

SAXS INVESTIGATION OF THE STRUCTURE REARRANGEMENT DURING THE SOL-GEL PROCESS OF SOLS OF HYDRATED OXIDES USING SYNCHROTRON RADIATION^{*}

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Abstract

The method of simulating the process of formation of new crystalline phase during solid state reactions is proposed. Sols of some electrochemically produced hydrated oxides (original sols) and their mixtures (binary sols) are studied by SAXS method using synchrotron radiation (SR). The presence of $1 \div 2$ nm scattering entities (primary particles) is a characteristic property of the investigated sols. During gelation and concentration of the original sols the interparticle distance varies in different ways. The binary sols gelate without concentration of the system. Different changes of the primary particles take place in the binary sols with the different component relation. Particles with different sizes are observed in the binary sols.

I. INTRODUCTION

The mechanism of phase formation during the solid state chemical transformation is one of the most intriguing problems in reactivity of solids. It is considered that reaction product appears from the intermediate amorphous substance. But nobody as a rule knows the structure of this intermediate substance. There are only several physical-chemical models of the arrangement of the intermediate substance.

The hypothesis on the existence of the vacancy structure - a distorted crystalline lattice of the initial reagent with the vacancies and pores left by the removed atoms or molecules of the initial reagent - is a foundation of the modern knowledge of the arrangement of the intermediate states. These models are not experimentally confirmed. Because practically the direct methods (especially X-ray diffractometry using the traditional X-ray sources) for investigating the intermediate substance structure during the process may not be applied.

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Development of the works at the Siberian Synchrotron Radiation Center (SSRC, storage ring VEPP-3, Budker Institute of Nuclear Physics, Novosibirsk) allows us to improve considerably the time and spatial characteristics of the X-ray diffraction methods (1). Investigation of the intermediate states during some solid state chemical reaction became possible (2,3). However in this case the task about the structure rearrangement during the solid state reaction remains very complex. To simplify the problem we simulate only the stage of new phase formation in another model system. In the model system the stage of the amorphous intermediate state formation is absent. As a model system we chose the sol-gel process.

Several results concerning the sol-gel process were obtained by SAXS method. Gelation of sols of hydrated oxides was studied (4). In this paper the results will be described and discussed considering the simulating method.

