STUDY OF TETRAETHOXYSILANE CLUSTERS IN BASIC ETHANOL/WATER SOLUTIONS BY SANS CONTRAST VARIATION

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Abstract. Small-angle neutron scattering has been applied to observe a cluster structure and specify its growth in ethanol-based solutions of hydrolyzed silicon tetraethoxide. The contrast variation has been used to reveal the inner structure of the clusters and compare it with the data of the previous analogous experiments. The presence of hydroxyl groups in the clusters is discussed based on the scattering data.

Key words: Small-angle neutron scattering, branched polymers, colloidal solutions, silicon tetraethoxide.

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1. INTRODUCTION

The study of the structure of branched polymeric materials is of permanent interest because of their great role in various technologies. Among most useful features providing and facilitating the applications of this kind of materials are high efficiency thermal insulation [1], strong piezoelectric effect [2] and others. Silicon tetraethoxide (tetraethoxysilane, tetraethyl orthosilicate, Si(OC2H5)4, TEOS) is a material, which is widely used for producing silicon-based branched polymers [3–5]. TEOS is a tetrahedral molecule. Like its numerous analogues, it is derived by alcoholysis of silicon tetrachloride. Silicate clusters grown in basic ethanol/water solutions of hydrolyzed
TEOS exhibit a diverse range of structures, from weakly cross-linked polymers [6] to dense colloidal particles [3] depending on the number of parameters like pH, temperature, H₂O/TEOS molar ratio (w) etc.

In the given paper basic solutions are considered. Silica condensation polymerization proceeds in two steps. First, functional groups – SiOH are generated by the hydrolysis of alkoxide groups:

\[
\text{Si(OC}_2\text{H}_5\text{)}_4\text{(OH)}_{k-1} + \text{H}_2\text{O} = \text{Si(OC}_2\text{H}_5\text{)}_4\text{(OH)}_{k} + \text{C}_2\text{H}_5\text{OH.} \quad (1)
\]

Then, the condensation of these species results in silicate polymers through formation of the Si–O–Si linkages like:

\[
\text{Si(OC}_2\text{H}_5\text{)}_4\text{Si(OH)}_i + \text{Si(OC}_2\text{H}_5\text{)}_4\text{Si(OH)}_j \rightarrow \text{(OH)}_{i-1}\text{SiO}_j \text{Si(OH)}_{j-1}\text{Si(OC}_2\text{H}_5\text{)}_4\text{Si(OH)}_{k} + \text{H}_2\text{O,} \quad (2)
\]

and so forth. Always 1 \leq i, j, k \leq 4. The variety of possible structures is determined by the competition between two processes – hydrolysis and condensation. Keefer and Schaefer proposed [5] the so-called poisoned growth model to describe the formation of the observed clusters based on the results of small-angle X-ray scattering (SAXS) analysis. It was assumed that the hydrolyzed bonds included in the structure of the clusters do not take part further in the aggregation process. In accordance with this model, the content of OH-groups in the clusters determines their growth type and inner structure. Avdeev et al. used [7] small-angle neutron scattering (SANS) to confirm some critical behavior of the structural parameters of the partially hydrolyzed TEOS clusters in a vicinity of \( w = 2 \). However, the question of the inner structure remained open. The aim of the given paper was to clarify at what extent hydroxyl and/or other groups are included in the silicate clusters. The presence of hydroxyl groups which are not accessible to the solvent makes it possible to apply the H/D isotopic substitution and estimate the density distribution of these groups within the aggregates by means of the contrast variation in SANS [8–10], one of the most useful experimental technique to study heterogeneous nanosystems. The contrast is the difference in the scattering length density (SLD) of the dispersed particles and the solvent (\( \Delta \rho = \rho - \rho_s \)).

In the current experiments, D₂O or H₂O have been added into the initial TEOS/alcohol solutions for the hydrolysis initiation. We expected that hydroxyl groups in the structure of the clusters can be distinguished, because the presence of these groups in the cluster structure would substantially change the neutron contrast and, as a consequence, the scattering curves. At the same time, the D/H substitution can also be done in the ethanol-based buffer of the initial solution to realize the standard contrast variation scheme (outer contrast variation) [8–10].
2. MATERIALS AND METHODS

The samples were prepared according to the procedure described in Refs. [5–7]. Water was added with different proportions to the 10 % TEOS (Sigma Aldrich) ethanol solution keeping the condition \( w = 2 \). In this case, the volume fraction of water was below 1.5 %. Such concentration ensures that the influence of small amount of hydrolyzed groups on the solvent SLD after dissolution is insignificant. Hydrolysis was base-catalyzed (\( \approx 0.01 \text{ M NH}_4\text{OH} \)). After the clusters were formed (7 days after the hydrolysis initiation), SANS experiments were carried out at the YuMO time-of-flight small-angle diffractometer at the IBR-2 pulsed reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) [11, 12].

The two-detector setup with ring wire detectors was used. The scattered intensity (differential cross section per sample volume) isotropic over the radial angle \( \phi \) was obtained as a function of the modulus of momentum transfer, \( q = (4\pi/\lambda)\sin(\theta/2) \), where \( \theta \) is the scattering angle and \( \lambda \) is the incident neutron wavelength. The neutron wavelengths within a range of 0.05–0.5 nm and the sample-detector distances of 4 and 16 m were used to obtain SANS spectra in a \( q \)-range of 0.07–4 nm\(^{-1}\). The calibration procedure was made using vanadium. The liquid samples, as well as the dried powder were measured in 1 mm thick flat quartz cuvettes (Hellma).

