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Influence of Iron Cations on Tetraethoxysilane Hydrolysis and Gelation Process

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Abstract—The influence of small additives of Fe^{3+} ions on tetraethoxysilane hydrolysis and subsequent polycondensation of products has been studied by the viscometry and dynamic light scattering methods. Experiments have been carried out at 50°C. Hydrolysis has been carried out at pH 1.5, 2.5, 5.0, or 7.0. The amount of the dopant cations has been varied from 1.5 to 3.8 at %. In the absence of the dopant cations, the gelation time grows with increasing pH from 1.5 to 5.0, while polycondensation occurs without gelation at pH 7.0. If the dopant is added at pH 1.5, the gelation time increases, but, at pH 2.5 and 5.0, it decreases. The gelation time increases with the dopant content at all three pH values. The size of the particles formed during the polycondensation process depends on the pH and the amount of the dopant. The smallest particles with a median diameter of about 10 nm are formed at pH 2.5. It is assumed that the cause of all observed effects is the incorporation of iron cations into the siloxane matrix. The degree of the incorporation depends on the degree of iron cation hydrolysis. This assumption is confirmed by the values of the electrokinetic potential of the studied systems and the dynamics of variations in the zeta-potential with varying pH and dopant content.

Keywords: tetraethoxysilane, hydrolysis, polycondensation, iron ions, gelation time, particle size, incorporation of iron into the siloxane framework

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INTRODUCTION

The sol–gel synthesis of silicas has found wide application, because it provides the feasibility of regulating the properties of resulting products and can be employed to produce diverse functional materials [1]. One of the most widely used precursors for the sol–gel synthesis of silicas is tetraethoxysilane (TEOS). TEOS hydrolysis followed by the polycondensation of orthosilicic acid monomers under various conditions has been studied in detail [2]. The characters of the hydrolysis and polycondensation processes, as well as the structure of gels produced from TEOS, depend on the hydrolysis pH. As a rule, three pH ranges characterized by different regularities of the polycondensation are distinguished: rather frequently, the process appears to be specific in the metastable range of pH < 2; acidic hydrolysis followed by the formation of siloxane bonds occurs at pH 2–7, and silica particles grow without gelation at pH > 7 [3].

The problems concerning the effects of dopants on the hydrolysis process, silica formation, and the properties of the resulting products are occasionally studied for more than 30 years; however, there is no unambiguous opinion about the action mechanism of the additives to date. In [4], the influence of eight cations with different charges on the time and activation energy of gelation was studied, and it was, for the first time, found that these parameters of the process increased drastically in the presence of Cu^{2+}, Al^{3+}, La^{3+}, and Y^{3+}, while Li^+, Na^+, Mg^{2+}, Ca^{2+}, and Sr^{2+} reduced the gelation time but had no effect on the activation energy. The author explained the observed difference by either participation or nonparticipation of metal ions in the formation of the three-dimensional network of a gel during polycondensation: the cations of the first group were capable of forming metal–oxygen tetrahedrons and incorporating them into the silicon–oxygen matrix, while the cations of the second group were incapable.

Iron cations in the tetrahedral coordination are known to be incorporated into the silicon–oxygen matrices. This fact has been known for rather a long time as applied to various zeolite structures [5]. Moreover, there are evidences for the incorporation of iron ions having the tetrahedral coordination into silicas. For example, the authors of [6] used a set of methods to obtain silica doped with iron cations in the tetrahedral coordination. In recent work [7], the incorporation of iron–oxygen tetrahedrons into silica was confirmed with the help of X-ray absorption spectroscopy. At the same time, it was shown that the introduction of an iron(II) salt (which was oxidized during the process) accelerated the gelation process in the course of alkaline TEOS hydrolysis [8]. In the authors' opinion, iron ions catalyzed the polycondensation process.

Subsequent studies of diverse dopants were devoted to specific silica materials (amorphous nanoparticles [9], thin films [10], etc.) and were, to a substantial extent, focused on their properties (particle sizes, film uniformity, etc.). However, they also confirmed the ability of dopants to affect the aggregative stability and gelation time of TEOS-based systems. It was found that the incorporation of multicharged metal cations (strontium, lead, cobalt) into TEOS-based sols can accelerate their gelation [10]. Such effect is also inherent in inorganic salts of platinum and palladium [11]. To explain the observed phenomena, the authors of the aforementioned works assumed that the presence of the additives decreased the degree of the hydration of silica sol particles and facilitated the approach of the particles by changing the viscosity of the obtained sols.

