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Influence of Indifferent Electrolytes on Formation of Coagulative Structures in Aqueous Silica Dispersions

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Effects of indifferent electrolytes (NaCl, KCl, LiCl, NaI, $NaNO_3$, $CaCl_2$, and $MgCl_2$) on the electrical double layer (EDL), aggregation, gelling, and rheological properties of aqueous dispersions of nanosilica were investigated. All examined indifferent electrolytes enhance interactions between nanoparticles of fumed silica through the coagulation mechanism. The critical concentration of gelation and gelling time decrease in the presence of the electrolytes, while the effective viscosity of the dispersions and average size of aggregates (D_{ef}) increase in series of chlorides: $Li^+ < Na^+ < K^+ < Ca^{2+} < Mg^{2+}$. That corresponds to an increase in the cation radius and reduction of the hydration shell. The nature of anions and cations significantly affects the values of D_{ef} and viscosity. For sodium salts, the viscosity increases in series $I^- < NO_3^- < Cl^-$ corresponding to an increase in the hydration shell.

Introduction

Nanosilica is used in aquatic systems, especially in medicine as adsorbent and drugs carrier [1]. In this case, the adsorption processes occurring at the surface of silica nanoparticles can play an important role in regulations or migration of metal ions in biosystems [2]. Some applications of nanosilica in medicine are based on the dispersions with saline (0.9 wt.% NaCl) or other buffers. Buffered solutions can include a variety of cations and anions, since their content and composition depend on application features. Therefore, the behavior of silica nanoparticles in the presence of different electrolytes is of importance from practical point of view [1- 4].

Changes in the characteristics of the EDL and surface charging in the aqueous suspensions due to variations in pH and salinity caused by ionic compounds (acids, bases, and salts) strongly affect the behavior of colloidal systems. Nanosilica is a convenient object to study coagulation processes affected by the particulate morphology and surface structure, namely, the small size of primary particles (~10 nm) and relatively homogeneous distribution of active surface sites (silanols). There are a number of papers in the literature devoted to study of the stability of aqueous dispersions of fumed silica in the presence of various electrolytes [3, 5-13].

The properties of nanoparticulate colloids (such as aggregative stability, particle size distributions (PSD), viscosity, turbidity, aging effects, etc.) depend on inter-particle interactions, the concentration, aggregation degree and particle shapes [14-16]. The processes of formation of coagulative structures in aqueous dispersions of nanooxides are determined by the balance of interparticle interaction forces. Electrostatic and structural components of the disjoining pressure play a significant role, depending on the structure of the particulate surface and near-surface layer. Effects of electrolytes on the processes of structure formation are generally caused by increasing concentrations of counterions and compression of the EDL, which in turn reduces the energy barrier that prevents the coagulation of nanoparticles. Location of ions in the EDL is due to electrostatic attraction forces depending on their position in lyotropic series [17, 18]. In turn, equal-valence ion position in the lyotropic row is determined by their radius and hydration. Coagulation and structure formation in the dispersions of fumed nanooxides depend on the aforementioned properties. It is known that salts, according to their position in the lyotropic series, have different ability to bind water and change its structure and properties (density, viscosity, etc.), and for cations and anions such impact is additive [19, 20]. The structure of hydration shells around the nanoparticles plays a significant role in the formation of coagulation structures in lyophilic disperse systems, including aqueous dispersions of nanosilica. Cosmotropic (promoting the formation of structures) or chaotropic (structure destroying) effects of electrolytes change the characteristics of coagulative contacts between the silica nanoparticles. Additionally, electrolytes significantly affect the electrostatic component of the interparticle interactions. Therefore the aim of this work was to study the effects of indifferent electrolytes (with such cations as Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, as well as anions Cl^-, I^-, NO_3^-) on the formation of coagulate structures in dilute free-disperse systems, i.e. the formation of aggregates of nanoparticles, their rheological properties, and gelling process in concentrated dispersions.

