Regularities of Flocculation of Silica Hydrosol at Acrylamide Copolymers of the Magnaflok Brand

N. A. Shabanova, I. A. Belova, and M. N. Markelova

Mendeleyev University of Chemical Technology of Russia, Miusskaya pl. 9, Moscow, 125047 Russia
e-mail: irinabelova@yandex.ru
Received March 14, 2014

Abstract—The aggregative stability of binary mixtures of silica hydrosols of the Ludox TM brand and solutions of acrylic polymers of the Magnaflok brand have been studied by the methods of viscometry, turbidimetry, electrophoresis, and dynamic light scattering. A decrease in the aggregate stability of colloidal silica and conformational contraction of macromolecular coils with the introduction of the electrolyte leads to the formation of polymer–silica floccules. Flocculation of silica particles at macromolecules proceeds via the mechanism of heterocoagulation. When forming the hybrid polymer–silica particles, the aggregative stability of the dispersed systems grows, the coagulation rate decreases, and the time of gelation increases.

Keywords: silica hydrosol, polyacrylamide, aggregative stability, heterocoagulation, nanoparticles, flocculation, gelation

**DOI:** 10.1134/S1087659615050168

INTRODUCTION

In this work, the results of the study of sol–gel processes in the binary mixtures of colloidal silica and water-soluble acrylamide polymers of the Magnaflok brand (M-351 and M-3127) (Allied Colloids Limited, England) are presented. Nanochemistry opens up new opportunities for preparing composite materials from particles of the organic and inorganic nature of a core–shell type at least when using binary sols. Mixing nanocomponents of organic and inorganic nature, between which no covalent bonds are formed in an aqueous media, is the simplest way for obtaining hybrid nanocomposites. Mixed colloidal systems may contain particles of a different chemical nature with respect to their size and shape, magnitude and sign of the surface charge, and other characteristics. The stability of such dispersions is of interest from both the theoretical and applied points of view. The uniformity of the distribution of the components in a dispersed system depends on the aggregative stability and kinetics of coagulation of the sol and determines the morphology of the gels and properties of the materials. These issues are important in the technologies for the sol–gel synthesis of porous materials, as well as silicate glass and coatings, because water-soluble polymers often play the role of templates [1–4]. Processes occurring at the early stages of the mixing of the components of the system affect the properties of the final materials (films, powders, suspensions, ceramics, etc.) in many ways.

The extremely widespread application of silica hydrosols (colloidal silica) is determined by the polymeric structure of the particles and by the presence of a highly developed surface and functional (silanol) groups, which provides high reactivity and the possibility for the adsorption modification of the surface of the particles. The fact that a large variety of silica hydrosols are produced by international manufacturers is motivating. In this work, the choice of polymers is determined by the fact that aqueous solutions of polyacrylamide and its copolymers are most often used in the composition of various compounds [5–10].

EXPERIMENTAL

Commercially available silica hydrosol of the Ludox TM-40 brand (Grace Davison) was used in the work. The concentration of the initial sol was 510.0 g/L and NaOH served as the stabilizer. The ionic strength was provided using chemically-pure-grade sodium chloride. Acrylic copolymers of the Magnaflok brand (M-351 and M-3127) (Allied Colloids Limited Acrylic, England) with various degrees of hydrolysis and molecular masses were used in the work. Magnaflok M-351 is an acrylamide homopolymer with the structural formula

$$\left[-CH_2-\underset{\underset{CONH_2}{|}}{CH}- \right]_n.$$
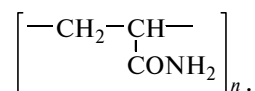
Magnaflok M-3127 is a partially hydrolyzed polymer (copolymer of acrylamide and sodium acrylate) with the structural formula

$$\left[\begin{array}{ccc} -CH_2-CH- & \cdots & -CH-CH_2- \\ | & & | \\ CONH_2 & & COONa \end{array} \right]_n .$$
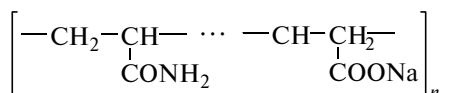
The commercial samples of the polymers were not preliminarily treated. Their characteristics were determined via the methods of viscometry and potentiometric titration.

