

# Deep insight in the processes occurring during early stages of the formation and room temperature evolution of the core(amorphous SiO<sub>2</sub>)@shell(organocations) nanoparticles

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## ABSTRACT

Assuming that the processes governing the formation, properties and evolution of core(amorphous silica)@shell(organocations) nanoparticles occur during short-time, room-temperature (*rt*) stirring/aging of homogeneous reaction mixtures (HmRMs) formed by hydrolysis of TEOS in solutions of Org(OH)<sub>n</sub>, we investigated these processes by various experimental methods (pH, ionic conductivity, <sup>29</sup>Si-NMR, DLS and AFM). Detailed and careful study of the model HmRMs (xTEOS:0.25TPAOH:20H<sub>2</sub>O; TPAOH = tetrapropylammonium hydroxide; x = 0.05 – 1) provides some new elements for grasping of the mechanism of formation and *rt* evolution of the core@shell silica nanoparticles: 1) There is a strong evidence for the formation of stable, about 1.2 nm sized core(amorphous SiO<sub>2</sub>)@shell(TPA<sup>+</sup> ions) nanoparticles below the critical aggregation concentration. 2) Due to the intensive particulate processes (growth, aggregation, disaggregation, dissolution) which occur during *rt* aging of the studied HmRMs, the “equilibrated” core@shell SiO<sub>2</sub> nanoparticles do not exist as individual primary particles, but as aggregates (≈2 – 20 nm) composed of 1 – 2 nm sized primary nanoparticles. 3) Despite general opinion that the nanoparticle shell is composed of free TPA<sup>+</sup> ions adsorbed on the surface of the nanoparticle core, the results of this study show that the nanoparticle shell can be formed mainly by attachment of polysilicate anions (silicate oligomers) associated with TPA<sup>+</sup> ions on the surface of nanoparticles cores.

## INTRODUCTION

Zeolites are crystalline silica or silica-alumina materials with periodic 3-D framework and well-defined microporous structure. Due to their unique properties such as acidity, porosity, and molecule-sieving ability, they have been widely used as catalysts, adsorbents, ion exchangers and micro-reactors in petroleum refining and fine chemical industry,<sup>1-3</sup> but also in electronic, optics, sensing and medicine.<sup>4</sup> The properties of zeolites, relevant for their different applications, are largely determined by their structural, chemical, particulate and morphological properties.<sup>2, 5</sup> Because the mentioned properties can be controlled by thorough understanding of the critical processes (nucleation, crystal growth) occurring during crystallization, the very complex processes, which at molecular level occur during crystallization of zeolites,<sup>6</sup> were in the focus of zeolite researchers since early days of zeolite synthesis.<sup>7-9</sup> Since then, many different approaches of the critical processes of zeolite crystallization (formation of hydrogel, nucleation, crystal growth) were established during the years of intense investigations.<sup>4, 5, 10-17</sup>

A new burst in the understanding of mechanism of zeolites crystallization happened at the end of 20<sup>th</sup> century and the beginning of 21<sup>st</sup> century, when several research groups reported formation of the stable, 2 – 5 nm sized, amorphous silica nanoparticles (amorphous precursor species – PPSs) in homogeneous systems (clear solution) SiO<sub>2</sub>-TAAOH-AlkyOH-H<sub>2</sub>O (TAA = tetraalkylammonium, AlkyOH = alkyl alcohol) at room temperature, formed by hydrolysis of TEOS (tetraethyl orthosilicate) in the systems, TEOS-TAAOH-H<sub>2</sub>O.<sup>18-23</sup> It also has been found that the addition of Al into reaction mixture leads to the formation of the stable, nanosized aluminosilicate particles.<sup>24-28</sup> These findings provided an additional significance of these investigations by the fact that hydrothermal treatment of such homogeneous systems results in the formation of different nanosized zeolites,<sup>18, 19, 23, 26-36</sup> and

in addition, that the sub-colloidal precursor species (PPSs) have a crucial role at the early stage of crystallization of zeolites in heterogeneous systems (hydrogels).<sup>37-42</sup>

Following Iler's original ideas on silica nanoparticles<sup>43</sup> and knowing the possibility of the stabilization of silica by organic molecules,<sup>44-46</sup> several research groups suggested that the PPSs have a core@shell structure with amorphous silica at the core and organic molecules at the shell.<sup>20-22, 23, 25, 33, 47-51</sup> On the basis of numerous studies of the formation of silica nanoparticles in homogeneous systems, TEOS-Org(OH)<sub>n</sub>-H<sub>2</sub>O<sup>20-23, 25, 28, 35, 47-56</sup> [Org(OH)<sub>n</sub> is organic base, most frequently TAAOH (n = 1),<sup>20, 22, 50</sup> but also other organoammonium hydroxides<sup>23, 27, 28, 50</sup> were used as organic bases], it was concluded that silica-Org(OH)<sub>n</sub> solutions have well defined critical aggregation concentration (CAC) of silica for OH<sup>-</sup>/SiO<sub>2</sub> ≈ 1. Prior to this critical point (below the CAC; OH<sup>-</sup>/SiO<sub>2</sub> > 1) no nanoparticles are detected in the solution.<sup>20, 22, 25, 27, 28, 35, 49, 53-57</sup> Namely, at the excess of OH<sup>-</sup> ions below the CAC, all the Si(OH)<sub>4</sub> monomers, formed by hydrolysis of TEOS, are deprotonated<sup>20-22, 25, 43, 49, 53, 55</sup> and then, mutual reactions of the deprotonated monomers result in the formation of silicate oligomers.<sup>20-22, 24, 25, 27, 28, 35, 47, 53-57</sup> On the other hand, the Si(OH)<sub>4</sub> monomers formed above the CAC (OH<sup>-</sup>/SiO<sub>2</sub> < 1), together with the dissolved oligomers and TAA<sup>+</sup> ions, are the possible building blocks of the nanoparticles.<sup>20</sup> The size of the inorganic core (SiO<sub>2</sub>) is nearly independent on the diameter of the TAA<sup>+</sup> ion, but decreases with pH, suggesting that the electrostatic forces are a key factor controlling their size and stability.<sup>20, 22, 32, 49, 55</sup> The independence of the core size and shape upon changes in the cation size are good indications that the core is mostly cation free.<sup>22</sup> Hence it is reasonable to assume that the TAA-containing nanoparticle shell is formed by attachment of TAA<sup>+</sup> ions from solution to the surface of nanoparticle core.

In spite of enormous amount of the data obtained during these studies, and great contribution to the knowledge on the “structure” and properties of silica nanoparticles<sup>18-25, 27,</sup>

28, 35, 41, 42,47-65 as well as in the understanding the mechanism of their formation,<sup>22-25, 28, 35, 51-54, 66, 67</sup> some inconsistencies and “grey zones” relating to the mechanism of nanoparticles formation (addition of silica monomers,<sup>51</sup> aggregation of oligomers,<sup>54, 66</sup> or both the mechanisms<sup>67</sup>), state of TAA<sup>+</sup> – especially TPA<sup>+</sup> ions in the nanoparticle shell and consequently, mode of formation and “structure” of nanoparticle shell,<sup>20, 44-46, 49, 53, 55, 59, 60, 65</sup> are still persisting in the published data. In addition, on the basis of the analysis of SAXS (Small-Angle X-ray Scattering) patterns of the nanoparticles formed above the CAC (OH<sup>-</sup>/SiO<sub>2</sub> < 1), Fedeyko *et al.*,<sup>20</sup> Eilertsen *et al.*,<sup>28</sup> Rimer *et al.*,<sup>49</sup> and Provis *et al.*<sup>51</sup> concluded that the number density of nanoparticles increases, but their size remains nearly constant with decreasing ratio OH<sup>-</sup>/SiO<sub>2</sub>, at nearly constant pH. On the other hand, using the same method (SAXS), Yang and Navrotsky<sup>21</sup> concluded that both the number and size of nanoparticles increase with decreasing ratio OH<sup>-</sup>/SiO<sub>2</sub>. Finally, in spite of widely accepted thinking that silica nanoparticles can be formed only above the CAC,<sup>20, 25, 27, 28, 35, 44, 45, 49, 51, 52, 54-57, 63</sup> some results based on SAXS<sup>21, 22</sup> and DLS (Dynamic Light Scattering)<sup>24, 53</sup> measurements indicate that the silica nanoparticles can also be formed at, and below the CAC. Here, it must be noted that in most cases, the clear solutions (homogeneous reaction mixtures – HmRMs) were aged at room temperature for at least 12-24 h<sup>22-25, 28, 33, 35, 49, 53, 55</sup> and even longer<sup>44, 52, 54</sup> after the preparation and before the measuring of the characteristic values (pH, ionic conductivity, particle size, distribution of different LMW silicate species and “oligomers” in the liquid phase, connectivity of Si in “oligomers and nanoparticles, etc.). Since it is our opinion that crucial processes governing the formation of PPSs take place during the hydrolysis of TEOS and immediately after the hydrolysis is finished (i.e., before the system is “equilibrated”), it is reasonable to assume that the observed inconsistencies and “grey zones” are caused by insufficiency of the knowledge on just the processes occurring at the early stage (time) of the PPSs formation. For this reason, pH and ionic conductivity of the investigated “model”

HmRMs (IM-HmRMs) having the starting chemical composition:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ , were, in this paper, measured (collected) continuously at various times,  $t_A$ , after mixing of TEOS and TPAOH solutions ( $t_A = 0$ ), while the other data (particle size distribution, AFM images,  $^{29}\text{Si}$ -NMR) were collected at different times,  $t_A$ , after the entire amount of TEOS has been hydrolyzed (see Experimental methods). Then, the obtained data were used for the analysis of the mechanism of the nanoparticles (PPSs) formation and their evolution during room-temperature aging.

## EXPERIMENTAL METHODS

### Preparation and of TEOS-TPAOH-H<sub>2</sub>O systems

The investigated (“model”) homogeneous reaction mixtures (IM-HmRMs) having the initial chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$  ( $x = 0.05 - 1$ ), were prepared at room temperature (*rt*) by adding the appropriate amounts of tetraethylorthosilicate (TEOS, Aldrich, 98 %, reagent grade) to a water solution of tetrapropylammonium hydroxide (TPAOH, 1M aqueous solution, Alfa Aesar). For this purpose, the appropriate amount (mass) of TPAOH solution was added into plastic vessel containing appropriate amount (mass) of deionized water stirred by magnetic bar. Then, the appropriate amount (mass) of TEOS was quickly added to the stirred TPAOH solution. The moment of addition of TEOS into TPAOH solution was taken as the zero time, ( $t_A = 0$ ) of the hydrolysis/aging processes. Further treatment of such prepared reaction mixtures was conformed to the experimental method used for characterization (see below).

### Characterization

$^{29}\text{Si}$  NMR experiments were carried out on a Bruker Avance 600 spectrometer (600,13 MHz,  $^1\text{H}$ ; 119.22 MHz,  $^{29}\text{Si}$ ). The samples of IM-HmRMs with  $x = 0.1, 0.2, 0.25, 0.3, 0.5, 0.75$  and  $1.0$  were prepared in the way described in 2.1., and then, the samples were

transferred into 5 mm NMR tubes after; (i) *rt* stirring for  $t_A = t_s = 3$  h and (ii) additional *rt* aging under static condition for  $t_a = 21$  h ( $t_A = t_s + t_a = 24$  h). Typically, spectra at a spectral width of 50 kHz and a digital resolution of 1.5 Hz per point were measured with 512 scans. A  $30^\circ$  pulse was used with a repetition rate of 7 s. All experimental data were zero-filled to double the number of experimental points. The software TopSpin (Bruker BioSpin) version 2.1 was used for all acquisition and processing.  $^{29}\text{Si}$  NMR quantification was performed by spectral deconvolution using the Dmfit software.<sup>68</sup>

The pH and ionic conductivity of the IM-HmRMs with  $x = 0.05, 0.1, 0.125, 0.15, 0.175, 0.2, 0.22, 0.25, 0.35, 0.5, 0.75$  and  $1.0$  were measured under stirring at *rt*, in the vessels in which the reaction mixtures have been prepared. For this purpose, pH electrode or conductivity cell was immersed into stirred solution (reaction mixture), about 1.5 min after addition of TEOS into TPAOH solution. Then, pH was continuously recorded at various times  $t_A = t_s$  ( $t_s$  is the time of stirring) from  $t_A = t_s \approx 1.5$  min to  $t_A = t_s = t_{\text{end}} = 50 - 70$  min, at which the measuring of pH was stopped. On the other hand, due to high starting alkalinity of the investigated IM-HmRMs ( $\text{pH} > 13.6$ ), the conductivity cell was, between two consecutive recording of conductivity, pulled out from the vessel with IM-HmRM, rinsed with deionized water and deleted (dried) with filter paper. Depending on  $x$ , the last value of the ionic conductivity of the IM-HmRMs were recorded at  $t_A = t_s = t_{\text{end}} = 50 - 76$  min.

The pH of the IM-HmRMs was measured using a Corning Pinnacle 555 pH/ion meter. The pH meter was calibrated with pH 9.0 and 12.0 buffer solutions at  $25^\circ\text{C}$ . The accuracy of the pH meter was  $\pm 0.01$  pH units

The ionic conductivity of the IM-HmRMs was measured using a Metrohm 712 Conductometer. The conductometer was calibrated with KCl standard.

The size distribution of the nanoparticles formed/present in the IM-HmRMs was determined by means dynamic light scattering (DLS), using a photon correlator

spectrophotometer equipped with a 532 nm “green” laser (Zetasizer Nano ZS, Malvern Instruments, UK). Intensity of scattered light was detected at the angle of 173°. To avoid overestimation arising from the scattering of larger particles, the hydrodynamic diameter ( $D_h$ ) was obtained as a value at peak maximum of size number distribution function. The samples of the IM-HmRMs with  $x = 0$  (0.694 M solution of TPAOH ), 0.05, 0.1, 0.15, 0.2, 0.25, 0.275, 0.35, 0.5, 0.65, 0.75 and 1.0, used for DLS measurements, were prepared by the way described in previous section and stirred for the time  $t_A = t_s$  and/or additionally aged under static for the time (in hours)  $t_a = 24 - t_s$ , before the measurement. Each sample was measured 10 times and the results were expressed as the average value. All measurements were conducted at  $25 \pm 0.1$  °C. The data processing was done by Zetasizer software 6.32 (Malvern instruments).