3. RESULTS AND DISCUSSIONS

The measured scattering curves are presented in Fig.1. Two power-law regions can be observed in the double logarithmic scale as linear dependences for two H-ethanol samples (maximal contrast), which can be interpreted as volume and surface scattering [7], respectively. The curves show the scattering from a set of subunits with diffusive surface [13, 14] combined in mass fractal clusters [15]. The corresponding power-law exponents are similar to those from Ref. [7]. Thus, the fractal dimension is \( D = 2.1(1) \), and the surface scattering exponent is 4.7(2). Still, in this case the clusters have somewhat smaller size (see below), which was not observed in the curves in the previous experiments. A slight difference in the corresponding pairs of the curves is not clear for the moment. It could be connected with possible slight deviations in the preparation procedure from that in Refs. [5–7] including the temperature regime, especially for NH\(_4\)OH additive, whose influence is to be clarified. It is clearly seen that the scattering curves differing only by the content of D\(_2\)O and H\(_2\)O practically overlap. Thus, the data obtained indicate that there are no ‘immured’ hydroxyl groups in the cluster structure, because, as it was mentioned above, their presence would change largely the scattering curve. That is, the vast majority of hydrolyzed bonds take part in the condensation reaction with the formation of Si–O–Si linkages.
Fig. 1 – (Color online). SANS contrast variation for two types of systems under study based on light and heavy water. The inset shows the experimentally obtained values of $I(0)^{1/2}$ against the D-ethanol volume content ($\eta$) with the parabolic approximations and corresponding match points.

In order to determine the match-point of the clusters (a volume fraction of the deuterated component in the solvent where the forward scattering intensity is minimal), the scattering intensity averaged over the range of 0.07–0.1 nm$^{-1}$, $I(0)$, was analyzed. The choice of this range is justified by the minimal sensitivity of the scattering intensity to the residual background within it. The dependence of the $I(0)$ parameter on the D-ethanol volume fraction in the solvent, $\eta$, is illustrated in the inset in Fig. 1. The corresponding match-point obtained via parabolic fitting is 0.74(4) on the average. This value corresponds to the mean SLD of the clusters, $\bar{\rho} = 4.4(3) \times 10^{10}$ cm$^{-2}$, which is slightly higher than the calculated SLD for pure SiO$_2$ (4.19 $\times 10^{10}$ cm$^{-2}$) but still coincides with it within the experimental error.

Thus, our results are not described by the previously proposed model of the poisoned bonds [5], but points to other reasons for the variety of the structure of this type of silicate clusters. Most likely, a cause of the effect is the conformational diversity of polymer structures which are formed from hydrolyzed tetraethoxysilane in basic solutions due to nucleophilic substitution mechanism [3, 16].

According to Stuhrmann [9] the scattered intensity as a function of the contrast has the form:

$$I(q) = I_s(q) + (\Delta \rho) I_{cs}(q) + (\Delta \rho)^2 I_c(q),$$

(3) where $I_c(q)$, $I_s(q)$, $I_{cs}(q)$ are the so-called basic functions which can be found from
at least three experimental scattering curves obtained for different contrasts. The $I_c(q)$ function corresponds to the scattering from the particle shape, while the $I_s(q)$ and $I_{cs}(q)$ functions correspond to the scattering from the density fluctuations inside the particles. The basic functions obtained for our system are presented in Fig.2. $I_{cs}(q)$ differs from zero, which indicates that the particles in the liquid system under study are quite inhomogeneous from the viewpoint of neutron scattering. The $I_c(q)$ basic functions are separately represented in Fig.3 in the double logarithmic scale. They can be well described by the Guinier approximation in the low $q$-range, which makes it possible to apply the indirect Fourier transform [17, 18] and represent the correlations in the systems in terms of the pair distance distribution functions, $p(r)$, comprising the size characteristics such as gyration radius and maximum size. One can observe that the size characteristics of the dispersed particles are close for both solutions based on D$_2$O and H$_2$O and give just a small difference in the concentrations according to $I(0)$. Contrary to H-ethanol samples (squares in Fig.1), the Porod-type limit at high $q$-values is indicative of the smooth surface of the silicate clusters. In addition, it shows that the diffuse type of the scattering is determined primarily by the inhomogeneities of the SLD under the cluster surface, and not by specific roughness of the surface of homogeneous clusters [19].

![Fig. 2 – (Color online). Basic functions determined by the scattering curves in Fig.1 in accordance with (3).](image)
4. CONCLUSIONS

To summarize, the ethanol-tetraethoxysilane-water system has been investigated by the SANS contrast variation. Clusters of hydrolyzed silicon tetraethoxide having a structure of the mass fractal type are assembled from subunits with diffuse surface. The obtained data clearly indicate that the number of closed hydroxyl groups in the structure of the clusters is negligibly small. Thus, the most of the hydrolyzed bonds participate in the condensation reaction to form Si–O–Si bonds.

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