Previously, our research group studied the influence of a wide spectrum of single-, double-, and triple-charged metal cations on the acidic hydrolysis of TEOS at pH < 1 [12]. The effect of the addition of the cations on the rheological properties manifested itself as an increase in the lifetime of a stable sol, which precedes the formation of a gel network for the majority of the studied cations, including iron(III) cations. An exception was Ni^{2+} cation.

The goal of this work was to study in detail the effect of iron(III) additives on the sol–gel process accompanying TEOS hydrolysis at different pH values. The interest in the products of this process, i.e., iron-containing silicas, is, primarily, due to the prospects of their application as biomaterials for the targeted drug delivery in an organism and contrasting images in the course of diagnostics. Moreover, iron present in silicas increases the biodegradability of these materials [13–15]. In the literature, there are evidences that silicas doped with iron compounds are also used in other fields. For example, the authors of [16] described the use of coatings obtained by the sol–gel method on the basis of TEOS and iron oxide nanoparticles for the preplant treatment of seeds with the aim of stimulating the plant growth and increasing the resistance to pathogens.

EXPERIMENTAL

Silicas were obtained by hydrolyzing TEOS of the extrapure grade in the presence of iron(III) ions, with iron(III) nitrate nonahydrate (reagent grade) serving as a source of the ions. The process was implemented in a water–alcohol solution. All samples were obtained by mixing the main components in TEOS : ethanol : water molar ratios of 1 : 4 : 16. The amounts of the iron salt added to the reaction mixture were calculated in a manner such that the iron contents in the final dry doped silicas were 1.5, 2.3, and 3.8 at %, which, being recalculated for iron(III) oxide, corresponded to 2, 3, and 5 wt %, respectively. Hydrolysis was carried out at 50°C and pH values of 1.5, 2.5, 5.0, and 7.0. The temperature was selected proceeding from the previously determined temperature dependences of the rates of the hydrolysis and polycondensation in TEOS-based systems [12]. Necessary pH values were reached using a 0.1 M nitric acid solution and a 0.01 M ammonium hydroxide for strongly and weakly acidic pH values, respectively.

The dynamics of variations in the viscosity during hydrolysis/polycondensation of the considered systems was monitored using an SV-10 oscillatory viscometer. After all precursors were mixed and a necessary pH value was reached, the mixture was placed into a quartz cell, and the measuring plates of the viscometer were immersed into the mixture. The measurements were carried out beginning from the moment of reaching the required pH value to the complete transformation of the mixture into the gel.

The aggregation/disaggregation processes of particles accompanying the hydrolysis and polycondensation reactions were studied by dynamic light scattering using a ZetaSizer Nano ZS instrument. The dynamics of variations in the particle sizes during the hydrolysis and polycondensation reactions was measured at 50°C every 10 min from the moment of reaching a required pH value to the moment of the complete transformation of the mixture into the gel. In this case, the intensities of laser beam reflections from particles with different hydrodynamic radii were recorded. Such representation of the measurement results makes it possible to record particles with sizes of at least 1 nm. The electrokinetic potentials of the samples annealed at 600°C were also measured with the ZetaSizer Nano ZS instrument. In order to ensure the constant electrical conductivity of the system, a 0.1 M potassium chloride solution was used as a dispersion medium.

All synthesized samples were analyzed by the FTIR spectroscopy method. The IR transmission spectra were recorded with an FSM 2201 FTIR spectrometer. The samples were prepared by pressing a 1 : 0.04 mixture of potassium bromide with silica, respectively.

RESULTS AND DISCUSSION

When hydrolyzing TEOS in the absence of the iron salt as a dopant, the system had initially (immediately after mixing of the precursors but before reaching a selected pH value) a two-phase structure with a distinct interface between the liquid phases. After acidification to pH ~ 2.65 and below, a one-phase system was formed and retained its homogeneity until the onset of its transformation into a gel. In the experiments performed at pH 5.0 and 7.0, the system retained its two-phase structure. Stirring led to the formation of an emulsion, which remained to be stable for 10–20 min during the first 6–10 h; then the stability of the emulsion increased, and, by the onset of the aggregation processes, it reached 90–120 min.

