|-----------------|
| HLB                               | 10–12           |
| Density at 20 °C                   | 0.65 g/cm³      |
| Fractional composition: 95% is distilled at a temperature < | 70 °C           |
| Sulfur content                     | 0 %             |

The obtained nanosilica solution is mixed with oil, which is damped with oleophilic components (surfactants) and subsequently floats to the surface, while the oleophobic nanosilicon remains in solution, partially precipitated. Based on the studied parameters of viscosity, surface adsorption, difference in HLB values, the optimal volume concentration of petroleum ether in the emulsion was selected - 35%.

To emulsify the oil, a Silverson laboratory mixer with a cooling thermostat-circulator was used (refer with figure 6).
Figure 6. Laboratory setup for emulsion preparation by phase inversion method at a temperature

An aqueous solution of nanosilica with surfactant and oil added to it was placed in a tumbler glass, previously connected to a thermostat at 20 °C. Then dispersed at the maximum speed (10,000 rpm) to the constancy of turbidity (10 minutes). Then the solution was settled for 3 days until its complete separation. For intensification, a centrifugation can be applied at 3000 rpm, which will reduce the exposure time to 60 minutes.

A separated TWIN-80 solution can be cleaned from the petroleum ether by distillation of the latter at a temperature of 70–80 degrees (thermal resistance of TWIN-80 > 105 °C).

As a result of a comprehensive study of optical density (in wavelengths from 190 to 1100 nm), determination of dispersed composition using the method of laser Fourier diffractometry, final drying and roasting, the dependence of particle size and SiO2 concentration was determined (refer with fig. 7). The concentration of dilute working solutions (100x) was determined as a coefficient k from the Geller equation (3):

\[ \ln D = \ln k - \chi \ln \lambda \]  

where, \( \lambda \) is the wavelength, \( D \) is the optical density, \( \chi \) is the dimensional coefficient.

Figure 7. Dependence of the concentration of coarse and fine silica fraction on total SiO2 content in the solution
The coarse fraction was SiO$_2$, which scatters light at wavelengths $\lambda=540–740$ nm with an average particle size of $d=600$ nm. The fine fraction was nanosilicon with a particle size of up to $d=100$ nm, which scatters light at wavelengths $\lambda=305–340$ nm (refer with Fig. 8). For the latter, due to falling into the light range from $1/10$ to $1/3 \lambda$, it turned out to choose the dependence of the size coefficient $\chi$ and the actual particle size, obeying the equation $\chi=-0.0151d+3.3805$ (refer with Fig. 9). The small curvilinearity in small particle sizes is due to the proximity of the refractive indices of amorphous SiO$_2$ and water.

Summary
Thus, as a result of the study, a fundamentally new method was developed for obtaining aqueous solutions of silica nanoparticles. Besides, a hardware and technological design were selected. The following operations were involved into the process:

- obtaining alcohol solutions of nanosilica with surfactants using classical methods of sol-gel technology;
- distillation of alcohol under vacuum for 2 hours at a temperature of 60 °C, adding liquid water to dry steam;
–emulsification of the resulting solution with the petroleum ether (35% by volume) for 10 minutes while maintaining the temperature of 20 °C;
–oil flotation in natural conditions (3 days) or centrifugation at 3000 rpm - 60 minutes.

The obtained offal, such as distilled alcohol and a solution of surfactant in petroleum ether can be reused. Both concentration and particle size can be determined wisdom inexpensive and affordable means, such as a single-beam spectrophotometer, which supports measurements in the wavelength range from 305 to 740 nm. To optimize the increased yield of silica nanoparticles and prevent the release of coarse fractions, it is recommended to ensure the concentration of SiO₂ not higher than 0.15% by weight during rectification and further.

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