The macromolecules are negatively charged in neutral and alkaline media due to the presence of the ionized $-COO^-Na^+$ groups. All measurements were carried out in the alkaline region of pH values (8.0–9.5).

The viscosity of the polymers, silica hydrosols, and their mixtures was determined on a VPZh-2 capillary viscometer with the diameter of the capillary of 0.86 mm at $25 \pm 0.1°C$. The relative error was less than 2.5%.

The time of gelation in the silica sol and binary mixtures was determined via the visual method by the loss in the fluidity [1].

The acid indices and hydrolysis rate of the polymers (the molar percents of hydrolyzed amide groups relative to their total concentration) were determined via the method of potentiometric titration on a pH-213 pH meter (Hanna) according to the standard procedure [11]. Solutions of 0.1 M KOH were used within pH values ranging from 2.5 to 9.0 at 20°C.

Dynamic light scattering was used for determining the hydrodynamic radius of the particles in silica hydrosols, polyacrylamide solutions, and their mixtures on a Zetatrac laser dynamic light scattering instrument (Microtrac Co.) with the wavelength of the impinging radiation of 780 nm and scattering angle of 180° at 25°C; the measurement time was 90 s. The refractive index of the liquid phase corresponded to the refraction of distilled water of 1.333 and was 1.49 for the particles of the M-351 polymer and 1.46, for SiO₂.

The size of the particles of silica sol determined via the method of potentiometric titration (Sears method) was 22.0 ± 0.6 nm [12].

The electrophoretic mobility of the sols was determined via the method of moving the boundary in a *U*-shaped cell according to the standard procedure [2]. The solution of NaCl, which corresponded to the sol under study with respect to the electric conductivity and pH value, was used as the coupling fluid. Table 1 shows the examples of the electrokinetic potentials of the sol particles calculated according to the Helmholtz−Smoluchowski equation, taking into account the Wiersema−Loeb−Overbeck corrections for the polarization of particles under electric field [13]. The relative error did not exceed 5%.

Table 1. The effect of the electrolyte on the electrokinetic potential of silica hydrosol ($C_{SiO_2} = 4.0$ g/L)

	Concentration of NaCl, M			
	0.01	0.05	0.1	0.15
$-\zeta$ potential, mV	36.0	36.0	24.0	12.0

Silica of the Ludox TM-40 brand.

RESULTS AND DISCUSSION

It was demonstrated earlier that the viscosity of the solutions of polyacrylamide of the Magnaflok M-351 brand grows almost linearly up to the concentration of ~0.4 g/L. In the case of the partially hydrolyzed polymer (Magnaflok M-3127), this dependence is exponential [8]. As shown in Fig. 1, the electrolyte has an insignificant effect on the viscosity over the concentration of the solutions of polyacrylamide (Magnaflok M-351) ranging from 1.0 to 2.5 g/L. The viscosity of the solution of the M-3127 copolymer decreases notably and reaches the minimum value when the concentration of sodium chloride increases above 0.2 M (see Fig. 1, curve *5*).

The effect of the electrolyte on the viscosity is determined by the polyelectrolyte effect because the molecules of hydrolyzed polyacrylamide contain amide and carboxylic functional groups, thus forming negatively charged macroions and low-molecular-mass counterions. Adding an electrolyte to the solution of the polymer results in a decrease in the dissociation rate of the ionogenic groups, a change in the conformation of macrocoils, their contraction, a
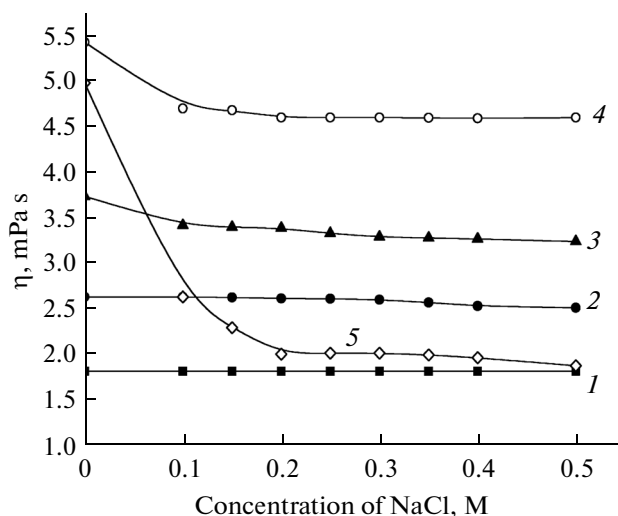