AFM imaging of the nanoparticles present in the investigated systems was performed in soft tapping mode using a MultiMode Scanning Probe Microscope with a Nanoscope IIIa controller (Bruker, Billerica, USA) with a vertical engagement (JV) 125 mm scanner. For this purpose, 5  $\mu$ L of each of the selected IM-HmRMs ( $x = 0.1, 0.2$  and  $1.0$ ;  $t_A = t_s = 3$  h and  $t_a = 24$  h, respectively), prepared as described in 2.1., was pipetted directly onto mica substrate and incubated for 10 min. Then, the excess of the IM-HmRM was removed from the substrate by filter paper and the mica sheets were placed in enclosed Petri dishes for several hours at a relative humidity of up to 50% to evaporate the excess water. Processing and analysis of images were carried out using the NanoScope™ software (Digital Instruments, Version 5.12r5, Digital Instruments, Tonawanda, NY, USA). All images are presented as raw data except for the first-order two-dimensional flattening. The NanoScope was allowed to equilibrate thermally for 1 h before imaging. Scanning rates were normally optimized around 1 Hz at a scan angle of 90°. Images were recorded under ambient conditions in air, by using

silicon tips (RTESP, Bruker, nom. freq. 320 nom. freq. 320 kHz, nom. spring constant of 42 Nm1). Images were processed and analyzed by means of the offline AFM NanoScope.

## RESULTS AND DISCUSSION

As already has been pointed out in the Introduction, the entire amount of silica, formed by hydrolysis of TEOS exists as a mixture of monomers and oligomers below the critical aggregation concentration (CAC) of silica, and as a mixture of monomers, oligomers and nanoparticles above the CAC.<sup>20-22, 24, 25, 27, 28, 44, 45, 49, 51-57</sup> Identification of different silicate species (monomers, oligomers, nanoparticles) and Si-O-Si connectivity (expressed as  $Q^n$ , where  $n$  is number of bridging oxygen atoms per  $SiO_4$ ) in the TEOS-Org(OH)<sub>n</sub>-H<sub>2</sub>O homogeneous reaction mixtures (HmRMs – clear solutions) were most frequently realized by <sup>29</sup>Si-NMR spectroscopy.<sup>24, 27, 28, 35, 43, 44, 52, 54, 56, 57</sup>

Figure 1 shows the <sup>29</sup>Si-NMR spectra of the investigated “model” homogeneous reaction mixtures, obtained by room-temperature hydrolysis of TEOS and aging of the reaction mixtures having the initial molar compositions: xTEOS:0.25TPAOH:20H<sub>2</sub>O (IM-HmRMs in the further text; see Experimental methods). The <sup>29</sup>Si-NMR spectra were measured after  $t_A = t_s = 3$  h (Fig. 1A) and after  $t_A = t_s + t_a = 24$  h (Fig. 1B); here,  $t_s$  is the time of the room-temperature (*rt*) stirring of the IM-HmRMs and  $t_a = 21$  h is the time of the additional *rt* aging of the IM-HmRMs under static conditions (without stirring; see Experimental methods). Presence of only sharp lines, characteristic for dissolved silicate oligomers below the CAC ( $x < 0.25$ ) and the appearance of broader bands above the CAC ( $x > 0.25$ ), are consistent with the results of previous studies.<sup>24, 27, 28, 35, 54, 57</sup> Consequently, the distribution of Si between oligomers and nanoparticles (see Figs. S1Aa and S1Ba in the Supporting Information SI-1), types of oligomers and their distributions (Figs. 2Aa and 2Ba) as well as connectivity of the Si atoms in the silicate species distributed in the clear solutions,



investigated in this work (Figs. S1Ab and S1Bb in SI-1), are also in large extent consistent with the results of the corresponding previous studies.<sup>27, 28, 54, 57</sup> Some differences in the distributions of oligomers and their  $Q^n$  values between these, shown in Figs. 2Aa, 2Ba and S1 and ones, presented in the comparing studies<sup>27, 28, 54, 57</sup>, as well as the differences in the distributions of oligomers and their  $Q^n$  sites between the IM-HmRMs aged at  $rt$  for  $t_A = t_s = 3$  h (Figs. 2Aa and S1A) and for  $t_A = t_s + t_a = 24$  h (Figs. 2Ba and S1B) are in more details discussed in SI-1. In addition, Fig. 2Bb shows that  $Q^3$  sites are dominant in the nanoparticles for each value of  $x$  at  $t_A = 24$  h, which is consistent with the results of previous studies.<sup>27, 28, 54, 55</sup> On the other hand, Fig. 2Ab shows that the ratio  $Si-Q^3/Si-Q^4$  is close to 1 for all the measured values of  $x$ ; this effect, already observed in the silica nanoparticles formed in concentrated HmRMs,<sup>43, 66, 69</sup> will be discussed and explained further in the paper.

Measuring of ionic conductivity and pH are widely used for determination of the critical aggregation concentration (CAC) of silica in the TEOS-Org(OH)<sub>n</sub>-H<sub>2</sub>O HmRMs. However, while the conductivity,  $S$ , and pH were usually measured after longer  $rt$  aging ( $t_A = 12 - 24$  h or longer; see Introduction<sup>22,25, 49, 53, 55</sup>), the values of  $S$  and pH were, in this work, measured continuously during hydrolysis of TEOS and additional  $rt$  aging of the IM-HmRMs (see Experimental methods). Figure 3 shows the changes of the ionic conductivity,  $S_{x,t}$ , during the hydrolysis of TEOS in TPAOH solutions (preparation and aging of the IM-HmRMs) under the  $rt$  stirring. Ionic conductivity,  $S_{x,t}$ , is almost constant ( $S_{x,t} \approx S_{x,0} = 48.8$  mS/cm, which corresponds to 0.7 M TPAOH solution; 0.25TPAOH:20H<sub>2</sub>O) or slightly decreases during the first 5 – 7 minutes of stirring. Thereafter the values of  $S_{x,t}$  rapidly decrease until reaching approximately constant (“equilibrium”) value,  $S_{x,t} = S_{x,eq}$  at the time  $t_A = t_s = t_{eq}$  and to the value  $S_{x,t} = S_{x,24h}$  at  $t_A = t_s + t_a = 24$  h, respectively (see Fig. 3 and Table 1).

Here,  $t_a = 24 - t_{eq}$  is the time (in hours) of additional  $rt$  aging of the IM-HmRMs (after stirring), under static condition (see Experimental methods). The initial rapid linear decrease

of both  $S_{x,m} = S_{x,eq}$  and  $S_{x,m} = S_{x,24h}$  (solid straight lines in Fig. 4A) from  $[\text{SiO}_2]_{x,tot} = 0$  ( $x = 0$ ) to  $[\text{SiO}_2]_{x,tot} \approx 0.6$  mol/kg ( $x = 0.28$  for  $S_{x,m} = S_{x,eq}$ ;  $\circ$ ) and to  $[\text{SiO}_2]_{x,tot} \approx 0.56$  mol/kg ( $x = 0.26$  for  $S_{x,m} = S_{x,24h}$ ;  $\bullet$ ), respectively, followed by the slow decrease of both  $S_{x,m} = S_{x,eq}$  and  $S_{x,m} = S_{x,24h}$  (dashed straight lines in Fig. 4B), are consistent with the results of previous studies.<sup>20, 22, 25, 49, 53, 55</sup> Here must be noted that the value of  $[\text{SiO}_2]_{x,tot}$  represents the molality concentration of the  $\text{SiO}_2$  formed by complete hydrolysis of TEOS and thus,  $[\text{SiO}_2]_{x,tot} = [\text{TEOS}]_{x,0}$  is proportional to  $x$  (see Table 1), where  $[\text{TEOS}]_{x,0}$  is the starting molality concentration of TEOS at  $t_A = 0$ .

Figure 5 shows the changes of the molality concentrations,  $[\text{OH}^-]_{x,t}$ , of  $\text{OH}^-$  ions during *rt* preparation and aging (with stirring) of the IM-HmRMs. The concentrations  $[\text{OH}^-]_{x,t}$  are calculated by the relation:  $[\text{OH}^-]_{x,t} = 10^{(14-\text{pH})}$ , from the corresponding values of  $\text{pH} = \text{pH}_{x,t}$  (Fig. S4 in SI-2), measured as it is described in the Experimental methods, and corrected by the method described in SI-2. The change of the concentration,  $[\text{OH}^-]_{x,t}$ , is characterized by its initial slow decrease, whereupon the value of  $[\text{OH}^-]_{x,t}$  changes with a higher, but decreasing rate till the “breakthrough” time,  $t_A = t_s = t_b$ . The “breakthrough” time  $t_A = t_s = t_b$  is characterized by the intersections of the solid and the dashed curves (see Figs. 5a and 5b), in which the concentration of  $\text{OH}^-$  ions reaches the specific (pseudo-equilibrium) value, i.e.,  $[\text{OH}^-]_{x,t} = [\text{OH}^-]_{x,b}$ .

From previous studies<sup>20-22, 25, 49, 53, 55</sup> and the relationships expressed by Eqs. (S2) and (S3) in SI-2, it is evident that the changes in conductivity and concentration of  $\text{OH}^-$  ions below the CAC ( $x \leq 0.25$ ,  $[\text{SiO}_2]_{x,tot} \leq 0.5397$  mol/kg for the IM-HmRMs) can be rationalized on the basis of the acid-base chemistry of silicic acid and silica oligomers. Both the conductivity and concentration of  $\text{OH}^-$  ions drop because the consumption of  $\text{OH}^-$  ions for deprotonation of the silica monomers formed during hydrolysis of TEOS [see Eqs (S2) and (S3) in SI-2]. On the basis of Eq. (S2), it is evident that the rate,  $d[\text{OH}^-]_{x,t}/dt_A$ , of consumption

of  $\text{OH}^-$  ions for deprotonation is proportional to the product of the concentration,  $[\text{OH}^-]_{x,t}$ , of “free” (unspent)  $\text{OH}^-$  ions and the concentration,  $[\text{Si}(\text{OH})_4]_{x,t} = [\text{SiO}_2]_{x,t}$ , of the  $\text{Si}(\text{OH})_4$  monomers at any stirring (aging) time,  $t_A = t_s$  i.e.,

$$d[\text{OH}^-]_{x,t}/dt_A = -k_1 \times [\text{OH}^-]_{x,t} \times [\text{SiO}_2]_{x,t} \quad (1)$$

Since  $[\text{SiO}_2]_{x,t} = [\text{TEOS}]_{x,S,t}$ , where  $[\text{TEOS}]_{x,S,t} = [\text{TEOS}]_{x,0} - [\text{TEOS}]_{x,t}$  is the amount (molality concentration) of the TEOS, hydrolyzed and spent for the formation of  $\text{Si}(\text{OH})_4$  and other silica species (oligomers below the CAC and nanoparticles above the CAC), and  $[\text{TEOS}]_{x,t}$  is the amount (molality concentration) of the non-hydrolyzed TEOS at time  $t_A > 0$ , Eq. (1) can be rewritten in the form,

$$d[\text{OH}^-]_{x,t}/dt_A = -k_1 \times [\text{OH}^-]_{x,t} \times \{[\text{TEOS}]_{x,0} - [\text{TEOS}]_{x,t}\} \quad (2)$$

On the other hand, Matsoukas and Gulari<sup>58</sup> observed that in the systems of high water content, such as those of interest here, hydrolysis is relatively fast process, largely independent of water concentration and pseudo-first-order in the concentration,  $[\text{TEOS}]_{x,t}$ , of the non-hydrolyzed TEOS, i.e.,

$$d[\text{TEOS}]_{x,t}/dt_A = -k_2 \times [\text{TEOS}]_{x,t} \quad (3)$$

On the basis of these findings, the changes of  $[\text{OH}^-]_{x,t}$  and  $[\text{TEOS}]_{x,t}$  during *rt* stirring (aging) of the IM- HmRMs, were calculated by simultaneous numerical solutions of the differential equations (2) and (3) using a fourth-order Runge-Kutta method and corresponding numerical

values of appropriate constants and initial conditions, as explained in the Supporting Information SI-3.

Almost perfect agreement of the measured values of  $[\text{OH}^-]_{x,t}$  (symbol  $\circ$  in Fig. 5) and the values of  $[\text{OH}^-]_{x,t}$  calculated by simultaneous numerical solutions of the equations (1) and (2) (solid curves in Fig. 5) in the time interval from  $t_A = 0$  to  $t_A = t_s = t_b$  shows that Eqs. (2) and (3) satisfactorily describe the relevant processes (hydrolysis of TEOS and deprotonation of the  $\text{Si}(\text{OH})_4$  monomers formed during hydrolysis of TEOS) occurring in the mentioned time interval. Since the backward reaction (protonation of the  $\text{Si}(\text{OH})_3\text{O}^-$  monomers and other deprotonated silicate species) is not included in Eq. (2), the agreement between measured and calculated values of  $[\text{OH}^-]_{x,t}$  shows that the effect of the backward reaction on the concentration of  $\text{OH}^-$  ions is negligible at least to  $t_A = t_s \approx t_b$ . On the other hand, a sudden achieving of the pseudo-equilibrium concentration,  $[\text{OH}^-]_{x,t} = [\text{OH}^-]_{x,b}$ , at  $t_A = t_s = t_b$  (see Fig. 5) indicates that in this point the rate of forward reaction (deprotonation) is considerably decreased and approached to the rate of the backward reaction (protonation of the  $\equiv\text{Si}-\text{O}^-$  groups of monomers and oligomers formed below the CAC). This is, at the same time, the reason that the measured (symbol  $\circ$  in Fig. 5) and calculated (solid curves in Fig. 5) values of  $[\text{OH}^-]_{x,t}$  starts to differ at  $t_A = t_s = t_b$  and that the difference between the measured and calculated values of  $[\text{OH}^-]_{x,t}$  increases with time  $t_A = t_s$ . However, a slow decrease of the concentration of  $\text{OH}^-$  ions from  $[\text{OH}^-]_{x,t} = [\text{OH}^-]_{x,b}$  at  $t_A = t_s = t_b$  to  $[\text{OH}^-]_{x,t} = [\text{OH}^-]_{x,24h}$  at  $t_A = t_s + t_a = 24$  h (see Fig. 4), indicates that the rate of the backward reaction (protonation) does not surpass the rate of the forward reaction (deprotonation), at least to  $t_A = 24$  h. As it can be expected from the results of previous studies,<sup>20, 22, 25, 49, 53, 55</sup> the values of  $[\text{OH}^-]_{x,n}$  linearly decrease with the increasing concentration,  $[\text{SiO}_2]_{x,\text{tot}}$  to  $[\text{SiO}_2]_{x,\text{tot}} = [\text{SiO}_2]_{x,\text{tot},b} \approx 0.6$  mol/kg for  $n = b$  and to  $[\text{SiO}_2]_{x,\text{tot}} = [\text{SiO}_2]_{x,\text{tot},24h} \approx 0.56$  mol/kg for  $n = 24$  h. Thereafter, the values of  $[\text{OH}^-]_{x,n}$  very slowly changes (decreases) with further increase of  $[\text{SiO}_2]_{x,\text{tot}}$  (Fig. 4).

