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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Regularities of the Change in Colloid-Chemical Properties of Silica Hydrosols in the Presence of Alkali Metal Hydroxides

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Abstract—The effect exerted by type of alkaline hydroxide additive on the change in turbidity and on the formation of silica hydrosol spatial structures was studied. Silica depolymerization in an alkaline solution to form active silicic acids was studied depending on the aging time of the system, size of sol particles, and the type of alkaline hydroxide additive.

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Over many decades silica hydrosols have aroused an ever-growing interest, which became especially pronounced in recent years owing to the development of sol-gel synthesis of materials used for various purposes. The sol-gel technology is the most suitable for silica-based materials. Readily accessible precursors of nanotechnology are solutions of alkali metal silicates and sols. Synthesis of silica sols from sodium silicate solutions is well known [1]. The processes proceeding in silica hydrosols in the presence of alkali metal hydroxides to form aqueous polysilicates or silicates have been studied to a lesser extent. Aging of silica in aqueous solutions at pH > 9, consisting in its intense dissolution and formation of singly charged anions ($H_3SiO_4^-$), and a reverse order of the alkali metal cations with respect to the sorption ability of silica gel at high pH values are well known [2, 3].

Subject under discussion is maximum on the zeta-potential vs. pH dependence [4], including that at small ionic strength (0.3 mmol l^{-1} KCl), and the shift of the isoelectric point (IEP) toward pH 5.0 for various types of silica, caused by specific effect of Cs^+, Rb^+, or K^+ cations [5, 6]. These findings show that the Cs^+, Rb^+, and K^+ ions are adsorbed non-specifically (non-electrostatically).

Among theories explaining a specific effect of cations on the amorphous silica properties, a concept [7] postulating formation of a gel layer upon silica depolymerization deserves a special attention [8, 9].

Virtually all aspects of the sol-gel technology of silica-based materials are determined by silica reactivity. Generalization of the above data suggests that interaction of alkali metal hydroxides with amorphous silica particles changes the structure of both a gel layer and a conjugate aqueous solution. In particular, presence of the Si–O–Si and Si–OH conjugated bonds affects kinetics of the colloid-chemical processes at various stages of passage of the sol to polysilicates or silicate solutions.

This study is concerned with the dissolution of colloidal silica particles in strongly alkaline solutions of lithium, sodium, and potassium hydroxides. The study was performed with the means of colorimetric analysis.

EXPERIMENTAL

Objects of study were silica hydrosols (Ludox AS-40 and Ludox HS-30) with the average particle size of 16 and 12 nm, respectively. The surface of sol particles was charged negatively. Ludox AS-40 was stabilized with ammonia**;** counterions in a double electric layer were ammonium ions and a minor amount of sodium ions. As a stabilizer of Ludox HS-30 served sodium hydroxide. The sols were diluted to a concentration of 41.02 g l^{-1} in all tests. The study was performed at the molal ratio (modulus value) $SiO_2/M_2O = 3$, where M is alkali metal cation (Na^+, K^+, or Li^+). Solutions of alkali metal hydroxides (chemically pure grade) were introduced into the sol upon agitation at a temperature of 298 K, which was

maintained constant. Test samples were taken beginning from the mixing of the system components. Change in the aggregative stability of the dispersion system was controlled by visual observations and by measuring the optical density at a wavelength of 540 nm. Sol turbidity τ was calculated by the relation $\tau = 2.3D/l$, where D is optical density and l, the thickness of a cuvette.

The concentration of active silicic acids was determined by the colorimetric analysis based on the reaction of silicic acids with ammonium heptamolybdate to give yellow colored β-silicon-molybdenum complex. Equation for the formation of silicomolybdic acid has the form:

$$7Si(OH)_4 + 12H_6Mo_7O_{24} \cdot 4H_2O + 2H_2O$$

$$\rightarrow H_8[Si(Mo_2O_7)_6] \cdot 28H_2O$$

The optical density at a wavelength of 400 nm was measured on a KFK-3 photoelectrocolorimeter. According to the literature data, the dependence of the optical density of a silicomolybdic acid solution on the initial concentration of SiO_2 may be nonlinear. Therefore, a calibration dependence of optical density on the concentration of dissolved silica was preliminarily constructed. To prepare the initial SiO_2 solution used for measuring a calibration curve, a specially pure SiO_2 (1 g) placed into a corundum crucible was dissolved in a 1 N NaOH solution (20 ml) at boiling temperature and then a distilled water was added to a total volume of 1^{-1}. After that, test solution (10 ml) was sampled from each of the prepared solutions and a 1N sulfuric acid was added to it to pH 2.5. From the initial solution ($c(SiO_2)$ = 1 g l^{-1}), aliquots (5, 10,...50 ml) were taken and a distilled water was added to V_{tot} = 50 ml to attain a necessary SiO_2 concentration. Then, test solution (10 ml) was sampled from each of the prepared solutions and the necessary amount of 1N sulfuric acid was added to it to pH 2.5.