Fig. 1. The effect of NaCl on the apparent viscosity of the solutions of the polymers at the concentration of M-351 of (*1*) 1.0, (*2*) 1.5, (*3*) 2.0, and (*4*) 2.5 g/L and (*5*) at the concentration of M-3127 of 0.25 g/L.

Table 2. Characteristics of polymers

	Polyacryl-amide M-3127	Polyacryl-amide M-351
Hydrolysis rate, %	32.00	0.04
Acid index, mg/g	25 200	700
Intrinsic viscosity [η], dL/g	10.5	3.4
Molecular mass $M \times 10^{-6}$, Da	25.1	3.4
Size of macrocoils d, nm	105	32

decrease in the hydrodynamic volume, and, hence, a decrease in the viscosity of the system.

The viscometric studies were used to obtain the hydrodynamic characteristics of the macromolecules in the aqueous medium. The intrinsic viscosity [η] was determined based on the Huggins equation [14]. For suppressing the electroviscous effect, the measurements of the viscosity were conducted in a 0.5 M solution of NaCl. The viscosity average molecular mass M_η of the polymers was calculated according to the Mark–Houwink–Kuhn equation [15, 16]:

$$[\eta] = K_M M_\eta^\alpha$$

at the values of the constants $K_M = 1.05 \times 10^{-3}$ and $\alpha = 0.54$ at 25°C [15]. The concentration range of the polymers was chosen based on the rheological studies on an Ubbelohde viscometer. In the presence of 0.5 M NaCl, the solutions of M-351 and M-3127 polymers belong to Newtonian fluids within the area of concentrations below 0.7 and 0.3 g/L, respectively. The sizes

Fig. 2. The effect of the concentration of NaCl on the apparent viscosity of the solution of (*1*) M-351, (*2*) SiO$_2$ sol, (*3*) freshly prepared M-351 polymer–sol binary mixture, and (*4*) binary mixture after the three-week ageing. $C_{SiO_2} = 65.0$ g/L and $C_{polymer} = 1.0$ g/L.

of the macrocoils d were estimated according to the formula

$$\left[\frac{d^2}{4}\right]^{3/2} = \frac{[\eta]M}{F},$$

where F is the Flory universal viscometric constant of 2.0×10^{24} mol^{-1}. Since the constants of the Mark–Houwink–Kuhn equation depend on multiple factors (the molecular mass of polymers, hydrolysis rate, concentration of electrolyte, and temperature), the choice of the constants affects the calculation of the viscometric parameters of the macrocoils to a considerable extent, which is why the data obtained should be considered as relative (see Table 2).

The macrocoils of polyacrylamide are fairly condensed in the aqueous medium due to the formation of intramolecular hydrogen bonds. The formation of polymolecular layers of water on the peripheral segments of the macrocoils is accompanied by their liophilization. The presence of negatively charged anions promotes the destruction of the system of hydrogen bonds and expansion of the macrocoils of the polymers. The sizes of the macrocoils of the studied polymers increase with the growth in their molecular mass and hydrolysis rate (the anionic character of the polymer). The molecular mass of the M-3127 polymer is higher approximately by a factor of eight than the corresponding value of M-351 low-hydrolyzed polyacrylamide, while the diameters of the macrocoils differ more than threefold. The studied polymers differ not only by their molecular masses but also by acid indices and, respectively, the hydrolysis rate of the amide groups, which is 0.04% for M-351 and 32.0%, for M-3127. This means that the macromolecules of both polymers contain carboxylic groups capable of dissociating in an alkaline medium, which imparts a negative charge on the polymer chains. The low hydrolysis rate indicates that Magnaflok M-351 is represented by acrylamide homopolymers.