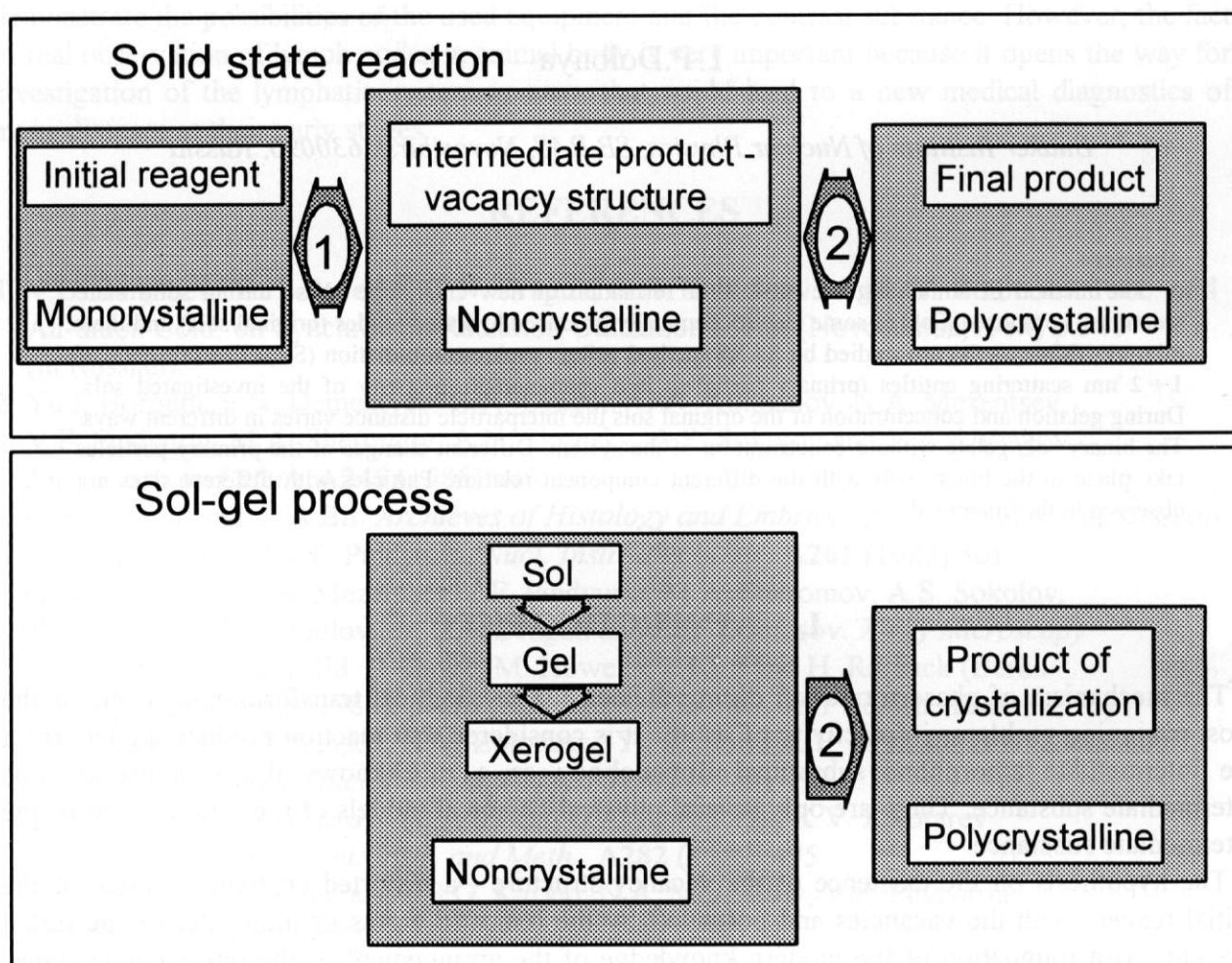


FIGURE 1. The schemes of the solid state reaction and of the sol-gel process. The stage of formation of the intermediate product is marked by figure 1. The stage of formation of the polycrystalline product from noncrystalline state is marked by figure 2. The stage 2 is common part of both processes.

II. SIMULATING METHOD

Figure 1 shows the schemes of solid state reaction and sol-gel process.

Sol-gel system has not the stage of formation of the noncrystalline state (process begins from the liquid state of the sol). Both processes have similarly states and stages. There is noncrystalline state in the solid state reaction (intermediate state) as well as in the sol-gel process (sol-gel-xerogel transformations). In both processes the product has polycrystalline structure.

The model of the vacancy structure of the intermediate product during the solid state reactions may be suitable and may be of use to sol-gel process too. It is known that during gelation viscosity of the sol is increasing up to very big value (not measured by a capillary method) (5). Nevertheless the process of the new phase formation takes place. It means that old particles and clusters are destroyed and the appearing fragments of molecules migrate to construct another molecule of the new phase. The possible mechanism of the fragment migration may be by vacancy mechanism.

So that it is logically to simulate the process (to find some regularities) of the new phase formation during the complex solid state process in the less complex model sol-gel system. Combination of small and wide angle X-ray scattering methods (SAXS and WAXS) will allow one to investigate the process of the structure rearrangement from noncrystalline state to polycrystalline state.

In this paper only the process of structure rearrangement in the noncrystalline state will be described and discussed. Studying by combined SAXS and WAXS method is the next step of our investigation.

III. EXPERIMENTAL

The SAXS experiments were carried out at the station "Anomalous Small Angle X-ray Scattering", Siberian SR Center, Novosibirsk. A Kratky small angle chamber with a one-coordinate position sensitive detector allows one to observe SAXS patterns of the sols-gel systems under study at a time resolution of $1 \div 2$ min. The size of a scattering entity and the interentity distance that may be defined from the experimental data are limited by a $1 \div 50$ nm range of values. The experiments on gelation kinetics were performed *in situ*.