Silicomolybdic acid of yellow color (silicon-molybdenum complex, SMC) is formed solely upon reaction with monosilicic acid. Therefore, the concentrations of a monomer and disilicic acids (active silicic acid) were estimated from the value of the optical density attained after 10 min of the color reaction using the calibration curve. In those cases, when the measured optical density went beyond the calibration curve, test solution was additionally diluted prior to the analysis.

The addition of alkali metal solutions to the sols leads to instantaneous formation of viscous suspensions in the

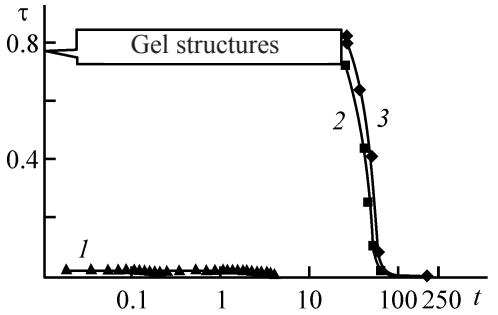

Fig. 1. Turbidity τ (cm^{-1}) of AS-40 hydrosol in the presence of alkali metal hydroxides vs. the aging time t (h). (*1*) KOH, (*2*) NaOH, and (*3*) LiOH; the same for Fig. 3.

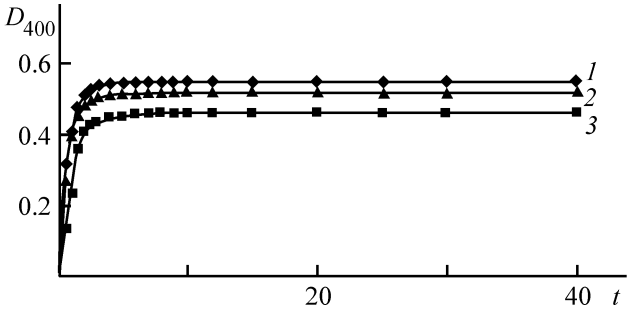

Fig. 2. Kinetic curves of growth of the optical density D upon formation of the β -silicon-molybdenum complex at various stages of aging of the system. (*t*) Time (min). Aging time: (*1*) 10 min, (*2*) 219.50 h, and (*3*) 456.25 h.

form of a white mass, which confirms sol coagulation. In the course of the aggregation, a gradual spontaneous dispersion (peptization) of the system, its clarification, and a decrease in the viscosity take place. Data characterizing a decrease in the sol turbidity in the presence of alkali hydroxide additives corresponding to the molal ratio SiO_2/M_2O = 3 are presented in Fig. 1. The analysis of the presented dependences shows that the turbidity of the systems under study decreases with time and the preliminarily formed aggregates decompose. However, the rate of this process depends on the type of alkali. For example, the time of attaining a deep clarification of the silicate system is approximately 1.5 h for the system containing potassium hydroxide, 22 h for that containing sodium hydroxide, and 40 h for that containing lithium hydroxide. Thus, the specific effect exerted by cations on the peptization process increases in the order $K^+ > Na^+ > Li^+$.

The colorimetric analysis was done on samples obtained after profound clarification of the sols. The comparison of the colorimetric analysis curves (Fig. 2) demonstrates a tendency of the optical density and the initial reaction rate to decrease as the aging time of the

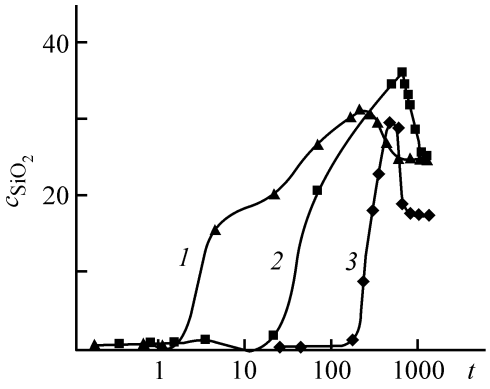

Fig. 3. Kinetic curves of growth of the active silicic acid concentration $c(SiO_2)$ (g l^{-1}) in silica hydrosol in the presence of alkali metal hydroxides. (*t*) Time (h); the same for Figs. 4, 5.