The differences in the hydrodynamic properties manifest themselves through the particularities of the change in the viscosity of the solutions of the polymers in the case of the addition of an electrolyte.

Figure 2 presents the dependences of the viscosity of the solutions of polyacrylamide (curve *1*), silica sol (curve *2*), and the binary mixture (curves *3* and *4*) on the concentration of sodium chloride. The measurements were performed over 1 h after adding the electrolyte. In the absence of the electrolyte, the viscosity of the initial solution of polyacrylamide is higher than the viscosity of the sol (curves *1* and *2*); however, the viscosity of the binary mixture of the silica sol and polyacrylamide (curve *3*) is higher than the viscosity of the initial sol (curve *2*) but lower than the viscosity of the solution of the polymer (curve *1*). One can note the decrease in the viscosity at low concentrations of NaCl (curve *3*) or in its absence (points on the *y* axis). At the concentration of the electrolyte above 0.2 M, the vis-
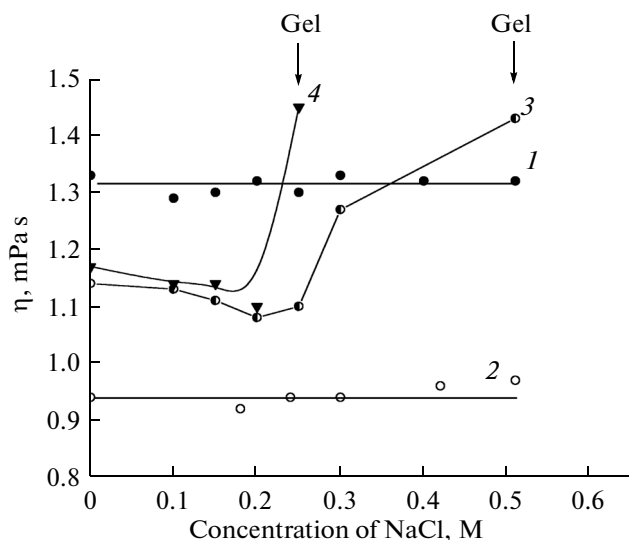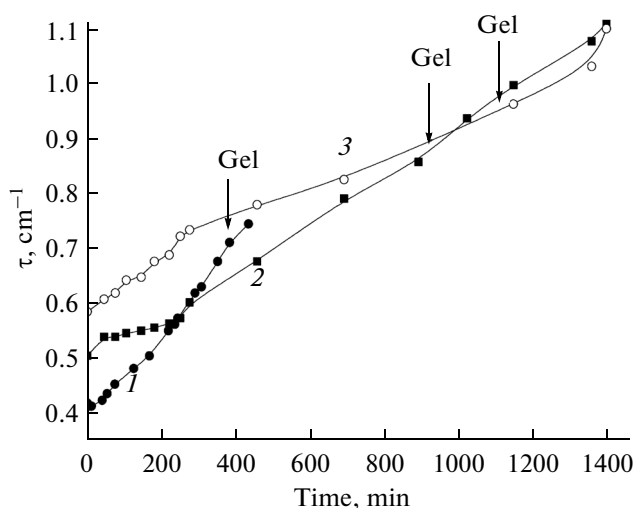
Fig. 3. Kinetics of the change in the turbidity: (*1*) SiO$_2$ sol, (*2*) SiO$_2$ sol + NaCl + M-351 polymer, and (*3*) SiO$_2$ sol + NaCl + M-3127 polymer. $C_{SiO_2} = 258.6$ g/L, $C_{NaCl} = 0.2$ M, and $C_{polymer} = 0.01$ g/L.