Analyzes of the data presented in Table 1 and Figs. 4 and 5 (see SI-4) lead to an assumption that the rate of formation of  $\text{Si}(\text{OH})_4$  monomers [see Eq. (S1) in SI-2] is higher than the rate of their deprotonation [see Eqs. (S2) and (S3) in SI-2] and thus, that the ratio  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  is lower than 1 during the hydrolysis of TEOS. This assumption is consistent with the previous postulations that “...TEOS hydrolysis is rapid compared to all other processes...,”<sup>59</sup> and thus that „...after a short period of time the mixture contains silicic acid ( $\text{Si}(\text{OH})_4$ ), ethanol ( $\text{EtOH}$ ), water, TPA cations and  $\text{OH}^-$  anions“.<sup>51, 53</sup> The slow initial decrease of both the ionic conductivity  $S_{x,t}$  (Fig. 3) and the concentration,  $[\text{OH}^-]_{x,t}$ , of the  $\text{OH}^-$  ions (see Fig. 5) also corroborate this assumption. Furthermore, to prove (or disapprove) this assumption, the values of  $[\text{SiO}_2]_{x,t}$  and  $[\text{OH}^-]_{x,s,t}$  were calculated by simultaneous numerical solutions of the differential equations (2) and (3) and then the calculated ratios  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  (solid curves in Fig. 6) were compared with the measured ratios  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  (symbol  $\circ$  in Fig. 6).

The obtained results (see Fig. 6) show that the calculated ratios  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  continuously increase from  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t} = 0$  at  $t_A = 0$  to  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t} > 0$  at the final time ( $t_A = t_s = 75$  min) used in the analysis, but that for all the analyzed cases, the measured ratios  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  are lower than 1 in the time interval from  $t_A = 0$  to  $t_A = t_s = 75$  min. In addition the last two columns in Table S5 in SI-4 show that the measured values of  $[\text{OH}^-]_{x,s,t}/[\text{SiO}_2]_{x,t}$  are lower than 1 at even  $t_A = 24$  h. Hence, it is evident that the rate of deprotonation of  $\text{Si}(\text{OH})_4$  monomers [Eqs. (S2) and (S3) in SI-2] is slower than the rate of their formation by hydrolysis of TEOS [Eq. (S1) in SI-2] and thus, that a certain amount of “free”  $\text{Si}(\text{OH})_4$  monomers is present in the investigated IM-HmRMs not only above the CAC, but also below the CAC. Fom the data in Fig. 6 it can be calculated that the molar ratio  $[\text{Si}(\text{OH})_4]_{x,t}/[\text{protonated monomers and oligomers}]_{x,t} \approx 40$  at  $t_A = t_s = 1$  min, and that the same ratio is about 8.5 at  $t_A = t_s = 5$  min. Hence, knowing that the presence of  $\text{Si}(\text{OH})_4$  monomers

is crucial for the formation of silica nanoparticles,<sup>20, 22, 51, 55, 58-61</sup> it is reasonable to assume that, in spite of a widely spread opinion that the formation of silica nanoparticles starts to occur above the CAC,<sup>20-22, 24, 25, 27, 28, 35, 44, 45, 49, 51, 53-57</sup> the silica nanoparticles can also be formed at the early stage of TEOS hydrolysis and thus, below the CAC. The nanoparticles are not observed in the corresponding <sup>29</sup>Si-NMR spectra for  $x \leq 0.25$  (see Fig. 1 as well as if Figs. S1Aa and S1Ba in SI-1), which is consistent with the results of previous studies.<sup>24, 27, 28, 35, 54, 56, 57</sup> The most possible reason is very small amount (fraction) of silica present in eventually formed nanoparticles, which is below the detection limit of the applied method (see Experimental methods). On the other hand, since DLS detects the presence of nanoparticles earlier than any other method,<sup>24</sup> selected reaction mixtures, stirred/aged at room temperature for the determined times  $t_A$ , were analyzed by DLS and, additionally by AFM.

The DLS analysis of SiO<sub>2</sub>-free “reaction mixture” 0.25TPAOH:20H<sub>2</sub>O (0.694 M solution of TPAOH) does not show the presence of the “particles” having the size (diameter)  $D \geq 1$  nm (see Fig. 7A and Table S6 in SI-5). Addition of SiO<sub>2</sub> in the reaction mixture (by hydrolysis of TEOS for  $t_A = t_s = 3$  h), even in minimum amount ( $x = 0.05$ ,  $[\text{SiO}_2]_{x,\text{tot}} = 0.12$  mol/kg; see Table 1), causes the formation of the nanoparticles having the size (diameter)  $D \geq 1$  nm (see solid curves in Fig. 7 and the data in Table S6 in SI-5). Here it is interesting that the average size,  $D_{\text{av}(\geq 1\text{nm})}$  of these nanoparticles is constant to  $x \leq 0.275$  ( $D_{\text{av}(\geq 1\text{nm})} \approx 1.2$  nm; see Table S6 in SI-5) and close to the „peak“ sizes ( $D_p = 1.25 - 1.35$  nm) of the discrete particles populations identified in the corresponding DLS-PSD curves by intensity (see Figs. S8Ac, S8Ad, S8Bc and S8Bd in SI-5). A linear increase of the relative number,  $N_{\text{np}}(\text{rel}) = N_{(D \geq 1 \text{ nm})}$ , of these nanoparticles with the amount,  $[\text{SiO}_2]_{x,\text{tot}} \propto x$ , of the SiO<sub>2</sub> formed by hydrolysis of TEOS<sup>20, 28, 49, 51, 54</sup> (see Table S6 and Fig. S7A in SI-5), leads to the reasonable assumption that the formation of nanoparticles below the CAC ( $0 < x \leq 0.25$ ) takes place by addition or removal of monomeric units, i.e., by the mechanism which has previously been suggested for

the formation of nanoparticles above the CAC.<sup>51</sup> On the other hand, the average size,  $D_{av(\geq 1\text{nm})} \approx 1.2 \text{ nm}$  (see Table S6 in SI-5) of the nanoparticles formed below CAC is comparable with the size,  $D < 1.5 \text{ nm}$ , calculated on the basis of one-step simulation procedure (silica polymerization from a random initial conditions without any pre-association with organic structure directing agents), using Monte Carlo method.<sup>59</sup> Hence, it is reasonable to conclude that, below the CAC, the nanoparticles form by polymerization via addition of  $\text{Si}(\text{OH})_4$  monomers which are not pre-associated with OSDA. This explains the linear relationship between  $x$  and  $N_{(D \geq 1 \text{ nm})}$  and constancy of  $D_{av(\geq 1\text{nm})}$  from one side,<sup>51</sup> and small size,  $D_{av(\geq 1\text{nm})} \approx 1.2 \text{ nm} < 1.5 \text{ nm}$ , of the formed nanoparticles from another side.<sup>59</sup>

Figs. 7B – 7D show that the PSDs, established below the CAC at  $t_A = t_s = 3 \text{ h}$  (solid curves), do not considerably change during prolonged  $rt$  aging to  $t_A = t_s + t_a = 24 \text{ h}$  (dashed curves). The high stability of the nanoparticles formed below the CAC is caused by at least three reasons: (1) Low concentration of the nanoparticles formed below the CAC substantially reduces the collision frequency between the nanoparticles and thus, reduces the formation of the nanoparticle aggregates. (2) High negative surface charge caused by the formation of deprotonated terminal silanol groups  $[(\text{NP})\text{Si-OH} + \text{OH}^- \rightarrow (\text{NP})\text{Si-O}^- + \text{H}_2\text{O}]$  at high concentration,  $[\text{OH}^-]_{x,t}$ , of the unspent  $\text{OH}^-$  ions at the early stage of TEOS hydrolysis ( $x \ll 0.25$ ). (3) Formation of  $\text{TPA}^+$  shell around negatively charged nanoparticles<sup>20, 22, 49, 53, 55, 59-61, 63-65</sup> by the attachment of “free”  $\text{TPA}^+$  ions from solution, present in the IM-HmRMs below the CAC. The  $\text{TPA}^+$  ions from the shell “block” the terminal silanol groups and thus, prevents the formation of  $(\text{NP})\text{Si-O-Si}(\text{NP})$  linkages between collided nanoparticles. Hence, it is evident that in this way, the stability of the nanoparticles is caused not only by concentration [1]) and electrostatic [2])<sup>32, 49, 55, 62</sup> reasons, but also by steric ones.<sup>32, 49, 64, 65, 70</sup> Since a part of electrically neutral  $\text{Si}(\text{OH})_4$  monomers participate in the formation of other oligomers<sup>59, 60, 71</sup> (see also SI-1), it can be assumed that only a small fraction of the  $\text{Si}(\text{OH})_4$  monomers directly

participates in the formation of the nanoparticles below CAC; this is, by the way, the reason for their low concentration and feasibility for detection by NMR.

Therefore, atomic force microscopy (AFM) visualization was primarily performed for the identification and presence of nanoparticles that are detected and measured by dynamic light scattering, particularly below the CAC. The AFM images were made for the selected IM-HmRMs, prepared at room temperature and then stirred at the same temperature for  $t_A = t_s = 3$  h and additionally aged for  $t_a = 21$  h under static conditions. Fig. 8 shows that a single deposition of colloidal suspensions of nanoparticles on the mica surface (see Experimental methods) is sufficient for their identification even at concentrations of nanoparticles below the CAC. The AFM cross-section analyzes (middle parts of Fig. 8), along the lines of the corresponding topographic 2D height image of the surface layer of nanoparticles on mica support (left part of Fig. 8) show that, in spite of the lateral half-widths between 35 nm and 50 nm, which indicates the association of the individual nanoparticles, the nanoparticles heights lie in the range from about 1 nm to about 2 nm. The AFM height images (right part of Fig. 8) confirm the presence of nanoparticles that have a relative narrow height distribution ranging from 1 to 2 nm, which is consistent with the results of other experiments, i.e., that silica nanoparticles, having the average size,  $D_{av(\geq 1\text{nm})} \approx 1.2$  nm (see Fig. 7 as well as Fig. S8 and Table S6 in SI-5) form below the CAC ( $x < 0.25$ ).<sup>21, 22, 24, 53</sup> Thus, the AFM analysis undoubtedly show that a short-time ( $t_A = t_s = 3$  h) *rt* stirring (aging) of the HmRMs, having the starting chemical compositions: xTEOS:0.25TPAOH:20H<sub>2</sub>O, results in the formation of silica nanoparticles below the CAC ( $x < 0.25$ ) (Figs. 8Aa and 8Ba,) and that the size of the nanoparticles formed at  $t_A = t_s \geq 3$  h does not change during prolonged ( $t_a = 21$  h) *rt* aging under static conditions. (Figs. 8Ab and 8Bb). In fact, taking into consideration existence of relatively large fraction of electrically neutral Si(OH)<sub>4</sub> monomers below the CAC (10 – 20 % of the [SiO<sub>2</sub>]<sub>x,tot</sub>, as was estimated from the data in Table 1 and Fig. 4) and their role in the



formation of silica nanoparticles,<sup>20, 22, 51, 55, 58-61</sup> the formation of silica nanoparticles below the CAC is rather necessity than the rarely expected event.

In contrast to independency of the size (1.2 – 1.3 nm) of the nanoparticles formed below the CAC ( $x \leq 0.25$ ) on both  $x$  and time of the *rt* stirring/aging of the IM-HmRMs (see the 6<sup>th</sup> column in Table S6 in SI-5), the solid curves in Figs. 7E to 7J and the corresponding data in the 6<sup>th</sup> column in Table S6 in SI-5 show that the size of the particles formed during the same short time stirring ( $t_A = t_s = 3$  h aging) of the IM-HmRMs, increases with increasing value of  $x$ , for  $x > 0.25$  (above the CAC). In addition, comparison of the DLS-PSD curves relevant for  $t_A = t_s = 3$  h (solid curves in Figs. 7E – 7J) and for  $t_A = t_s + t_a = 24$  h (dashed curves in Figs. 7E – 7J) and the results of analyzes of the relevant PSD data in Table S6 in SI-5, show that the nanoparticles present in the IM-HmRMs at  $t_A = t_s + t_a = 24$  h are generally smaller than the nanoparticles present in the IM-HmRMs at  $t_A = t_s = 3$  h. The above findings lead to an assumption that intensive particulate processes (growth,<sup>51</sup> dissolution,<sup>51</sup> aggregation<sup>53, 72</sup> and disaggregation<sup>56</sup>) simultaneously take place during the *rt* aging of the reaction mixtures, at least in the time interval from  $t_A = t_s = t_b$  to  $t_A = t_s + t_a = 24$  h. To prove (or disapprove) this assumption, the PSD of the particles formed in the HmRM, having the starting chemical compositions: 1TEOS:0.25TPAOH:20H<sub>2</sub>O, was measured at various times  $t_A = t_s$  (2, 2.5, 3, 3.5 4 and 6 h) and, for selected sample at  $t_A = t_s + t_a = 24$  h, where  $t_a = 21$  h is the time of additional *rt* aging under static conditions (see Experimental methods).