Original sols were prepared from water solutions by an electrochemical method in a diaphragm-free electrolyzer. The original sol of hydrated zirconium dioxide (HZD) was prepared from water solution of zirconil chloride. The original sol of hydrated aluminum oxide (HAO) was prepared from water solution of aluminum chloride. Binary sols with the different component relation ($n:m$ -HZD-HAO) were prepared by mixing n parts of the original sol of HZD and m parts of the original sol of HAO.

More details are described in (4).

IV. RESULTS AND DISCUSSION

During gelation of the original sols of HZD and of HAO the concentration of the sols takes place due to the evaporation of a solvent (water). The sols with different concentrations were studied to understand how the value of the particle number density C^N effects the sol structure. The different sols were made by thinning the source (100%) original sol with water.

The SAXS curves (with collimator corrections) $I(s)$ of the original sols of HZD and of the original sols of HAO with different concentrations and during gelation are shown in Figure 2a and Figure 3a. A broad diffraction maximum is observed on the diffraction patterns. This maximum characterizes an average distance r between the scattering entities (primary particles). One can estimate it from the corrected Bragg's relation (6):

$$r = 0.615 \cdot \frac{\lambda}{\sin(\vartheta)} = 0.615 \cdot \frac{4\pi}{s}, \quad (1)$$

where λ is the radiation wavelength, 2ϑ is the diffraction angle of the diffraction maximum, $s = \frac{4\pi}{\lambda} \cdot \sin(\vartheta)$ is a value of the scattering vector.

One can estimate the size of the particle using the distance distribution function $p(r)$ (7):

$$p(r) = r^2 \gamma(r) \quad (2)$$

This function describes quantitatively the set of the line segments connecting the volume elements in the particle. The function $p(r)$ is related both with the particle form and the particle inner structure. Function $\gamma(r)$ is the correlation function of electron density:

$$\gamma(r) = \frac{1}{2\pi^2} \int_0^{s_{\max}} I(s) \frac{\sin(sr)}{sr} s^2 ds + \delta\gamma(r), \quad (3)$$

where $\delta\gamma(r)$ is an additional part that can be calculated using asymptotic behavior of $I(s)$ at big values of s (7). Figure 2b and Figure 3b show the distance distribution functions $p(r)$ calculated from experimental curves. The first negative values of $p(r)$ indicate the maximum value of the particle size. The symbol (\times) in Figure 2b and Figure 3b indicates the distance r_{\max} on which the distance distribution function $p(r)$ (and correlation function $\gamma(r)$) becomes negative. In this case one can estimate the size of the primary particle d as r_{\max} : $d \approx r_{\max}$.

The dependences of the average interparticle distance r and the particle size d , calculated using (1), (2) and (3), on the normalized particle number density $[C_{\text{norm}}^N]^{1/3} = [C^N/C_0^N]^{1/3}$ during thinning the original sols with water and during gelation of the source original sols are given in Figure 4. C_0^N is taken as a particle number density of the source (100%) original sol. The values of C_{norm}^N were calculated on the assumption of non-interacting and non-changing particles in a solution. These values are shown in Figures 2 and Figures 3 between brackets. In the case of non-interacting and non-changing particles in a solution the following dependence of the average interparticle distance r on the normalized particle number density C_{norm}^N should be observed:

$$r = \left(\frac{B}{C_{\text{norm}}^N} \right)^{1/3}, \quad (4)$$

where B is a constant. For comparison, the solid lines in Figure 4 indicate the interparticle distance r , which is calculated from (4) with $B=252\text{nm}^3$ for the sol of HZD and $B=54\text{nm}^3$ for the sol of

HAO, versus the normalized particle number density $[C_{norm}^N]^{1/3}$. It is clear (Figure 4) that during the dilution of the original sols the average interparticle distance r changes approximately according to the relation (4) (the range of the normalized particle number density values is $0 \leq C_{norm}^N \leq 1$). In the process of gelation (the range of the normalized particle number density values is $1 < C_{norm}^N$) the change in the average interparticle distance differs considerably from the change of that calculated from the relation (4).

In the case of the original sol of HZD, during concentrating the system the interparticle distance r decreases slower than in the ideal system (solid curve in Figure 4a). This behavior may be explained by the existence of a shell around the primary particle nucleus. We consider that the shell consists of water molecules. During concentrating the sol the size of primary particle d decreases too from the value of 3.7 nm to 2.5 nm (Figure 2b). The thickness of the shell in this case is about $0.5 \div 0.6$ nm. In the initial stage of the gelation r and d sharply decrease (Figure 2b, Figure 4a).