Fig. 4. The effect of the concentration of the sol on the electrophoretic mobility in the presence of polyacrylamide. The concentration of M-351 is (*1*) 0, (*2*) 0.001, and (*3*) 0.01 g/L.

cosity of the binary system grows sharply and a fluidity loss occurs. After three days, the position of the viscosity minimum shifts towards the smaller concentration of the electrolyte (see Fig. 2, curve *4*).

The kinetic dependences of the change in the turbidity are obtained both for the initial concentrated sol (see Fig. 3, curve *1*) and for the mixtures of the sol with the polymers (Fig. 3, curves *2* and *3*) in the presence of 0.2 M sodium chloride.

The turbidity of the binary system changes immediately after mixing the components of the system. The changes in the viscosity and the growth in the turbidity of the dispersed systems over time are signs of the aggregation of the particles. It should be kept in mind that the growth in the turbidity in the case of the addition of the electrolyte is determined by the decrease in the aggregative stability of alkaline sols as a result of the ion exchange and dehydration of the surface layer. However, in the presence of polymers, the rate of the growth in the turbidity becomes lower than the rate of turbidization of the initial silica sol. In addition, the gelation in sols containing polymers occurs on reaching close values of turbidity, i.e., during the formation of a critical mass of large particles in the system. The obtained regularities can be explained by the flocculation of silica particles in the polymer resulting in the formation of polymer–silica associates. Such a conclusion also follows from the data of the electrophoresis.

In the case of an increase in the concentration of the polymer, the electrophoretic mobility of the particles in the binary system decreases (see Fig. 4). Here, the viscosity of the solution of the M-351 polymer within the specified range depends slightly on the con-
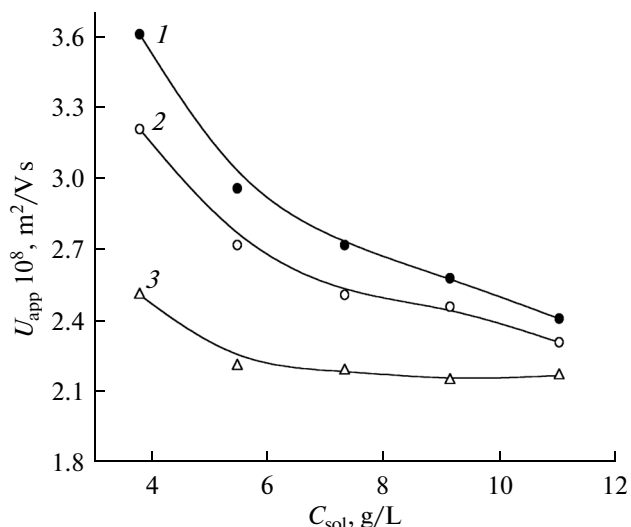
centration. Therefore, the decrease in the electrophoretic mobility can result from the flocculation and shielding of the charge of the surface of silica particles with the macromolecules. The macromolecules lyophilize the silica particles, which results in a slowdown in the coagulation process and an increase in the time of gelation (see Fig. 5).

Summarizing the data obtained, the following can be noted. The studied systems are the mixtures of two sols differing with respect to both the nature of the dispersed phase and character of the aggregative stability.
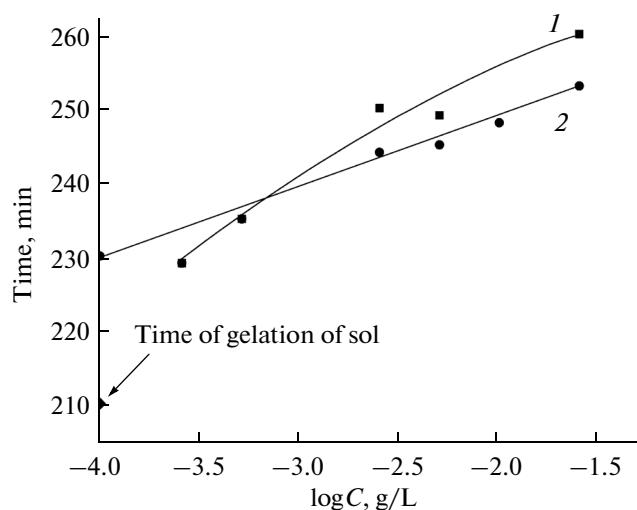