Experimental part

Material and methods

Fumed silica A-300 (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine, specific surface area S = 300 m^2/g) was used as the initial powder. The specific surface area of fumed silica was determined using low temperature desorption of argon.

2.1. Particle size distribution

Particle size distribution (PSD) measurements for the nanosilica dispersion were carried out using a Zetasizer Nano ZS (Malvern Instruments) apparatus with a universal dip cell (ZEN1002) [21].

Nanosilica dispersions in distilled water or in salt solutions (with concentrations of 0.001-0.1 M of NaCl, NaI, $NaNO_3$, LiCl, KCl, $CaCl_2$, $MgCl_2$) were sonicated for 2 min using an ultrasonic disperser (Sonicator Misonix, power 500 W, and frequency 22 kHz). The dispersions were equilibrated for 24 h.

The PSD with respect to intensity of scattered light (PDS_I), particle number (PDS_N) and particle volume (PDS_V) of silica alone and in the electrolyte presence were studied using photon correlation spectroscopy (PCS) described in detail elsewhere [22].

2.2. Rheological measurements

The rheological properties of the dispersions were studied using a rotational viscometer Rheotest 2.1 (cylinder system S/N) at a shear rate of 9-1312.2 s^{-1}. To determine the thixotropic properties of the dispersions, the rheological measurements were performed with stepwise increasing shear rate and exposure at maximal shear rate (1312 s^{-1}) up to a constant viscosity, and finally stepwise decreasing shear rate. The results are shown as 3D graphs of the effective viscosity *vs.* shear rate and time. This allows us to describe the destruction and restoration of the dispersion structures during the measurements. To compare different dispersions, the viscosity at the maximal shear rate (i.e. effective viscosity of the dispersion with most destroyed structure) was analyzed.

Results and discussion

The primary nanoparticles of fumed silica are non-porous, have a spherical shape of 10-20 nm in diameter. They have surface silanols as the main type of surface active sites [23, 24]. It should be noted that during the pyrogenic synthesis the primary silica particles tend to form such secondary structures as aggregates and agglomerates [23, 25]. However, chemical bonds between silica nanoparticles are practically absent in aggregates. The interactions are mainly determined by van der Waals attraction and electrostatic repulsion forces [22, 26]. Therefore, ultrasonic treatment of aqueous dispersions makes it easy to destroy the initial agglomerates and aggregates. The average aggregate size (effective diameter D_{ef}) decreases with increasing the treatment time (Fig. 1).

However, the colloidal systems are unstable due to high surface energy and tend to secondary aggregation in the aquatic environment (so-called coagulation), when the interactions between silica nanoparticles occur in a secondary (distant) minimum of the interparticle interaction energy vs. distance plot through a thin layer of water, i.e. water shell of nanoparticles [26].

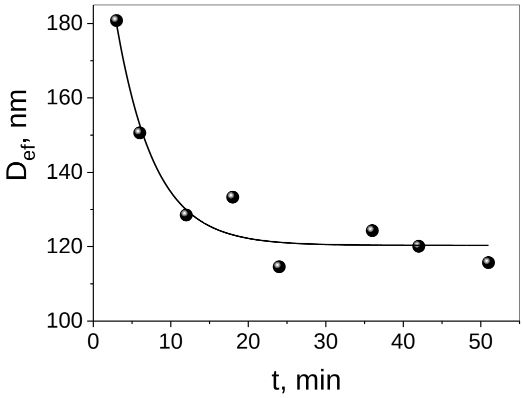

Figure 1. Dependence of the average size of silica aggregates (D_{ef}) in dispersion on sonication time

The PSD of nanosilica in the aqueous dispersions demonstrates the presence of primary nanoparticles (~10 nm), formation of their aggregates (30 nm ≤ D ≤ 1μm) and agglomerates (D > 1 μm) with the main contribution of aggregates (Fig. 2) [23-25].