The DLS-PSD profiles in Fig. 9A – 9C clearly indicate that the size of nanoparticles increases during the *rt* stirring of the HmRM from  $t_A = t_s = 2$  h (solid curve in Fig. 9A) to  $t_A = t_s = 3$  h (solid curve in Fig. 9C); in this time interval, the average particle size,  $D_{av}$ , increases from  $D_{av} = 4.60$  nm at  $t_A = t_s = 2$  h, through  $D_{av} = 6.75$  nm at  $t_A = t_s = 2.5$  h to  $D_{av} = 7.30$  nm at  $t_A = t_s = 3$  h. However, more interesting and important is that the particle size distribution, represent by the solid curve in Fig. 9C, does not represent distribution of the individual

(discrete) particles of different sizes (from  $D_{\min} \approx 2.3$  nm to  $D_{\max} \approx 22.7$  nm), but rather the aggregates of smaller, individual nanoparticles as can be seen in the AFM height image and its section analysis in Fig. 10. The AFM cross-section analyzes (middle parts of Fig. 10), along the lines of the corresponding topographic 2D height image of the surface layer of nanoparticles on mica support (left parts of Fig. 10), together with the AFM height images (right parts of Fig. 10) show that the individual nanoparticles, protruded above the supported mono-sized particles, have a relative narrow height distribution ranging from 1 to 2 nm (about 1.5 nm in average). On the other hand, since the lateral half-width is the same (between 10 nm and 15 nm) for the HmRMs stirred for  $t_A = t_s = 3$  h (middle part of Fig. 10A) and stirred/aged for  $t_A = t_s + t_a = 24$  h (middle part of Fig. 10B), it is evident that the lateral half-widths are related to the lateral dimensions of the aggregates formed during preparation of samples and not to the dimensions of the aggregates formed in the corresponding HmRMs (see Fig. 9C). The large lateral half-widths (between 35 nm and 50 nm) in the cross-section profiles of the individual nanoparticles formed below the CAC (see middle parts of Fig. 8), support this conclusion. Here must be noted that in all the presented images (Figs. 8 and 10), having the area of  $500 \text{ nm} \times 500 \text{ nm}$ , the surface-height differentiation, detected by AFM tip is order of magnitude of Å. Since the AFM height and lateral resolution is under 1 nm, and the curvature radius of the sharp AFM probe is below 8 nm, it could be used to characterize the small difference of the surface morphology and the dimensions of aggregates.

The formation of aggregates of the shell-less silica nanoparticles was predicted by Rivas-Cardona *et al.*<sup>53</sup> This implies that; (i) the individual, about 1.5 nm sized (primary) nanoparticles are formed by the same mechanism as already is described for the formation of about 1.2 nm sized nanoparticles below the CAC, namely by polymerization via addition of non-pre-associated  $\text{Si}(\text{OH})_4$  monomers<sup>51, 59</sup> and (ii) the aggregates of individual primary nanoparticles are formed by their stepwise nano-aggregation processes, similar to those,

described by van Tendeloo *et al.*<sup>72</sup> for the aggregation of primary nanoparticles in the presence of inorganic bases. On the basis of the above implications, the formation of the aggregates of primary nanoparticles (Figs. 9A – 9C and 10A) can be described/explained as follows: The increase of the amount of Si(OH)<sub>4</sub> monomers at reduced amount of “free” TPAOH, above the CAC (see Fig. 4), makes the conditions for the formation of increased number (amount) of nanoparticles (see Scheme 1-Ia as well as Figs. S1Aa and S1Ba in SI-1) during the hydrolysis of TEOS above the CAC.<sup>20-22, 24, 25, 27, 28, 35, 44, 45, 49, 51, 53-61</sup> It is reasonable to assume that the HmRM, obtained by the complete hydrolysis of TEOS (for  $t_A = t_s + t_a \approx t_b$ ; see Table 1) is composed of about 1.5 nm sized shell-less silica nanoparticles dispersed in the water-ethanol solution of TPA-bearing silicate oligomers (mainly 4R, D3R, D4R and D5R; see Figs. 2Aa and 2Ab) and small amount of “free” TPAOH, at least for  $t_b < t_A = t_s < 2$  h (see Scheme 1-Ia). Due to low concentration of the “free” TPAOH above the CAC<sup>[57]</sup> (see also Figs 4 and 5bD and Tables 1 and S1), the ≡Si-OH groups are dominant, and the fraction of the ≡Si-O<sup>-</sup> groups is considerably reduced on surfaces of the nanoparticles formed above the CAC [55] (see Scheme 1-Ib). By the same reason, the formed nanoparticles are not sterically stabilized by TPA<sup>+</sup> shell (or this stabilization is very limited) at least to  $t_A = t_s = 3$  h.

Relatively low ratio Si-Q<sup>3</sup>/Si-Q<sup>4</sup> ( $\approx 1$ , see Fig. 2Ab) of the nanoparticles indicates that the nanoparticle core is formed mainly by polymerization of Si(OH)<sub>4</sub> monomers<sup>51, 55</sup> and that negatively charged silicate monomers and oligomers does not directly participate in the formation of nanoparticle core, as was assumed in some studies.<sup>20, 21, 27, 54, 66</sup> However, still large fraction (about 50 %) of Si with Q<sup>3</sup> sites, is caused by a large amount of the surface (terminal) Si atoms, e.g. (NP)Si-OH and (NP)Si-O<sup>-</sup> (see Scheme 1-Ib),<sup>49, 60</sup> but also internal (bulk) ≡Si-OH groups (bordered by red ellipses in Scheme 1-Ic). As already has been mentioned, the ratios Si-Q<sup>3</sup>/Si-Q<sup>4</sup>  $\approx 1$  were observed in the silica nanoparticles formed in the concentrated HmRMs.<sup>66, 69, 74</sup>

Collisions of the non-stabilized (shell-less) silica nanoparticles results in the formation of aggregates; their sizes gradually increase from  $t_A = t_s > t_b$  to  $t_A = t_s = 3$  h (solid curves in Figs. 9A – 9C and Schemes 1-Ia, 1-IIa and 1-IIIa). A wide distribution of sizes of the aggregates, established at  $t_A = t_s = 3$  h (solid curve in Fig. 9C), indicates that the processes of aggregation (ag in Scheme 1) and disaggregation (d-ag in Scheme 1) are in dynamic equilibrium; however, the forward reaction (ag) is dominating in the time interval from  $t_A = t_s > t_b$  to  $t_A = t_s = 3$  h (see Schemes 1-I – 1-III). On the other hand, since the AFM images and their cross-section analyzes in Fig. 10 show that the nanoparticles present at both  $t_A = t_s = 3$  h (solid curve in Fig. 9C) and  $t_A = 24$  h (dashed curve in Fig. 9C) represent the aggregates of about 1 nm to 2 nm sized primary nanoparticles, it is evident that the decrease in the particle size from  $D_{av} = 7.30$  nm at  $t_A = t_s = 3$  h to  $D_{av} = 3.85$  nm at  $t_A = t_s + t_a = 3$  h + 21 h = 24 h is caused by a stepwise disaggregation (d-ag) of the aggregates formed in the time interval from  $t_A = t_s > t_b$  to  $t_A = t_s = 3$  h. Only reasonable explanation of the process of disaggregation at constant or even decreasing alkalinity (see Figs. 4 and 5bD as well as Table S1 I SI-2) is blocking of the terminal (NP)Si-OH groups and thus, preventing the formation of new (NP)Si-O-Si(NP) bonds between the colliding nanoparticles, i.e., stoppage of the aggregation. This blocking can be realized by the formation of the shell on the surface of the silica nanoparticles. It is reasonable to assume that the shell is firstly formed on the individual nanoparticles and their small(est) aggregates (see Schemes 1-IIIa and 1-IV); such sterically stabilized NP-Sa are excluded from the further aggregation processes. Since, as already has been postulated, the aggregation and disaggregation are in dynamic equilibrium (see Schemes 1-Ia, 1-IIa, 1-IIIa and 1-IV), the excluded NP-Sa are “replaced” by the disaggregation of the larger aggregates. Formation of the shells on the newly-formed Np-Sa and their exclusion from the aggregation processes causes further disaggregation. These processes (exclusion of the stabilized Np-Sa and their replacement by disaggregation) continue until entire amount of

NP-Sa has been sterically stabilized by the formation of shells (at  $t_A = t_s + t_a \leq 24$  h; see Scheme 1-V) and thus, become unable for aggregation. Such formed, stabilized NP-Sa have the size in the range from  $D_{\min} \approx 1.6$  nm to  $D_{\max} \approx 10.9$  nm with  $D_p = 3.1$  nm and  $D_{av} = 3.85$  nm at  $t_A = t_s + t_a = 24$  h (see dashed curve in Fig. 9C and Table S6 in SI-5). The AFM image and its cross-section analysis (Fig. 10B) show that the Np-Sa of different sizes (from about 1.6 nm to about 10.9 nm) are composed of the smaller, about 1 nm to about 2 nm sized primary nanoparticles.

Very often, the nanoparticle shell is considered as organic cations ( $\text{Org}^{n+}$ ), usually tetraalkylammonium ( $\text{TAA}^+$ ) and most frequently,  $\text{TPA}^+$  ions, adsorbed on the surface of  $\text{SiO}_2$  nanoparticle core.<sup>49, 53, 55, 59, 60, 65, 74, 75</sup> This consideration includes association of the  $\text{Org}^{n+}$  ( $\text{TAA}^+$ ,  $\text{TPA}^+$ ) ions with deprotonated silanol groups<sup>74</sup> and formation of a Stern layer of the adsorbed cations, that is effectively part of the liquid phase of the system.<sup>49, 55</sup> On the other hand, analysis of the interactions of  $\text{TAA}^+$  ions with oligomers and nanoparticles (see SI-6) has shown that most of the  $\text{TPA}^+$  ions, originally arising from  $\text{TPAOH}$ , are associated with the polysilicate anions (silicate monomers and oligomers), formed below the CAC.<sup>20-22, 24, 25, 28, 47, 53-57</sup> In addition, from the data presented in Figs. 4 and 5b and Tables 1 and S1, it can be easily calculated that more than 90 % of  $\text{TPAOH}$  has been spent for deprotonation of the  $\text{Si}(\text{OH})_4$  monomers, formed during hydrolysis of  $\text{TEOS}$ , and for the formation of the polysilicate anions (oligomers) associated with  $\text{TPA}^+$  ions, below the CAC. Hence, less than 10 % of “free” (unspent)  $\text{OH}^-$  ions  $[(\text{OH})_{x,U,av}]$ ; see Table S7 in SI-6] and consequently, less than 10 % of the “free” (unspent)  $\text{TPA}^+$  ions  $[(\text{TPA}^+)_{x,U,av}]$ ; see Table S8 in SI-6], are present in the IM-HmRMs above the CAC ( $x \geq 0.25$ ). Finally, knowing that the  $\text{TPA}$ -silica nanoparticles contains 7 – 15  $\text{TPA}^+$  ions per 100  $\text{SiO}_2$  molecules,<sup>59, 63</sup> it can be easily calculated that  $(\text{TPA}^+)_{x,U,av} < (\text{TPA}^+)_{\text{shell}}$  and thus, that amount of the remaining “free”  $\text{TPA}^+$  ions is not sufficient for the formation of the nanoparticle shell (see also SI-6); here,

$(\text{TPA}^+)_{\text{shell}}$  is the fraction (percentage) of the  $\text{TPA}^+$  ions needed for the formation of the  $\text{TPA}^+$  shell, relative to the starting amount of  $\text{TPAOH}$ , (see Table S8 in SI-6). Hence, only very small fraction of the  $\text{TPA}^+$  ions in the nanoparticle shell is directly bonded to the deprotonated terminal (surface) silanol groups (see Scheme 1-IIIb). On the other hand, since the majority of the  $\text{Org}^{n+}$  ( $\text{TAA}^+$ ,  $\text{TPA}^+$ ) ions are associated with the polysilicate anions (oligomers; see SI-6), it is reasonable to conclude that the major part of the nanoparticle shell is formed by the attachment of the polysilicate anions (silicate oligomers), associated with  $\text{TPA}^+$  ions, on the surfaces of the nanoparticles cores. This attachment may be realized by the formation of the  $(\text{NP})\text{Si}-\text{O}-\text{Si}(\text{Ogm})$  linkages between the protonated silanol groups of silica nanoparticles  $[(\text{NP})\text{Si}-\text{OH}]$  and the protonated silanol groups of silicate oligomers ( $\text{OgmSi}-\text{OH}$ ) associated with the  $\text{Org}^{n+}$  ( $\text{TAA}^+$ ,  $\text{TPA}^+$ ) ions (see Schemes 1-IIIb and 1-Vb).