Fig. 5. The effect of the concentration of the polymers on the time of gelation: (*1*) M-3127 and (*2*) M-351. $C_{SiO_2} = 340.0$ g/L and $C_{NaCl} = 0.05$ M.
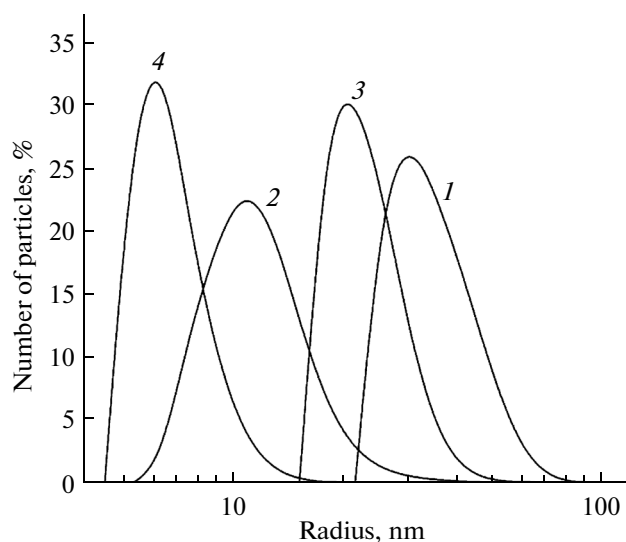
Fig. 6. Differential curves of the number average particle radius distribution: (*1*) M-351 polymer, (*2*) SiO$_2$ hydrosol, (*3*) SiO$_2$ hydrosol + polymer, and (*4*) SiO$_2$ hydrosol + polymer after one week. C_{SiO_2} 65.0 g/L and C_{M-351} 2.0 g/L.

Silica hydrosols are highly lyophilized but, nevertheless, lyophobic (thermodynamically unstable) dispersed systems, whose aggregative stability is determined by the structure and properties of the surface layers. In the presence of an electrolyte, the aggregative stability of the alkaline silica hydrosol decreases, first of all, because of the compression of the electrical double layer and a decrease in the value of the ζ potential (see Table 1).

The solutions of the polymers belong to a class of lyophilic (thermodynamically stable) dispersed systems, whose heterogeneity is provided by the ability of the macromolecules to be in the state of macrocoils, the sizes and conformation of which change continuously depending on the properties of the medium.

The formation of hybrid associates (floccules) retaining the aggregative stability for a long time is possible in binary sols.

As shown in Fig. 6, the curves of the average number of the particle distribution in the initial systems have a monomodal character. The average value of the hydrodynamic radius of the polyacrylamide macrocoils is ~25 nm, while that of the silica particles is ~10 nm. Close results were also obtained for the volume average particle distribution (see Table 3). The monomodal character of the particle distribution is retained in the binary systems but the shift of the maximum towards a more highly dispersed sol can be noted. This trend strengthens after the ageing of the mixed system (see Fig. 6, curve *4*) and indicates the occurrence of flocculation.

In the presence of an electrolyte, the average radiuses of the particles in the binary system grow with the increase in the ionic strength; here, the monomodal distribution is only observed for the average number of values (see Table 3). In the case of average volume values, three fractions with the average values of the radiuses of 52, 390, and 1540 nm are observed.

As shown in Table 3, the increase in the concentration of NaCl in the silica hydrosol results in an increase in the average radiuses of the particles in the binary system and has no effect on the radiuses of the polyacrylamide macrocoils.

It is difficult to explain the regularities of the formation of floccules in binary systems from the viewpoint of the "bridge bond" theory or expelling mechanism [17]. The more so, as binary sols are nanodispersed systems, in which the sizes of the polymer macrocoils are comparable to or severalfold large than the size of silica particles.