It is essential that, in the experiments carried out in the presence of the dopant cations, the reaction systems remained to be one-phase until the onset of the transformation into a gel at all studied pH values.

To estimate the effect of the dopant on the rheological properties of the systems during the polycondensation of the TEOS-based gels at different pH values, variations in the viscosity with time were recorded. Similar curves were obtained for time variations in the viscosity at three pH values. An exception was pH 7.0, at which the sol–gel transition occurred almost instantaneously upon reaching the preset pH value. For all other pH values, the viscosity at the initial stage varied slowly from 2 to 8–12 mPa s. This metastable state lasted from 1 to nearly 10 h depending on pH. Then, a sharp step occurred in the viscosity, and the gel formation became visible. The time of the onset of the intense increase in the viscosity was denoted as the gelation time. Viscosity value of 400 mPa s was conventionally taken as the point of the complete gel formation. The data obtained reflect the difference in the mechanisms of TEOS hydrolysis occurring at different pH values. It is known that, at low pH values, the rate of the polycondensation exceeds the rate of the hydrolysis [17]. In this case, the gel structure is formed by long polysiloxane chains, while the degree of polymer crosslinking is low [1, 17, 18]. Seemingly, the contribution of the hydrolysis via the alkaline mechanism becomes noticeable already at pH 5.0, with this mechanism being characterized by a high rate of hydrolysis with the formation of small and dense spherical particles [1]. This mechanism prevails at pH 7.0. It should be emphasized that the aforementioned facts refer to TEOS hydrolysis and polycondensation occurring in the absence of additives. However, even in the classical monograph by Ailer, it was noted that, upon the alkaline hydrolysis in the presence of salts, the morphology of particles and the character of a gel are rather similar to the results of the acidic hydrolysis [3].

It has appeared that the incorporation of even small amounts of the dopant cations at hydrolysis pH 1.5 increases the gelation time relative to that of the dopant-free system. On the contrary, at hydrolysis pH 2.5 and 5.0, the incorporation of the dopant cations reduces the gelation time of the systems. Moreover, at pH 5, it decreases manyfold. The pattern of the curves for time variations in the viscosity in the presence of the dopant is shown in Fig. 1, while the quantitative data are summarized in Table 1.

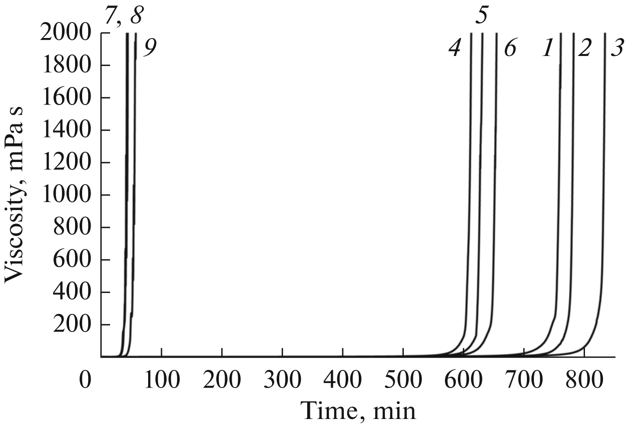

Fig. 1. Time dependences of viscosity for tetraethoxysilane-based systems at a temperature of 50°C and different pH values and contents of iron cations as dopants: (*1*, *4*, *7*) 1.5, (*2*, *5*, *8*) 2.3, and (*3*, *6*, *9*) 3.8 at %.

The difference in the mechanisms of the processes is confirmed by the results of determining the hydrodynamic diameters of the particles formed at different pH values within the time interval preceding the moment of the conditional time of gelation (Fig. 2). It is of interest that the smallest particles were formed at pH 2.5.

The amount of the added dopant substantially affects the gelation time in the system under investigation. At all three pH values, as the amount of Fe^{3+} ions increases, the gelation time grows (Table 1). This effect is especially strongly pronounced at pH 1.5. Moreover, the amount of the added dopant affects the sizes of the particles resulting from the polycondensation (Fig. 2).