Since silicate monomers and dimers are precursors for the formation of higher oligomers,<sup>58, 65</sup> it can be assumed that only smaller part of the core surface is covered by the  $\text{TPA}^+$ -bearing monomers and dimers and thus, that their participation in the formation of the nanoparticle shell is not crucial. However, it is reasonable to assume that these species contribute to  $\text{Q}^1$  and  $\text{Q}^2$  sites of the nanoparticles (see Figs. 2Ab and 2Bb and Scheme 1-IIIb as well as SI-6), together with the  $\text{Q}^1$  and  $\text{Q}^2$  sites formed in the bulk of nanoparticle core.<sup>27, 28, 54, 55</sup> Small percentages of the nanoparticles Si atoms having  $\text{Q}^1$  and  $\text{Q}^2$  sites and their little changes in the time interval from  $t_A = t_s = 3$  h (symbols  $\circ$  and  $\bullet$  in Figs. 2Ab) to  $t_A = 24$  h (symbols  $\circ$  and  $\bullet$  in Figs. 2Bb) confirm the assumptions that the only small amounts of the  $\text{TPA}^+$ -bearing monomers and dimers participate in the formation of the nanoparticles shells at the early stage of the process (see Scheme 1-IIIb; for the sake of simplicity, only  $\text{TPA}^+$ -bearing monomers and “free”  $\text{TPA}^+$  ions are displayed as the shell-containing  $\text{TPA}^+$  ions). On the other hand, the analysis of the relationships between the “types” of oligomers attached on the nanoparticle core and their contribution to the distribution of Si-Q sites in the

nanoparticles (see SI-6) indicates that the increase of the ratio  $\text{Si-Q}^3/\text{Si-Q}^4$  from 0.925 at  $t_A = t_s = 3$  h (Fig. 2Ab) to 1.23 at  $t_A = 24$  h (Fig. 2Bb) is caused by the attachment of the 4DR and 5DR oligomers on the surfaces of the nanoparticles cores. Hence, it can be concluded that the nanoparticle shell is composed of mainly  $\text{TPA}^+$ -bearing D4R and DR5 oligomers and, as already has been mentioned, smaller fractions of the  $\text{TPA}^+$ -bearing monomers and dimers, at  $t_A = 24$  h (see Scheme 1-Vb; for the sake of simplicity, only the simplified, “2D sketches” of the  $\text{TPA}^+$ -bearing D4R and D5R units are presented in the scheme). Assuming that the mobility of the Ogm-TPA species are considerably lower than the mobility of the  $\text{TPA}^+$  ions and that the mobility decreases with the increasing size of the Ogm-TPA species, the formation of the nanoparticle shell by the attachment of the larger oligomers (D4R and D5R), explains the “delaying” in the formation of the shell: It is reasonable to assume that the first Ogm-TPA species attached on the nanoparticle core are  $\text{Si}(\text{OH})_3\text{O}^{\cdots+}\text{TPA}$  (monomers) and/or  $(\text{OH})_3\text{Si-O-Si}(\text{OH})_2\text{O}^{\cdots+}\text{TPA}$ ,  $\text{TPA}^+\cdots\text{O}(\text{OH})_2\text{Si-O-Si}(\text{OH})_2\text{O}^{\cdots+}\text{TPA}$  (dimers) (see Scheme 1-IIIb). By the same principles, larger Ogm-TPA species, (D4R and D5R) attach to the surfaces of the nanoparticles cores later ( $t_A = t_s > 3$  h).

Finally, it is reasonable to assume that the  $\text{TPA}^+$  ions overlay not only directly interacting silanol groups of the attached oligomers, but also surrounding ones, (see Scheme 1-Vb). In this way, the “terminal” silanol groups of the TPA-containing oligomers (shell) are unable for the formation of (new)  $(\text{Np})\text{Si-O-Si}(\text{Np})$  linkages between eventually collided core@shell nanoparticles. As already has been pointed out, this is the reason that the steric stabilization of the nanoparticles, caused by the formation of shells, as described above, not only prevents the further aggregation, but provokes disaggregation of the already formed aggregates (see Fig. 9 and Scheme 1), which results in the establishing of the stable particulate system composed of small aggregates of primary silica nanoparticles (dashed curve in Fig. 9C, AFM image in Fig. 10B and Scheme 1-V).

## CONCLUSIONS

The clear solutions in the system,  $\text{SiO}_2$ -TPAOH-EtOH- $\text{H}_2\text{O}$ , prepared by room-temperature (*rt*) hydrolysis of TEOS (tetraethyl orthosilicate) in the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ , were characterized by different methods during the preparation (measuring of pH and ionic conductivity) and during subsequent *rt* stirring/aging ( $^{29}\text{Si}$ -NMR, DLS, AFM).

Careful analysis of the obtained data clearly shows that the results of this study offer some new „elements“ for the understanding of the mechanisms of formation and room temperature evolution of the core@shell silica nanoparticles:

(1) In spite of widely spread meaning that the silica nanoparticle cannot be formed below the critical aggregation concentration (CAC;  $x < 2.5$ ) of  $\text{SiO}_2$ , the resolute evidence of the formation of the stable, about 1.2 nm sized core(amorphous  $\text{SiO}_2$ )@shell( $\text{TPA}^+$  ions) nanoparticles below the CAC was found during realization of this study. The nanoparticle core, formed by polymerization via addition of the  $\text{Si}(\text{OH})_4$  monomers which are not pre-associated with OSDA ( $\text{TPA}^+$  in the studied case), are immediately stabilized electrostatically (deprotonation of the surface silanol groups at high  $[\text{OH}^-]/[\text{SiO}_2]$  ratio below the CAC) and sterically (formation of the  $\text{TPA}^+$  shell on the surface of the nanoparticle core at high  $[\text{TPA}^+]/[\text{SiO}_2]$  ratio below the CAC). Due to the small fraction of the  $\text{SiO}_2$  in the form of nanoparticles, below the CAC, they cannot be evidenced by  $^{29}\text{Si}$ -MNR, but can be clearly detected by DLS and observed by AFM.

(2) The nanoparticles formed above the CAC, aggregate into larger particles in the short time interval from  $t_A = t_s < 2$  h to  $t_A = t_s \leq 3$  h; the larger particles are composed of discrete (individual) 1 – 2 nm sized “primary” nanoparticle formed at  $t_A = t_s < 2$  h. This indicates that due to insufficient concentration of TPAOH, the nanoparticle formed above the CAC are not



stabilized either electrostatically or sterically, at least to  $t_A = t_s \approx 3$  h. Of course, the indicated time intervals are valid for the investigated IM-HmRMs having the starting chemical compositions: TEOS:0.25TPAOH:20H<sub>2</sub>O; it can be expected that the characteristic time intervals changes with the change of the (starting) hemical composition of HmRMs.

(3) Disaggregation of the particles (aggregates), formed above the CAC, in the time interval from  $t_A = t_s < 2$  h to  $t_A = t_s \leq 3$  h, as described in (2), start to disaggregate at  $3 \text{ h} \leq t_A = t_s \leq 3.5$  h as the consequence of the stepwise formation of the shell on the surface of the nanoparticle core (steric stabilization) and thus, by exclusion of the stabilized nanoparticles from further aggregation processes. Since the processes of aggregation and disaggregation are in dynamic equilibrium, the excluded nanoparticles and their small aggregates are “replaced” by the disaggregation of larger aggregates. These processes (exclusion of the stabilized nanoparticles and their replacement by disaggregation) continue until entire amount of nanoparticles and their small aggregates has been sterically stabilized by the formation of shells (at  $t_A \leq 24$  h) and thus, unable for aggregations. In this way, the stabilized core@shell nanoparticles are not individual (discrete) entities, but the nanoaggregates of the primary nanoparticles.

(4) On the basis of the estimated ratio  $[TPA^+]/[SiO_2]$  ( $[shell]/[core]$ ) in the core@shell silica nanoparticles and the known concentrations of the remaining („free“) TPAOH above the CAC, it is concluded that the nanoparticle shell can be formed only by attachment of the polysilicate anions (silicate oligomers), associated with  $TPA^+$  ions, on the surfaces of the nanoparticles cores. This gives a new insight in the “structure” of the nanoparticle shell, which is considerably different from the most frequently described one, i.e., “free”  $TPA^+$  ions adsorbed on the surface of the nanoparticle core.

Since the general mechanism of the formation of the core(amorphous silica)@shell(Org<sup>n+</sup> ions) nanoparticles does not depend on the nature of organic cation (Org<sup>n+</sup>) and the  $[TEOS]/[Org(OH)_n]$  and TEOS/H<sub>2</sub>O,<sup>28, 56</sup> it is reasonable to conclude that the

results obtained in this work are imminent not only for the investigated reaction mixtures, but also for other reaction mixtures in the systems, TEOS-Org(OH)<sub>n</sub>-H<sub>2</sub>O and thus, have the general significance.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional analyzes of <sup>29</sup>Si-NMR data; measurement and correction of pH values with respect to ethanol content; simulation (calculation) of the changes in the relevant concentrations during room-temperature stirring (aging) of the investigated homogeneous reaction mixtures; analysis of the changes in the concentrations, [SiO<sub>2</sub>], of silica and, [OH<sup>-</sup>], of OH<sup>-</sup> ions and of their relationships at various stages of hydrolysis of TEOS in the investigated homogeneous reaction mixtures; analysis of the DLS-PSD data; analysis of interactions of tetraalkylammonium (TAA<sup>+</sup>) ions with silica oligomers and nanoparticles; additional references (PDF)

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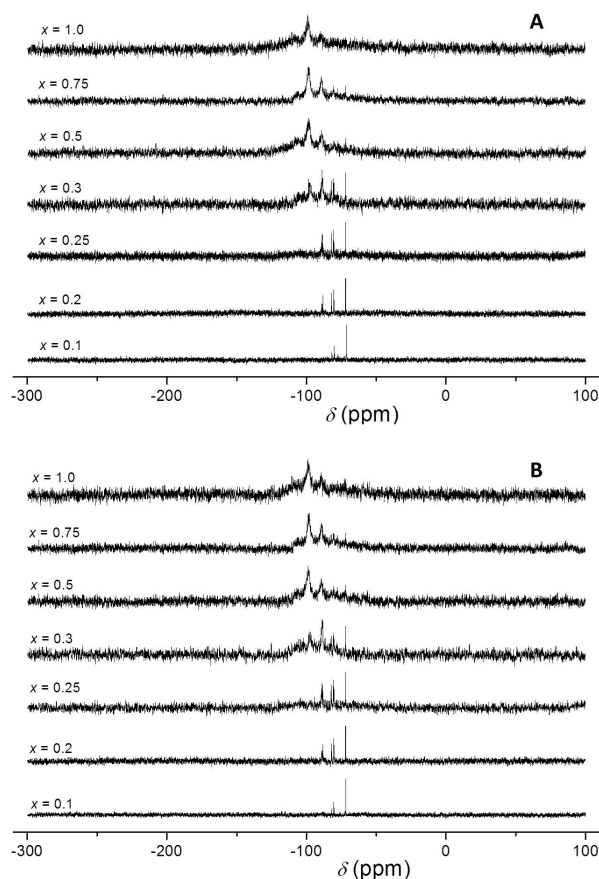
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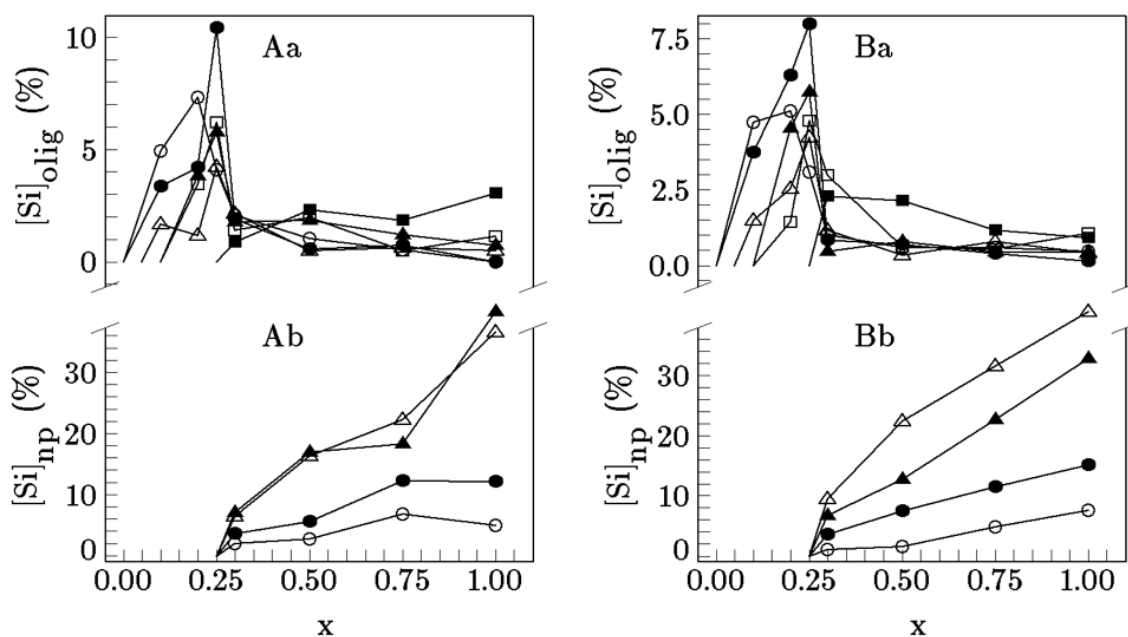
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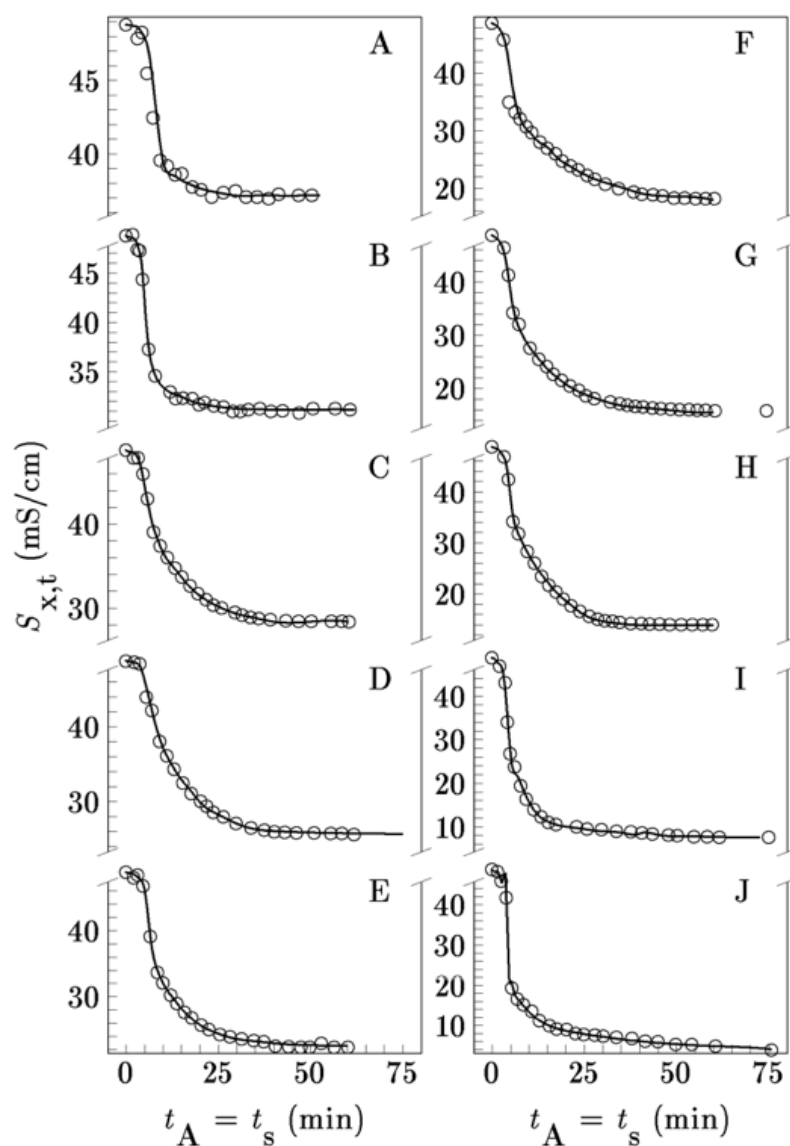


**Figure 1.**  $^{29}\text{Si}$ -NMR spectra of the homogeneous reaction mixtures (clear solution) obtained by room-temperature (*rt*) stirring for  $t_A = t_s = 3$  h (A) and then by additional room-temperature aging for  $t_a = 21$  h under static conditions (B), of the investigated “model” homogeneous reaction mixtures (IM-HmRMs) having the initial molar compositions: xTEOS:0.25TPAOH:20H<sub>2</sub>O (see Experimental methods).