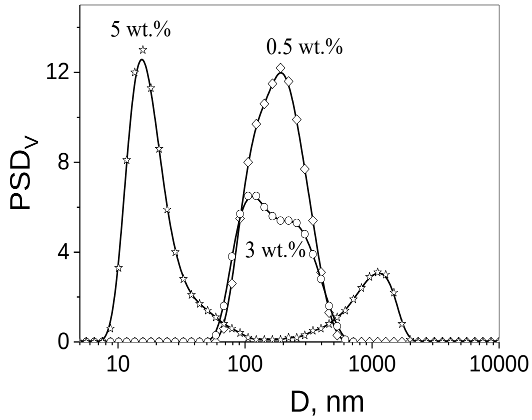

Figure 2. Particle size with respect to the particle volume (V) for nanosilica dispersions in distilled water with various content of silica

Bi- and trimodal size distributions of silica particles in the aqueous suspension without addition of any electrolyte are observed at different silica concentrations (Fig. 2). It is obvious that there are individual primary particles (16 nm), their aggregates and agglomerates thereof (300-1000 nm) also formed in the system.

The degree of nanosilica particle aggregation depends on the dispersion media (pH, salinity) and particle characteristics (PSD). The former influences the degree of dissociation of the surface silanol groups and, correspondingly, the surface charge density. Electrolyte addition to the $SiO_2 – H_2O$ system results in irregular charge distributions and changes in the EDL thickness in contradistinction to the salt-free $SiO_2 – H_2O$.

The addition of alkaline metal chlorides leads to significant changes in the PSD in nanosilica aqueous dispersions (Fig. 3). The size of aggregates considerably depends on the cation and especially anion characters. For chlorides with different cations, the PSD_V are close, while in the presence of $NaNO_3$ the secondary aggregates demonstrate the greatest sizes (Fig. 3). Nevertheless, it should be noted that the size of aggregates increases in the $Li^+ > Na^+ > K^+$ series, which is especially noticeable for 5% dispersions.

The aggregates of size less than 330 nm do not exist in the presence of more hydrated Li^+ cations (Fig. 3b). The diminution of cation hydrated radius leads to two phenomena: (i) conversion in the PSD from monomodal (LiCl) to bimodal (NaCl, KCl) distribution profiles; and (ii) addition of NaCl and KCl results in aggregates size changing vs. cation hydrated radius for R(Na^+) 50 nm and for R(K^+) 33 nm (Fig. 3b).

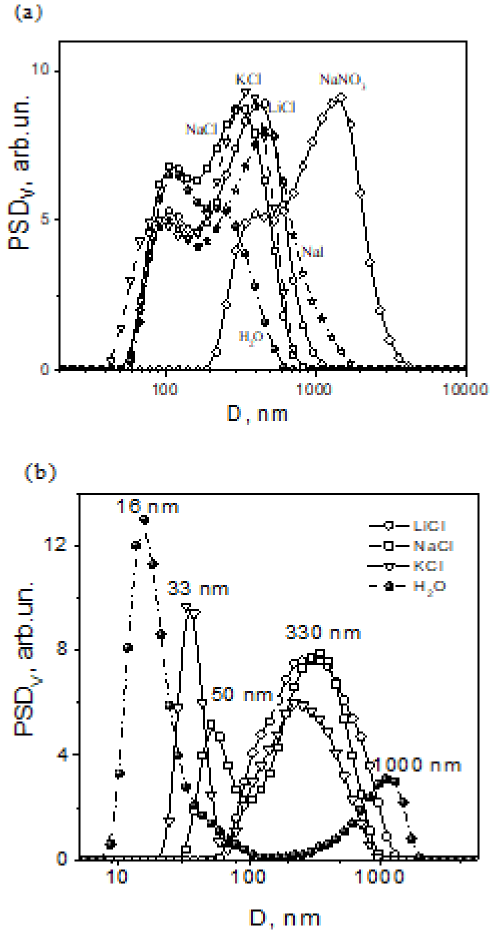

Figure 3. PSD_V of 3 wt.% (a) and 5 wt.% (b) silica dispersions in the presence of electrolytes with different cations and anions

It is worth noting that the salt addition into the SiO_2 – H_2O system causes destruction of large aggregates (~1 μm), which is observed in this system without any electrolytes, and formation of stable A-300 aggregates (330 nm) (Fig. 3b).