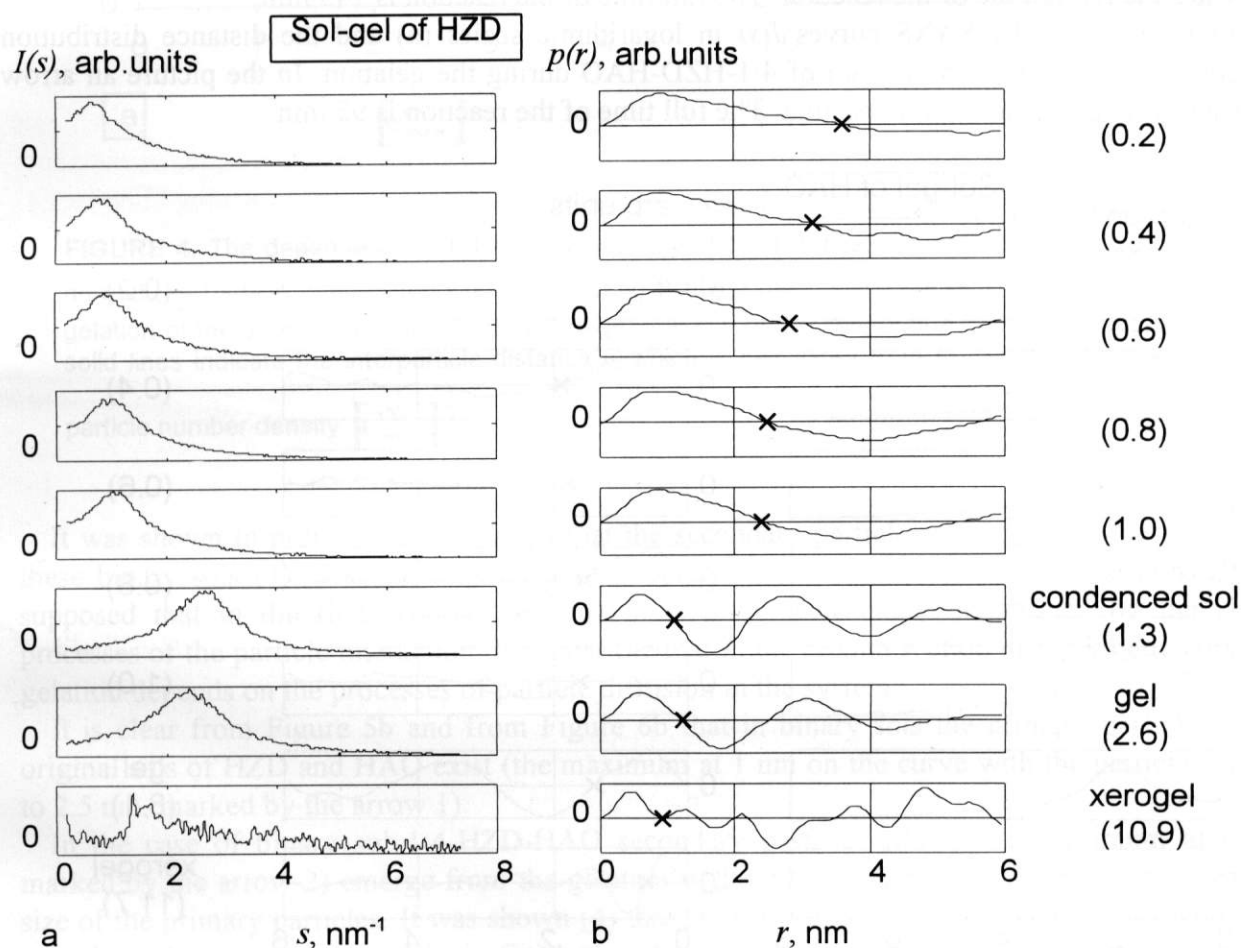


FIGURE 2. The SAXS curves $I(s)$ (a) and the distance distribution functions $p(s)$ (b) of the original sols of HZD with different concentrations and during the gelation. The values of the normalized particle number density C_{norm}^N , calculated on the assumption of non-interacting and non-changing particles in a solution, are enclosed in brackets. The values of the particle size are marked by symbol (x).