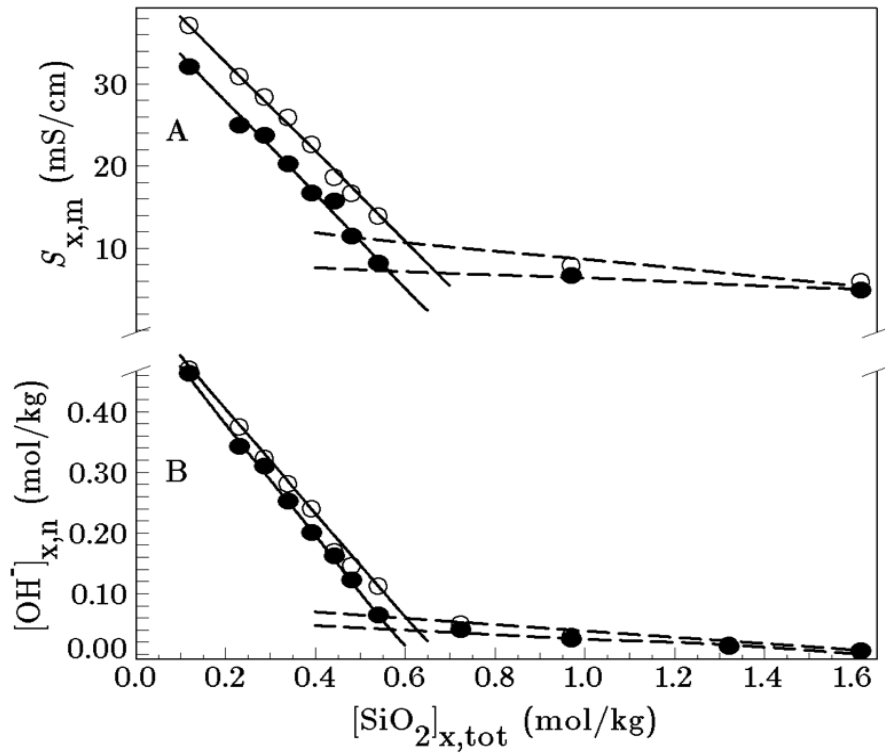


**Figure 2.** Si-distribution in oligomers (Aa, Ba) and distribution of  $Q^n$  Si atoms ( $Q^n$  sites) in nanoparticles (Ab, Bb), as functions of  $x$ , in the homogeneous reaction mixtures (clear solution) obtained by room-temperature (*rt*) stirring for  $t_A = t_s = 3$  h (Aa, Ab) and then by additional *rt* aging for  $t_a = 21$  h under static conditions (Ba, Bb) of the IM-HmRMs. The corresponding symbols in Figs. Aa and Ba are: ○ monomers, ● for dimers, △ for cyclic trimers (3R), ▲ for cyclic tetramers (4R), □ for double three rings (D3R), ■ for double four rings (D4R) and double five rings (D5R). The corresponding symbol in Figs Ab and Bb are: ○ for mixture of  $Q^1$  and  $Q^{2\Delta}$  sites, ● for mixture of  $Q^2$  and  $Q^{3\Delta}$  sites, △ for  $Q^3$  sites and ▲ for  $Q^4$  sites. Here  $Q^{n\Delta}$  corresponds to Si sites with  $n$  connectivity present in 3-membered rings.

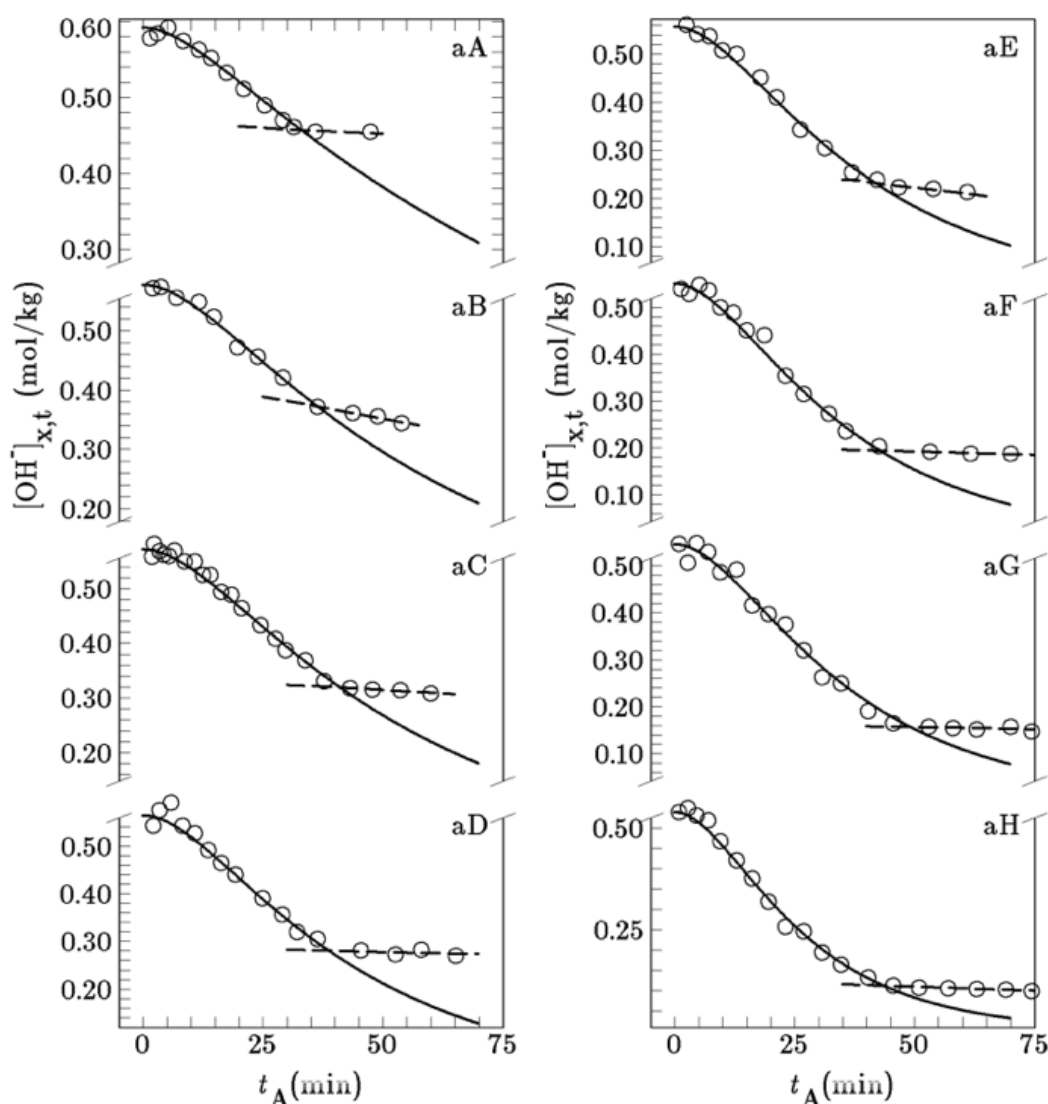




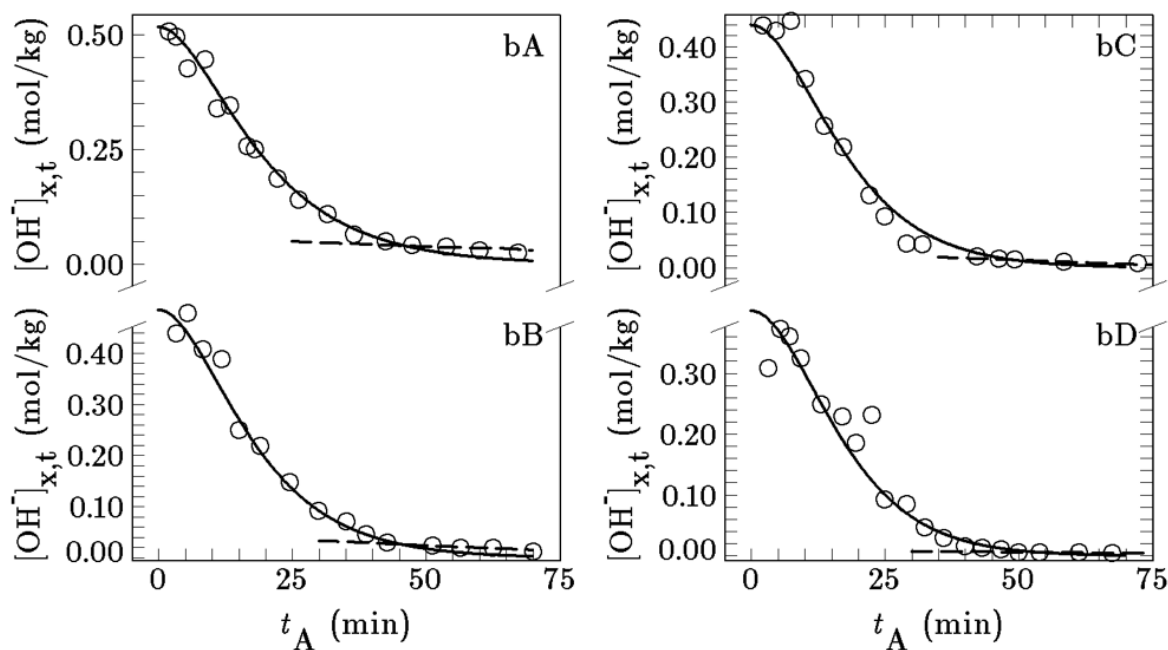
**Figure 3.** Changes of the ionic conductivity,  $S_{x,t}$ , measured during preparation and aging of the M-HmRMs with  $x = 0.05$  (A),  $0.1$  (B),  $0.125$  (C),  $0.15$  (D),  $0.175$  (E),  $0.2$  (F),  $0.22$  (G),  $0.25$  (H),  $0.5$  (I) and  $1.0$  (J). The IM-HmRMs were prepared by the *rt* stirring of the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ .  $t_A = t_s$  is the time of aging (with stirring) passed from the mixing of TEOS and TPAOH solutions (see Experimental methods).



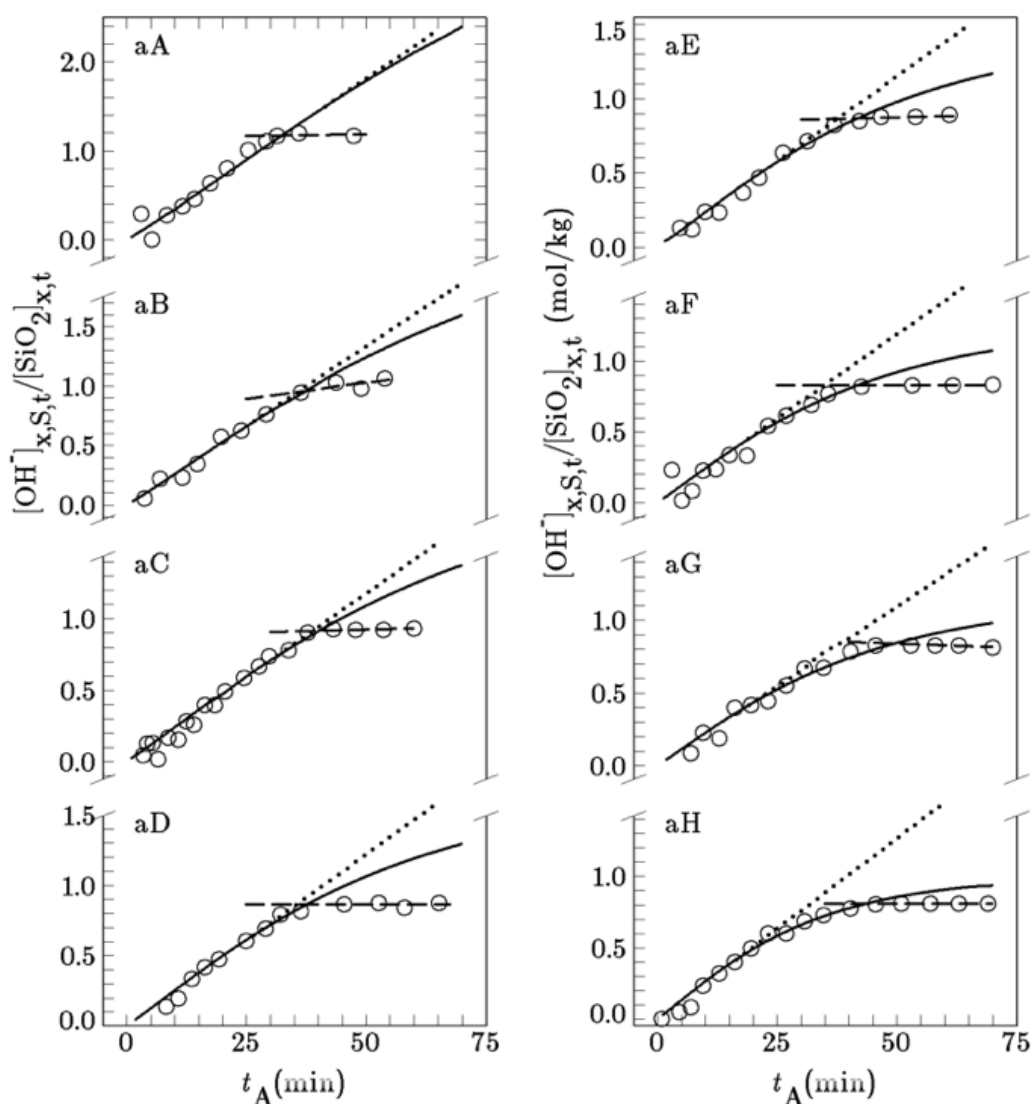
**Figure 4.** Changes of (A) the ionic conductivity,  $S_{x,m}$ , measured at “equilibrium” time  $t_A = t_s = t_{eq}$  (○;  $m = eq$ ; see Table 1) and at  $t_A = t_s + t_a = 24$  h (●,  $m = 24h$ ) and (B) the concentrations,  $[\text{OH}^-]_{x,n}$ , of the  $\text{OH}^-$  ions measured at the “breakthrough” time  $t_A = t_s = t_b$  (○;  $n = b$ ) and at  $t_A = t_b + t_a = 24$  h (●,  $n = 24h$ ), with the concentration,  $[\text{SiO}_2]_{x,\text{tot}}$ , of the  $\text{SiO}_2$  formed by hydrolysis of TEOS in the IM-HmRMs. The corresponding values of  $t_A = t_s = t_{eq}$  and  $t_A = t_s = t_b$  are listed in Table 1.