All revealed phenomena are in good agreement with the assumption on the incorporation of iron cations into the siloxane matrix. The character of the IR spectra for the silica samples doped with iron ions also does not contradict to this assumption.

The IR spectra of all obtained samples (including those synthesized at pH 7.1) are almost identical. Figure 3 exemplifies the spectra of the samples obtained by hydrolysis at pH 1.5. The absorption band of $(Fe,Si)O_4$ is located in a wavelength range of 400–465 cm^{-1} and coincides with the absorption band of

Table 1. The time of gelation in the TEOS-based systems at a hydrolysis temperature of 50°C

Hydrolysis pH	1.5				2.5				5.0			
Content of Fe^{3+}, at %	0	1.5	2.3	3.8	0	1.5	2.3	3.8	0	1.5	2.3	3.8
Gelation time, min	630	753	776	827	678	605	623	648	732	40	41	52

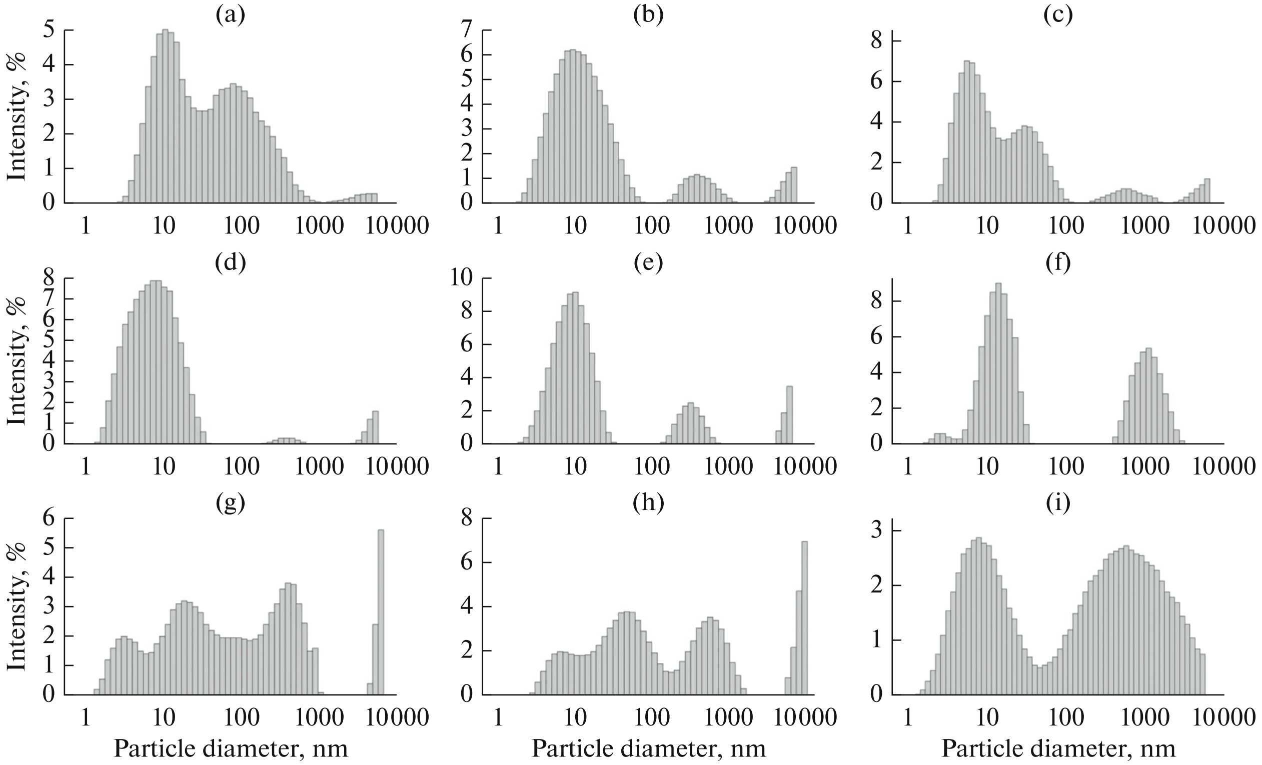

Fig. 2. Particle distributions over hydrodynamic diameters before the conventional gelation time is reached during TEOS hydrolysis at 50°C in the presence of Fe^{3+}: (a, d, g) 1.5, (b, e, h) 2.3, and (c, f, i) 3.8 at %; pH values: (a, b, c), 1.5, (d, e, f) 2.5, and (g, h, i) 5.0.