In the case of the original sol of HAO, during concentrating the system the same behavior of r and d takes place (Figure 3b, Figure 4b). The size of primary particle d decreases from the value of 2.2 nm to 1.7 nm. The similar explanation for this kind of behavior may be suggested. We consider that the water shell exists around the primary particle nucleus. The thickness of the shell in this case is about $0.2 \div 0.3$ nm. It is clear from Figure 3b that the size of the gel particle differs slightly from the size of the sol particle. One may conclude that in the gel state the primary particle is not destroyed. Only in the xerogel state the sharp decrease of r and d takes place (Figure 3b, Figure 4b). The thickness of the shell is about $0.5 \div 0.6$ nm. In this case one may conclude that the primary particle is destroyed in the xerogel state.

Another kind of the structure rearrangement is observed during the gelation of the binary sols of HZD-HAO with different component relations.

Figure 5 shows the SAXS curves $I(s)$ in logarithmic scales (a) and the distance distribution functions $p(r)$ (b) of the binary sol of 1:4-HZD-HAO during the gelation. In the picture an arrow indicates the rising time of the reaction. The full time of the reaction is 145 min.

Figure 6 shows the SAXS curves $I(s)$ in logarithmic scales (a) and the distance distribution functions $p(r)$ (b) of the binary sol of 4:1-HZD-HAO during the gelation. In the picture an arrow indicates the rising time of the reaction. The full time of the reaction is 95 min.