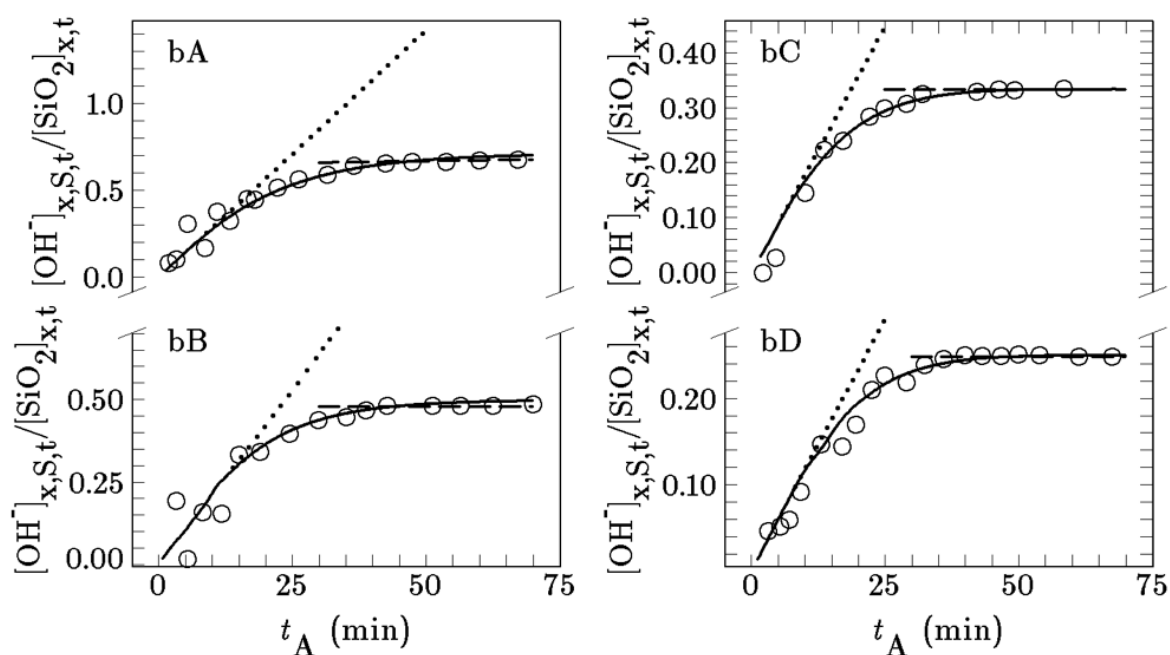
**Figure 5a.** Changes in the molality concentrations,  $[\text{OH}^-]_{x,t}$  of the  $\text{OH}^-$  ions during preparation and aging of the IM-HmRMs with  $x = 0.05$  (aA),  $0.1$  (aB),  $0.125$  (aC),  $0.15$  (aD),  $0.175$  (aE),  $0.2$  (aF),  $0.22$  (aG) and  $0.25$  (aH). The IM-HmRMs were prepared by the *rt* stirring of the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ . The values of  $[\text{OH}^-]_{x,t}$ , characterized by symbol  $\circ$ , are determined (calculated) from the corresponding measured and corrected pH values (see SI-2) and the values of  $[\text{OH}^-]_{x,t}$ , characterized by solid curves, are calculated by simultaneous numerical solutions of the equations (1) and (2).  $t_A = t_s$  is the time of aging (with stirring), passed from the mixing of TEOS and TPAOH solutions (see Experimental methods).



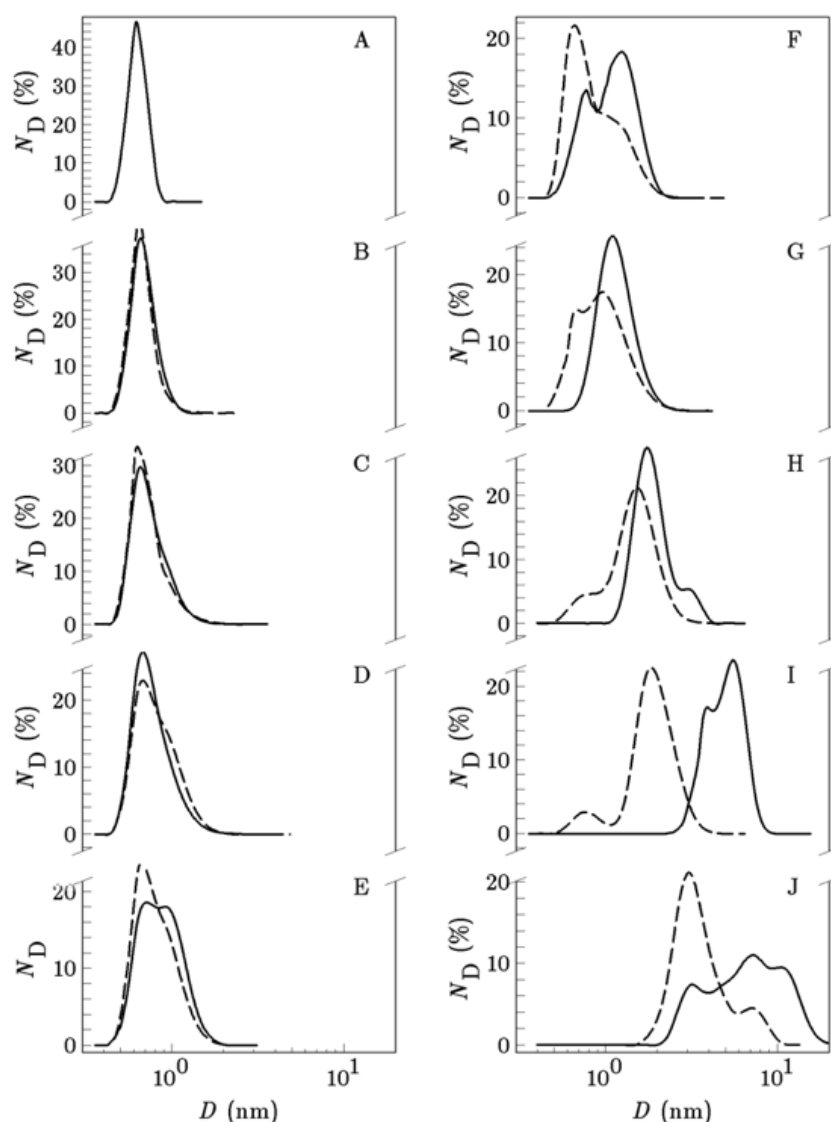
**Figure 5b.** Changes in the molality concentrations,  $[\text{OH}^-]_{x,t}$  of the  $\text{OH}^-$  ions during preparation and aging of the IM-HmRMs with  $x = 0.35$  (bA),  $0.5$  (bB),  $0.75$  (bC) and  $1.0$  (bD). The IM-HmRMs were prepared by the *rt* stirring of the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ . The values of  $[\text{OH}^-]_{x,t}$ , characterized by symbol  $\circ$ , are determined (calculated) from the corresponding measured and corrected pH values (see SI-2) and the values of  $[\text{OH}^-]_{x,t}$ , characterized by solid curves, are calculated by simultaneous numerical solutions of the equations (1) and (2).  $t_A = t_s$  is the time of aging (with stirring), passed from the mixing of TEOS and TPAOH solutions (see Experimental methods).



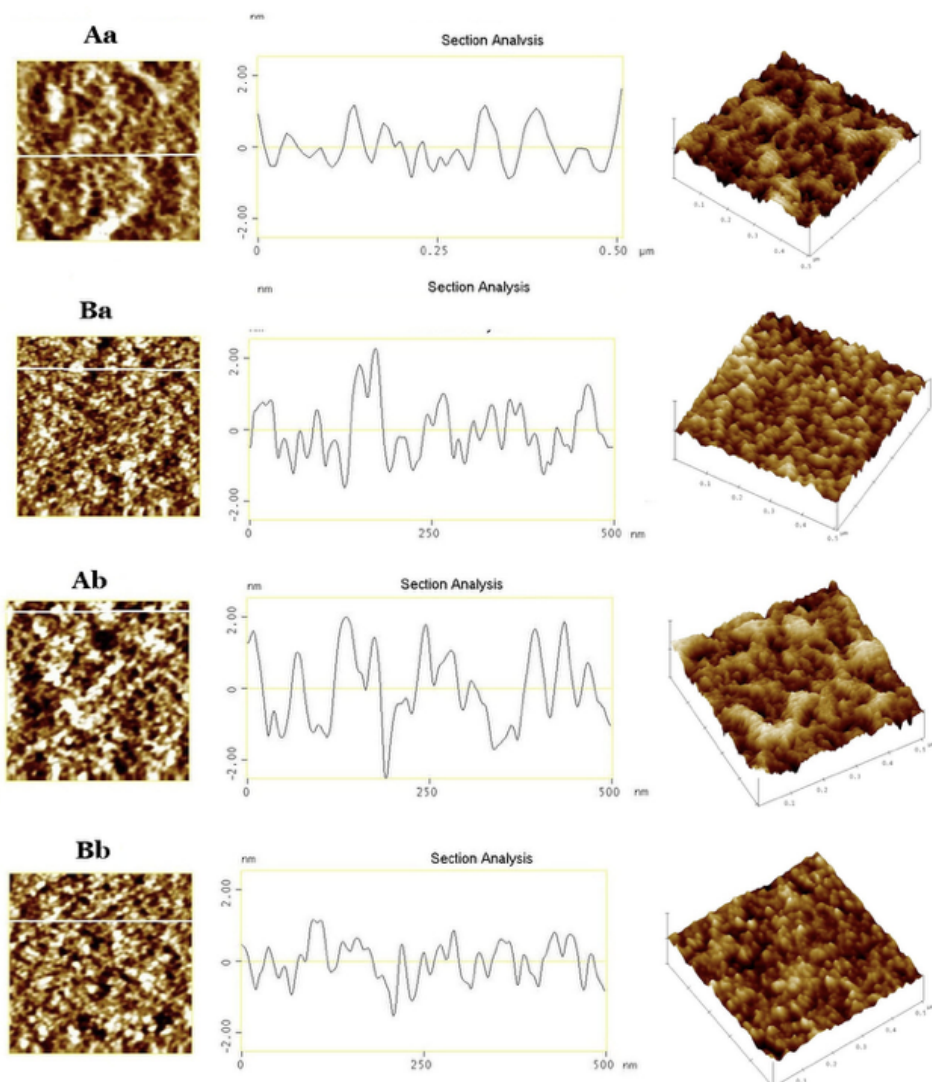
**Figure 6a.** Changes of the calculated (solid curves) and measured (symbol  $\circ$ ) ratios  $[\text{OH}^-]_{x,S,t}/[\text{SiO}_2]_{x,t}$  during preparation and aging of the IM-HmRMs with  $x = 0.05$  (aA), 0.1 (aB), 0.125 (aC), 0.15 (aD), 0.175 (aE), 0.2 (aF), 0.22 (aG) and 0.25 (aH). The IM-HmRMs were prepared by the *rt* stirring of the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ .  $t_A = t_s$  is the time of stirring (aging) passed from the mixing of TEOS and TPAOH solutions.



**Figure 6b.** Changes of the calculated (solid curves) and measured (symbol  $\circ$ ) ratios  $[\text{OH}^-]_{x,S,t}/[\text{SiO}_2]_{x,t}$  during preparation and aging of the IM-HmRMs with  $x = 0.35$  (bA),  $0.5$  (bB),  $0.75$  (bC) and  $1.0$  (bD). The M-HmRMs were prepared by the *rt* stirring of the reaction mixtures having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ .  $t_A = t_s$  is the time of stirring (aging) passed from the mixing of TEOS and TPAOH solutions.