It has been assumed earlier that heterocoagulation is the limiting stage of the flocculation in binary sols [9]. Heterocoagulation is provided by intramolecular attraction forces under the conditions of a decrease in the electrostatic repulsion of silica particles and macromolecular coils. The addition of the electrolyte leads to a change in the properties of the polymer solution (to a reduction in the electroviscous effect and a decrease in the viscosity of the polymer solution, contraction and compaction of the polymer macrocoils, and a decrease in the dissociation rate of the ionogenic

Table 3. Average hydrodynamic radius of the particles in SiO$_2$ sols, solutions of polyacrylamide, and their mixtures

Composition	Average radiuses of the particles, nm	
	MV—volume average distribution	MN—number average distribution
M-351 (1.0 g/L)	25.1 ± 0.3	20.3 ± 0.4
M-351(1 g/L)+ NaCl (0.1 M)	24.6 ± 0.7	19 ± 1.0
Ludox TM-40 (65.0 g/L)	11.1 ± 0.1	8.90 ± 0.05
Ludox TM-40 (65.0 g/L) + NaCl (0.1 M)	24.1 ± 0.7	19.2 ± 0.1
Ludox TM-40 (65 g/L) + M-351 (1.0 g/L)	15.4 ± 0.2	12.10 ± 0.05
Ludox TM-40 (65 g/L) + M-351 (1.0 g/L) + NaCl (0.3 M)	52; 390; 1540	45 ± 5.0

groups). At the same time, the aggregative stability of the alkaline hydrosol decreases during the addition of the electrolyte, which is associated with the ion exchange process and dehydration of the surface layer. All this promotes the heterocoagulation and formation of hybrid polymer−silica associates (floccules). A similar process was considered earlier in the colloidal silica−polystyrene latex systems [18−20]. Macromolecules lyophilize silica particles, which results in the decrease in the rate of coagulation. The mobility of the segments of the macromolecular coils promotes the structural rearrangement of the floccules and encapsulation of silica nanoparticles into a nanodispersed polymer matrix.

CONCLUSIONS

The colloidal nature of the solutions of polymers as lyophilic sols should be taken into account when considering the properties of polymer-containing dispersed systems. Under certain conditions, heterocoagulation, resulting in the formation of hybrid particles, can be the limiting stage of the interaction between macromolecules and particles of a different nature.

REFERENCES

1. Shabanova, N.A. and Sarkisov, P.D., *Zol'−gel' tekhnologiya. Nanodispersnyi kremnezem* (Sol−Gel Technology: Nanodispersed Silica), Moscow: BINOM Laboratoriya Znanii, 2012.

2. Shabanova, N.A., Popov, V.V., and Sarkisov, P.D., *Khimiya i tekhnologiya nanodispersnykh oksidov: Uchebnoe posobie* (Chemistry and Technology of Nanodispersed Oxides: A Higher Shool Textbook), Moscow: IKTs Akademkniga, 2006.

3. Moshnikov, V.A., Tairov, Yu.M., Khamova, T.V., and Shilova, O.A., *Zol'−gel' tekhnologiya mikro- i nanokompozitov: Uchebnoe posobie* (Sol−Gel Technology of Micro- and Nanocomposites), Shilova, O.A, Ed., St. Petersburg: Lan', 2013.

4. Gavrichev, V.D., Dmitriev, A.L., Anfimova, I.N., Kotova, E.I., Nikushchenko, E.M., and Antropova, T.V., Temperature sensors based on silicate porous glasses impregnated by organic compounds, *Glass Phys. Chem.*, 2014, vol. 40, no. 3, pp. 288−290.

5. Junto Ma, Ping Cui, Lin Zhao, and Ronghua Huang, Synthesis and solution behavior of hydrophobic association water-soluble polymers containing acrylalkyl group, *Eur. Polym. J.*, 2002, vol. 38, no. 8, pp. 1627−1633.

6. Ke Yang-Chuan, Wei Guang-Yao, and Wang Yi, Preparation, morphology, and properties of nanocomposites of polyacrylamide copolymers with monodisperse silica, *Eur. Polym. J.*, 2008, vol. 44, no. 8, pp. 2448−2457.