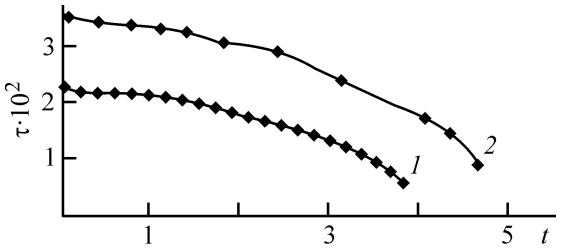

Fig. 4. Kinetic curves of change in the turbidity τ (cm^{-1}) of silica hydrosols containing (*1*) 16- and (*2*) 12-nm particles.

system is raised (from 10 min to 456.25 h). The results of the calorimetric analysis were used to calculate the concentrations of active silicic acid at the different aging stages of the system (Fig. 3). The kinetic dependences obtained show that the process passes several stages: after elapsing the induction period, the concentration intensely increases to the maximum value and then starts to decrease to a quasi-equilibrium concentration. The depolymerization of silica particles in an alkaline solution occurring via splitting of siloxane bonds (Si–O) and formation of a silanol group (Si–OH) causes silica to dissolve.

Breaking of siloxane bonds in the course of depolymerization increases silica reactivity, including that in reaction with sodium heptamolybdate. In the course of the aging of the system, the concentration of the active silica fraction increases in the order of alkaline hydroxides from LiOH to KOH (Fig. 3), i.e., in the order of increasing their basicity constants.

The time, at which the maximum concentration of active silicic acid is attained, is different for different sols (220, 530, and 695 h for sols containing KOH, NaOH, and LiOH, respectively). The concentration of active silicic

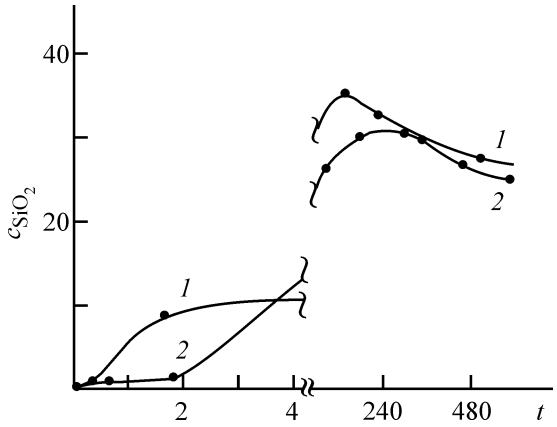

Fig. 5. Kinetic curves of change in the concentration of active silicic acid $c(SiO_2)$ (g l^{-1}) in silica hydrosols containing (*1*) 12- and (*2*) 16-nm particles.

acids first increases and then decreases. The maximum on the kinetic dependences is accounted for by conversion of silicic acids to higher order polymeric forms. On prolonged aging of the systems, quasi-equilibrium concentrations of the active fractions are established in the course of depolymerization (24.66, 25.40 and 17.39 g l^{-1} for LiOH-, NaOH-, and KOH-containing systems, respectively), which corresponds to 42.39, 61.53, and 60.12% of the total silica concentration. The fact that the above concentrations considerably exceed the values known for silica solubility shows that in the system aged for a long time, not only metal orthosilicate ions but also complex silicate anions containing silanol groups are formed in the course of polymerization and polycondensation in a liquid phase. The processes of coagulation-peptization and secondary polycondensation depend on the size of sol particles. For example, the initial turbidity of a KOH -containing sol (particle size 16 nm) is lesser than for a sol with 12-nm particles (Fig. 4). The rate of change in the concentration of active silicic acid during the initial aging period is also different, whereas the total run of the dependences for systems under study is the same (Fig. 5).

CONCLUSIONS

(1) The properties of colloidal silica in the presence of alkali metal hydroxides were studied. It was established that the type of alklaline hydroxide cation is one of the most important factors responsible for the colloid-chemical properties of hydrosols (aggregative stability in alkaline solutions and kinetics of depolymerization-secondary polymerization.

(2) The effect of alkali metal cations on the depolymerization and dissolution kinetics of the sol increases in the order $Li^+ < Na^+ < K^+$.

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