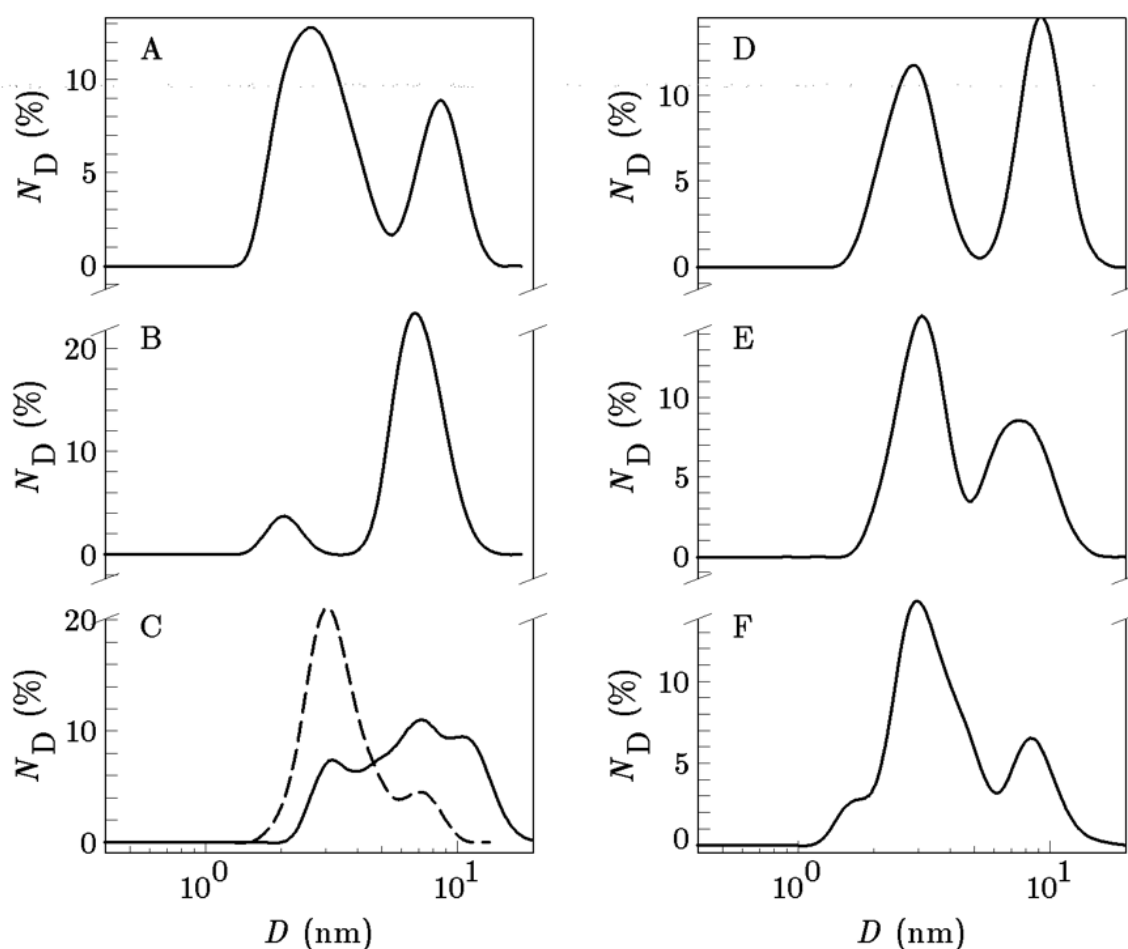


**Figure 7.** DLS-PSD curves by number measured in homogenous reaction mixtures (clear solutions) obtained by room-temperature stirring for  $t_A = t_s = 3$  h (solid curves) and then by additional room-temperature aging for  $t_a = 21$  h under static conditions ( $t_A = t_s + t_a = 24$  h, dashed curves) of the IM-HmRMs having the starting chemical compositions: xTEOS:0.25TPAOH:20H<sub>2</sub>O, with  $x = 0$  (A),  $x = 0.05$  (B),  $x = 0.2$  (C),  $x = 0.25$  (D),  $x = 0.275$  (E),  $x = 0.35$  (F),  $x = 0.5$  (G),  $x = 0.65$  (H),  $x = 0.75$  (I) and  $x = 1$  (J).  $N_D$  is the number percentage of the particles having the spherical equivalent diameter  $D$ .

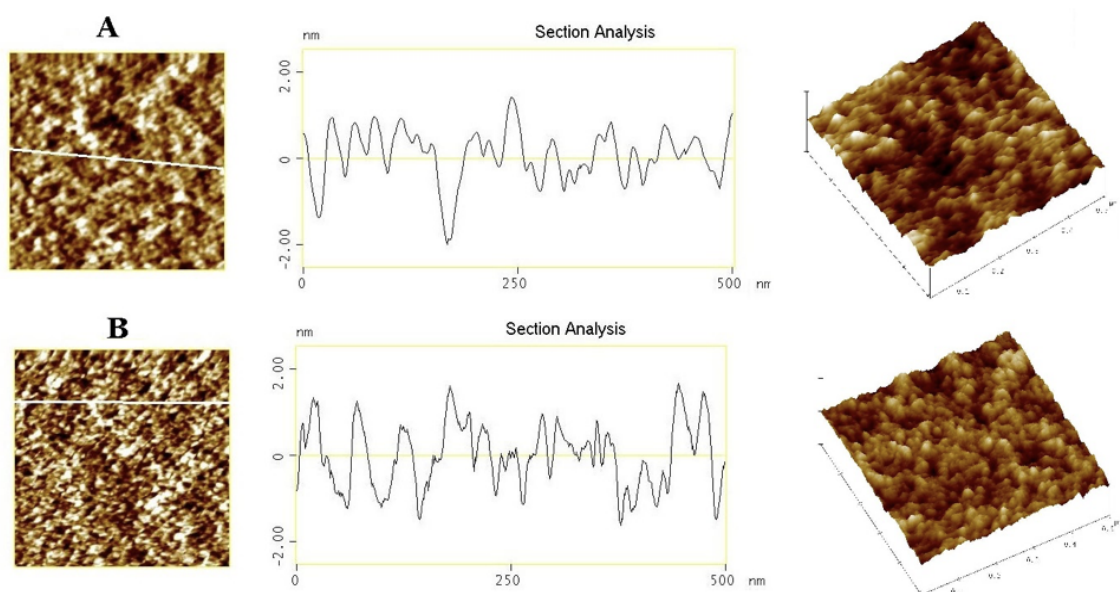


**Figure 8.** AFM topographic images and corresponding cross-section analyzes of the nanoparticles formed during room-temperature stirring for  $t_A = t_s = 3$  h (Aa, Ba) and then by additional room-temperature aging for  $t_a = 21$  h under static conditions;  $t_A = t_s + t_a = 24$  h (Ab, Bb) of the IM-HmRMs having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ , with  $x = 0.1$  (Aa, Ab) and  $x = 0.2$  (Ba, Bb). Images are presented as 2D height data (left), the cross-section through the line shown on the same scale: scan size of  $500\text{ nm} \times 500\text{ nm}$  and vertical scale of  $5\text{ nm}$  (middle) and as 3D height data are shown on the same scale: scan size  $500\text{ nm} \times 500\text{ nm}$  and vertical scale of  $5\text{ nm}$  (right).

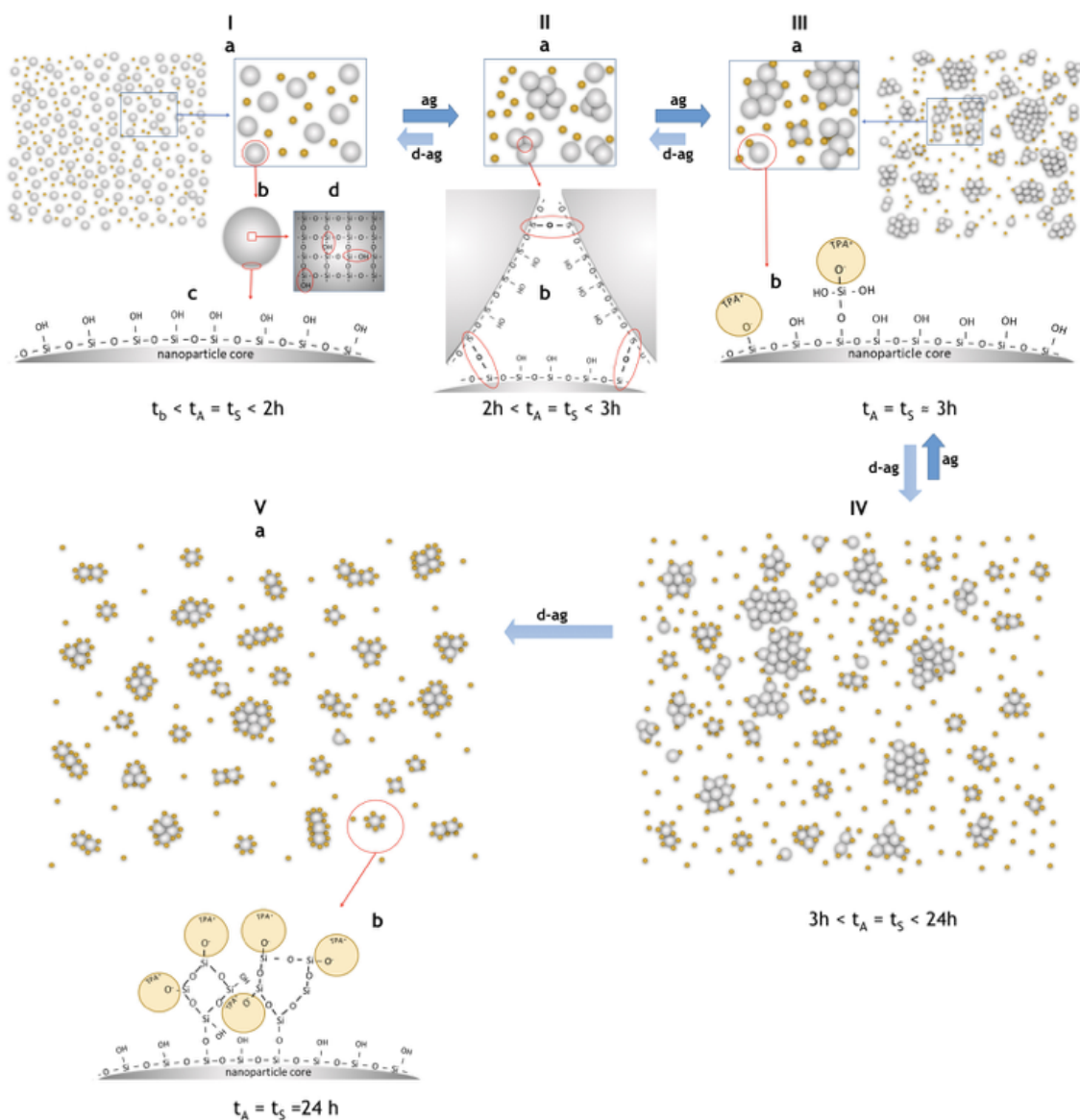




**Figure 9.** The size distributions by number (solid curves) of the nanoparticles formed during room-temperature stirring for  $t_A = t_s = 2$  h (A), 2.5 h (B), 3 h (C), 3.5 (D), 4.5 h (E) and 6 h (F), of the reaction mixture having the starting chemical compositions: 1TEOS:0.25TPAOH:20H<sub>2</sub>O. The dashed curve in the part (C) represent the size distribution of the particles obtained in the same homogeneous reaction mixture stirred at room temperature for  $t_A = t_s = 3$  h and then, by additional room-temperature aging under static conditions for  $t_a = 21$  h.  $N_D$  is the number percentage of the particles having the spherical equivalent diameter  $D$ .



**Figure 10.** AFM topographic images and corresponding cross section analyzes of the nanoparticles formed during room-temperature stirring for  $t_A = t_s = 3$  h (A) and then by additional room-temperature aging for  $t_a = 21$  h under static conditions;  $t_A = t_s + t_a = 24$  h (B) of the homogeneous reaction mixture having the starting chemical composition: 1TEOS:0.25TPAOH:20H<sub>2</sub>O. Images are presented as 2D height data (left), the cross-sections through the line are shown on the same scale: scan size of 500 nm  $\times$  500 nm and vertical scale of 5 nm (middle) and as 3D height data and are shown on the same scale: scan size of 500 nm  $\times$  500 nm and vertical scale of 10 nm (right).



**Scheme 1. Schematic presentation of the processes occurring in the HmRM having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$  ( $x > 0.25$ ; above the CAC) during room-temperature stirring/aging. The details are described in the text.**

Remarks: (1) For practical reason, only the nanoparticles (larger gray spheres) and  $\text{TPA}^+$ -bearing oligomers (red spots) are presented. (2) For practical reason, all the  $\text{TPA}^+$ -bearing oligomers are presented by the spots of the same size.

**Table 1.** Influence of the mole fraction,  $x$ , of TEOS in the homogeneous reaction mixtures, having the starting chemical compositions:  $x\text{TEOS}:0.25\text{TPAOH}:20\text{H}_2\text{O}$ , on the molality concentrations,  $[\text{SiO}_2]_{x,\text{tot}} = [\text{TEOS}]_{x,0}, [\text{OH}^-]_{x,0}, [\text{OH}^-]_{x,S,b}$  and  $[\text{OH}^-]_{x,S,24h}$  and the times  $t_{\text{eq}}$  and  $t_b$ . The definitions of  $[\text{SiO}_2]_{x,\text{tot}}, [\text{OH}^-]_{x,0}, [\text{OH}^-]_{x,S,b}, [\text{OH}^-]_{x,S,24h}, t_{\text{eq}}$  and  $t_b$  are explained in the text and omitted here for clarity reasons.

$x$	$[\text{SiO}_2]_{x,\text{tot}}$ (mol/kg)	$[\text{OH}^-]_{x,0}$ (mol/kg)	$t_{\text{eq}}$ (min)	$t_b$ (min)	$[\text{OH}^-]_{x,S,b}$ (mol/kg)	$[\text{OH}^-]_{x,S,24h}$ (mol/kg)
0.05	0.1186	0.5931	$\approx 31$	32.5	0.1230	0.1306
0.1	0.2315	0.5787	$\approx 35$	36	0.2037	0.2362
0.125	0.2859	0.5718	$\approx 40$	41	0.2488	0.2618
0.15	0.3391	0.5651	$\approx 40$	39	0.2841	0.3126
0.175	0.3910	0.5585	$\approx 45$	42.5	0.3185	0.3535
0.2	0.4416	0.5521	$\approx 43$	43.5	0.3824	0.3896
0.22	0.4814	0.5471	$\approx 50$	51	0.4010	0.4246
0.25	0.5397	0.5397	$\approx 50$	46	0.4277	0.4747
0.35	0.7230	0.5165	-	45	0.4660	0.4765
0.5	0.9703	0.4851	$\approx 55$	46	0.4555	0.4601
0.75	1.3220	0.4406	-	51	0.4256	0.4281
1	1.6140	0.4036	$\approx$	52	0.3975	0.3986

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