7. Schmidt, G. and Malwitz, M.M., Properties of polymernanoparticle composites, *Curr. Opin. Colloid Interface Sci.*, 2003, vol. 8, no. 1, pp. 103−108.

8. LeBaron, P.C., Wang, Zh., and Pinnavaia, Th.J., Polymer-layered silicate nanocomposites: An overview, *Appl. Clay Sci.*, 1999, vol. 15, nos. 1−2, pp. 11−29.

9. Shabanova, N.A. and Belova, I.A., Regularities of associate formation between water-soluble polymers and colloidal silica at early stages of sol−gel processes, *Glass Phys. Chem.*, 2012, vol. 38, no. 2, pp. 254−257.

10. Shabanova, N.A., Belova, I.A., and Markelova, I.A., Influence of the aggregation activity of binary salts of silica and polymers on the formation of hybrid nanoparticles, in *Tezisy dokladov XXII Vserossiiskogo soveshchaniya po neorganicheskim i organosilikatnym pokrytiyam, Sankt-Peterburg, 2014* (Abstracts of Papers of the XXII All-Russian Conference on Inorganic and Organosilicate Coatings), St. Petersburg: Lema, 2014, pp. 12−13.

11. Losev, I.P. and Fedotova, O.Ya., *Praktikum po khimii vysokomolekulyarnykh soedinenii* (Practical Works on the Chemistry of High-Molecular Compounds), Moscow: Goskhimizdat, 1962.

12. Sears, G.W. Jr., Determination of specific surface area of colloidal silica by titration with sodium hydroxide, *Anal. Chem.*, 1956, vol. 28, no. 12, pp. 1981−1983.

13. Wiersema, P.H., Loeb, A.L., and Overbeek, J.Th., Calculation of the electrophoretic mobility of a spherical colloid particle, *J. Colloid Interface Sci.*, 1966, vol. 22, no. 1, pp. 78−99.

14. Huggins, M.L., The viscosity of dilute solutions of long-chain molecules: IV. Dependence on concentration, *J. Am. Chem. Soc.*, 1942, vol. 64, no. 11, pp. 2716−2718.

15. Morawetz, H., *Macromolecules in Solution*, New York: Wiley Interscience, 1965. Translated under the title *Makromolekuly v rastvore*, Moscow: Mir, 1967.

16. Klein, J. and Conrad, K.-D., Molecular weight determination of poly(acrylamide) and poly(acrylamide-cosodium acrylate), *Macromol. Chem. Phys.*, 1978, vol. 179, no. 6, pp. 1635−1638.

17. Von Napper, D.H., *Polymeric Stabilization of Colloidal Dispersions*, New York: Academic, 1983. Translated under the title *Stabilizatsiya kolloidnykh dispersii polimerami*, Moscow: Mir, 1986.

18. Verezhnikov, V.N., Sergeeva, M.N., Shabanova, N.A., and Poyarkova, T.N., Investigation of the aggregation activity of mixtures of polystyrene latex and silica hydrosol using the photon correlation spectroscopy method, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2008, vol. 51, no. 9, pp. 56−58.

19. Shabanova, N.A. and Sergeeva, M.N., Aggregative stability and structure formation in binary mixtures of synthetic latex and silica hydrosol, *Russ. J. Appl. Chem.*, 2011, vol. 84, no. 8, pp. 1422−1425.

20. Sergeeva, M.N., Shabanova, N.A., and Verezhnikov, V.N., Specific features of the preparation of hybrid nanocomposites based on synthetic latexes and colloidal silica, in *Uspekhi v khimii i khimicheskoi tekhnologii: Sbornik nauchnykh trudov. Tom. XXI* (A Collection of Scientific Works: Advances in Chemistry and Chemical Technology: Volume XXI), Moscow: D.I. Mendeleyev University of Chemical Technology of Russia, 2007, no. 4 (72) pp. 26−30.

Translated by E. Boltukhina