The cation charge has a more pronounced effect on the aggregation of silica particles, which is expressed in a larger value of D_{ef}. This influence increases with growing electrolyte concentration (Fig. 4).

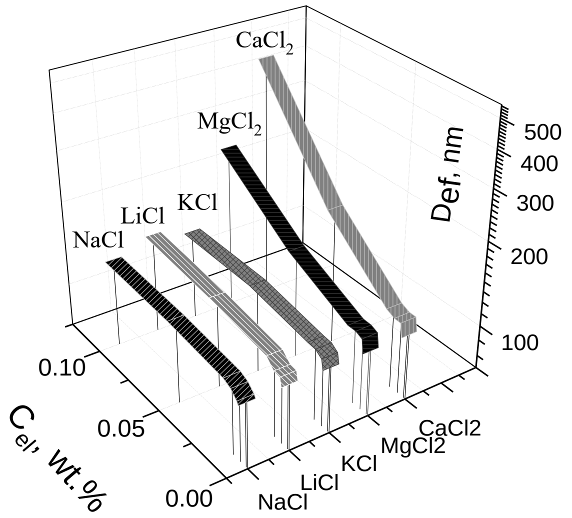

Figure 4. The dependence of effective diameter (D_{ef}) of the silica aggregates on concentration of chlorides of different metals.

During rheological investigations of such complex systems as structured aqueous dispersions of nanosilica, it is necessary to take into account the complex influence of several factors: the viscosity of the dispersion medium, the solid phase concentration, and the coagulation interactions between particles.

As mentioned above, both cations and anions may have cosmotropic or chaotropic character with respect to the structure of water. Fig. 5 shows the dependence of the viscosity of solutions of electrolytes in distilled water on their concentration. As can be seen, the effect of electrolytes on the viscosity of water varies significantly: while $NaNO_3$, NaCl, and LiCl increase the viscosity, but KCl and NaI decrease the viscosity in comparison with the distilled water.

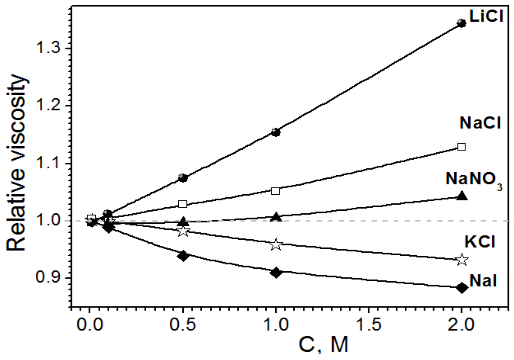

Figure 5. Dependence of the viscosity on indifferent electrolyte concentration in the solution

In the nanosilica dispersions, the effect of the dispersion medium viscosity is weakened, and the effect of the coagulation interactions between the particles on the effective viscosity enhances with increasing concentration of the solid phase. At relatively low solid phase concentrations of 3-5 wt.%, the difference in the effect of both cations and anions is not very noticeable. However, the viscosity of the dispersions in the presence of all the investigated electrolytes is higher than that for the dispersion of nanosilica in distilled water. With increasing concentration of the solid phase to 7.4 – 10 wt.% a noticeable increase in the effective viscosity can be noted in the presence of Cl^- and doubly-charged Ca^{2+} and Mg^{2+} cations, while for Cl^- and singly charged cations Li^+, Na^+, and K^+ it is smaller (Fig.6).