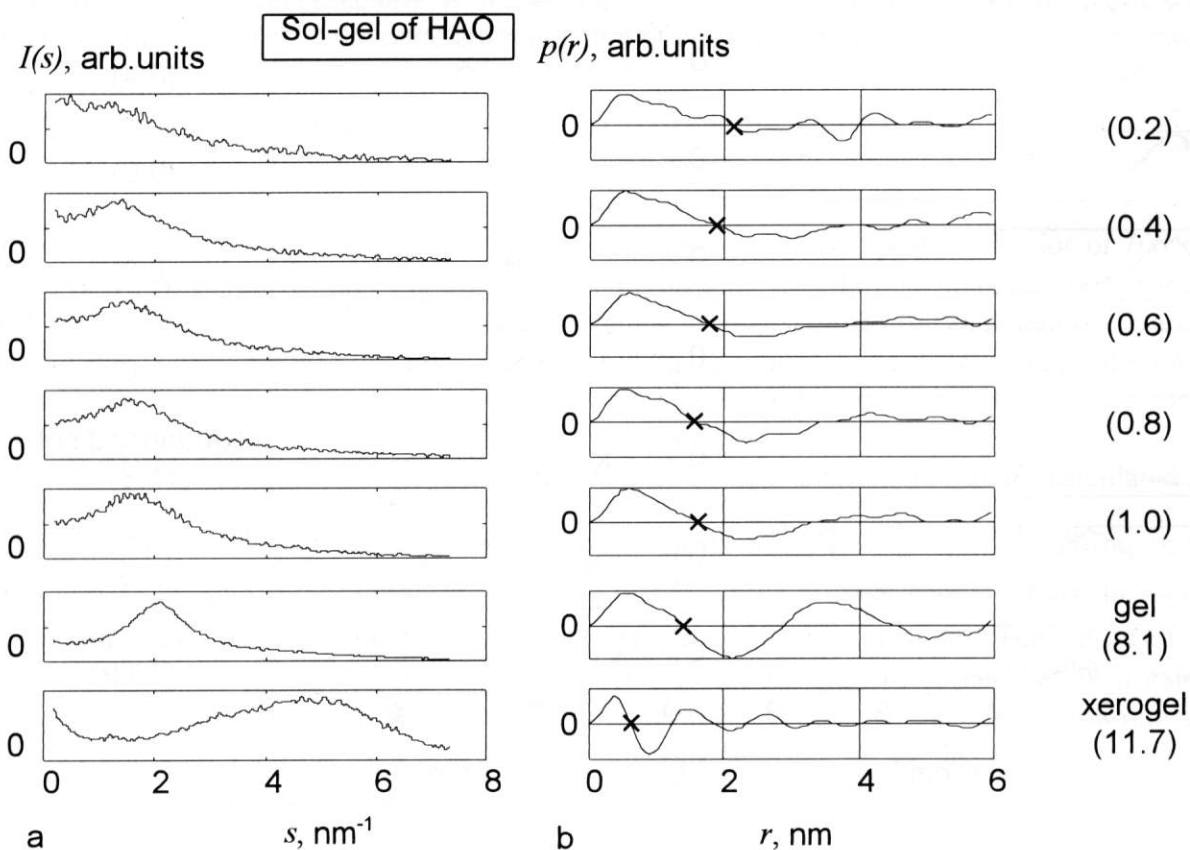


FIGURE 3. The SAXS curves $I(s)$ (a) and the distance distribution functions $p(r)$ (b) of the original sols of HAO with different concentrations and during the gelation. The values of the normalized particle number density C_{norm}^N , calculated on the assumption of non-interacting and non-changing particles in a solution, are enclosed in brackets. The values of the particle size are marked by symbol (x).

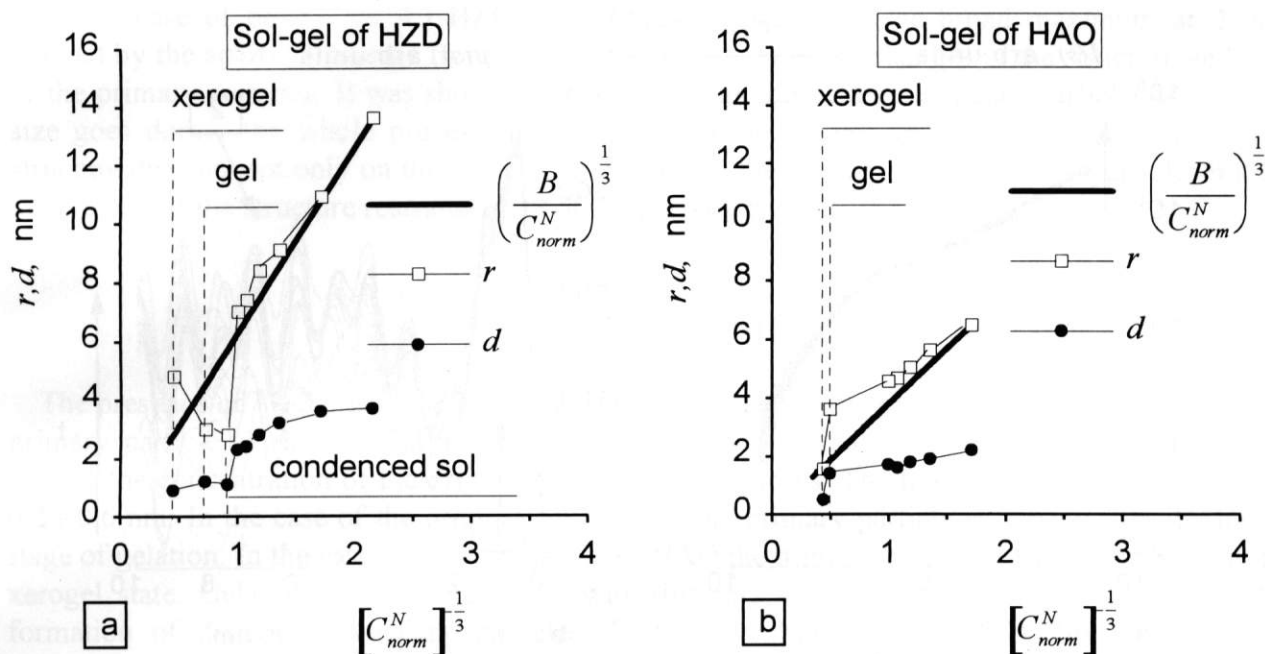


FIGURE 4. The dependences of the average interparticle distance r and the particle size d on the normalized particle number density C_{norm}^N during thinning the original sol with water and during the gelation of the source original sol: a) the sol-gel of HZD; b) the sol-gel of HAO. For comparison, the solid lines indicate the interparticle distance r , which is calculated from (3), versus the normalized particle number density $[C_{norm}^N]^{1/3}$.