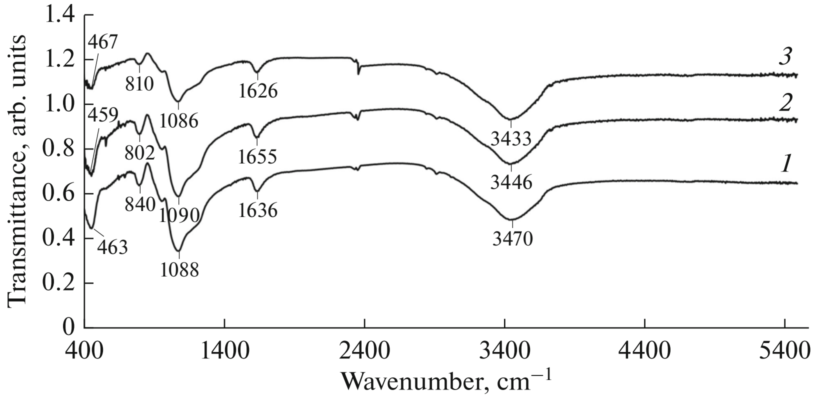

Fig. 3. IR spectra of silicas doped with iron cations at hydrolysis pH 1.5: (*1*) 1.5, (*2*) 2.3, and (*3*) 3.8 at %.

the siloxane matrix. It is essential that the spectra do not contain the absorption band at 667 cm^{-1}. The authors of [19] attributed this band to the stretching vibrations of Fe–O bonds and observed it in the samples with a high content of iron, which forms an oxide phase.

As has been noted above, an iron cation can be incorporated into the structure of silica as an iron oxide tetrahedron. Since iron cations are triple-charged, the iron oxide tetrahedrons are charged negatively and, being incorporated, provide siloxane polyanions with a negative charge. The results of measuring the zeta-potentials of the particles in the studied systems are presented in Table 2. It can be seen that all samples have negative zeta-potentials, while their absolute values depend on the pH values of sample synthesis and the contents of iron in reaction mixtures. The dependence on the iron content is explained by an obvious reason: the iron content in an initial solution determines the amount of iron in the resulting silica. A

Table 2. Electrokinetic potentials of samples obtained at different pH values

Hydrolysis pH	1.5			2.5			5.0		
Content of Fe^{3+}, at %	1.5	2.3	3.8	1.5	2.3	3.8	1.5	2.3	3.8
zeta-potential, mV	–12.1	–13.4	–14.8	–10.6	–12.3	–13.1	–8.76	–9.47	–10.1

decrease in the zeta-potential with a rise in pH seems to be associated with the ability of iron cations to the hydrolysis, which can be estimated using the Purbe diagram [20]. At pH 1.5, iron exists in a solution in the form of hydrated ions; at pH 2.5, first iron hydroxide ions arise in the system; while, at pH 5.0, the amounts of iron hydroxide and dihydroxide become sufficient to cause substantial hindrances for the incorporation into the siloxane matrix.

Thus, taken together, the results obtained agree with the ideas of the author of [4] about the structure-related reasons as the main factors affecting the gelation time in the system containing added metal cations at least in an acidic medium. The data of [8] on the acceleration of gelation in the course of alkaline TEOS hydrolysis are, most probably, associated with other mechanisms of the hydrolysis and polycondensation occurring under these conditions.

CONCLUSIONS

Proceeding from the data obtained on variations in the dynamic viscosity of a solution during the hydrolysis and polycondensation of tetraethoxysilane in the presence of Fe^{3+}, it has been assumed that the incorporation of iron cations into the siloxane matrix is the main reason for variations in the gelation time and particle sizes of a sol being formed. The influence of hydrolysis pH is explained by the pH dependence of the degree of iron cation hydrolysis. Seemingly, aquated iron ions rather than ions of iron hydroxide and dihydroxide can be incorporated into siloxane chains. The proposed assumption is in good agreement with the results of measuring the electrokinetic potentials of the studied systems. The character of the IR spectra does not contradict to this assumption.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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