It was shown in previous investigation that the secondary particles emerge from the gelation of these binary sols (4). The kinetic curves of structure parameters consist of two sections. It was supposed that in the first section the gelation is more than likely determined by the kinetic processes of the particle interaction. It is possible that in the second section of the kinetic curve the gelation depends on the processes of particle diffusion in the system.

It is clear from Figure 5b and from Figure 6b that in binary sols the primary particles of the original sols of HZD and HAO exist (the maximum at 1 nm on the curve with the particle sizes up to 2.5 nm, marked by the arrow 1).

In the case of binary sol 1:4-HZD-HAO secondary particles (the broad maximum at 6 nm, marked by the arrow 2) emerge from the gelation without significant changes in the structure and size of the primary particles. It was shown (4) that after forming the secondary particles with 6 nm size the gel formation generally is finished and the gelation supposedly goes from the kinetics regime to the diffusion one. The secondary particles supposedly interfere with the primary particles and hinder the primary particles moving. In this case the formation of the gel structure depends on the kinetics interaction of the primary and secondary particles.

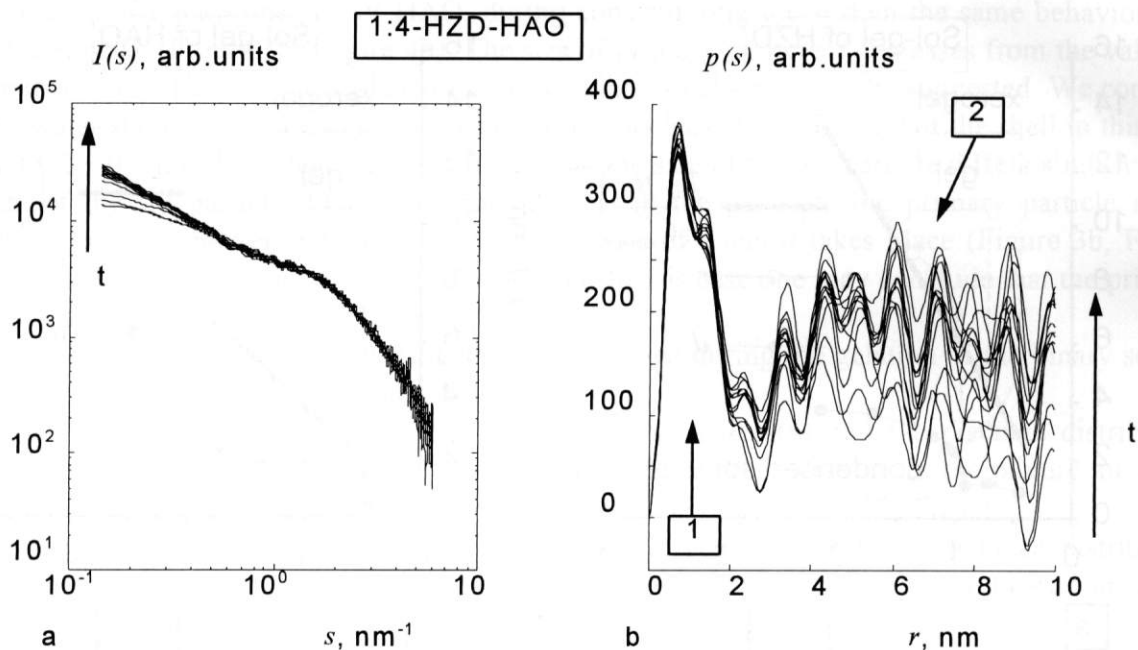


FIGURE 5. The SAXS curves $I(s)$ in logarithmic scales (a) and the distance distribution functions $p(r)$ (b) of the binary sol of 1:4-HZD-HAO during the gelation. Rising time is indicated by an arrow. Full gelation time is 145 min. The primary and the secondary particles are marked by the arrow with figure 1 and 2 respectively.

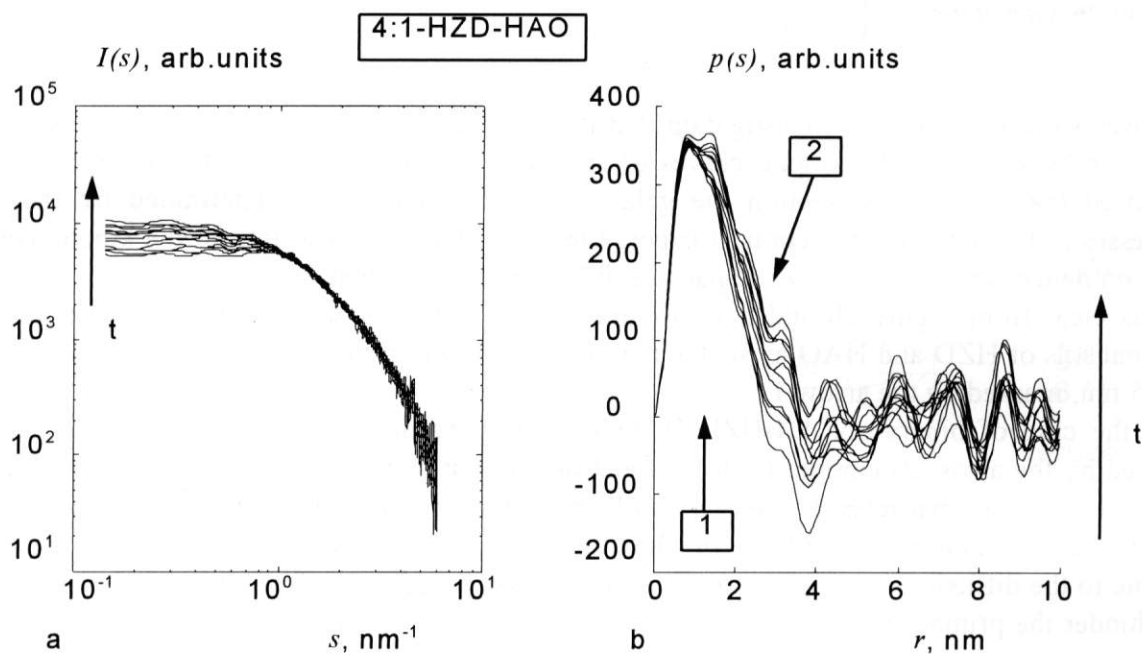


FIGURE 6. The SAXS curves $I(s)$ in logarithmic scales (a) and the distance distribution functions $p(r)$ (b) of the binary sol of 4:1-HZD-HAO during the gelation. Rising time is indicated by an arrow. Full gelation time is 95 min. The primary and the secondary particles are marked by the arrow with figure 1 and 2 respectively.

In the case of binary sol 4:1-HZD-HAO secondary particles (the broad maximum at 2 nm, marked by the arrow 2) emerge from the gelation with significant changes in the structure and size of the primary particles. It was shown (4) that the formation of the secondary particles with 3 nm size goes during the whole process of the gel formation. In this case the formation of the gel structure depends not only on the kinetics interaction of the primary and secondary particles but on the process of the structure rearrangement of the primary particles.

V. CONCLUSION

The presence of 1 ÷ 2 nm primary particle is a characteristic property of the investigated sols. The primary particle of the original sols is supposed to have a shell consisting of water molecules. During the concentration of the original sols the shell destroys. The thickness of the shell is about 0.2 ÷ 0.6 nm. In the case of the original sol of HZD the primary particle is destroyed at the initial stage of gelation. In the case of the original sol of HAO the primary particle is destroyed only in the xerogel state. Gelation of the binary sols with different component relations goes through the formation of different secondary particles. In the binary sol of 1:4-HZD-HAO forming the secondary particles goes without significant changes in the structure of the primary particles. Gelation supposedly depends on the kinetics interaction of the primary and secondary particles. In the binary sol of 4:1-HZD-HAO the secondary particle is formed with the significant changes in the structure of the primary during gelation. Gelation in this case supposedly depends not only on the kinetics interaction of the primary and secondary particles but on the process of structure rearrangement of the primary particle.

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