In the presence of sodium salts with different anions, the effective viscosity of nanosilica dispersion increases in the $I^- < NO_3^- < Cl^-$ series (Fig. 7).

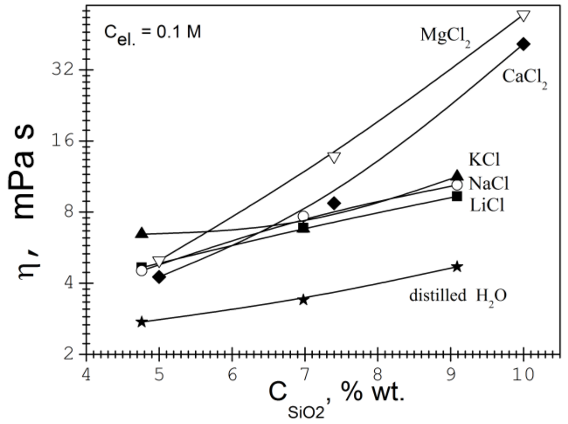

Figure 6. Effective viscosity (η) of silica dispersions at γ=1312 s^{-1} vs. C_{SiO2} in the presence of chlorides of different metals.

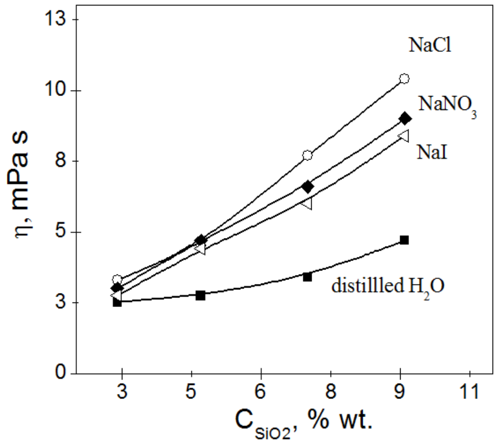

Figure 7. Effective viscosity (η) of silica dispersions at γ=1312 s^{-1} vs. C_{SiO2} in the presence of sodium salts.

In the concentration range of 3-9 wt.% for all investigated dispersions, the thixotropic behavior is typical (Fig. 8a). This is manifested in the destruction of the dispersion structure during the rheological studies with increasing shear rate (γ) and restoring it as far as reducing the shear rate.

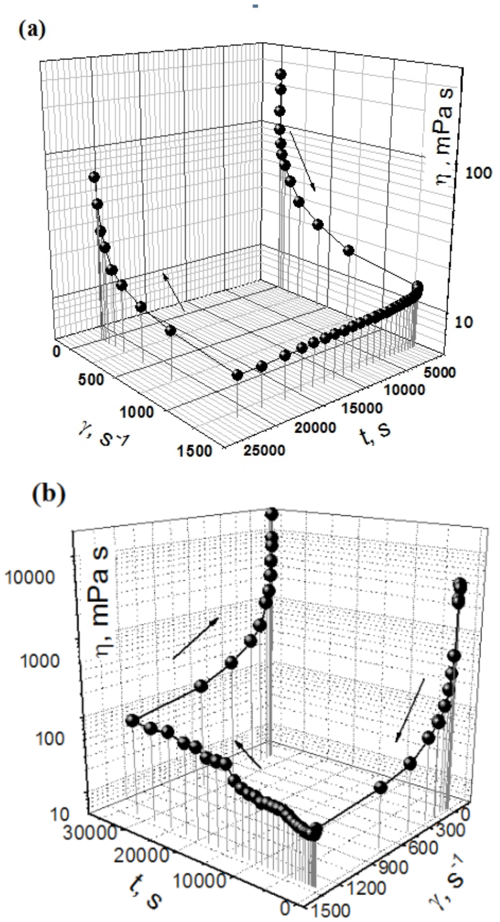

Figure 8. The dependence of viscosity on shear rate in time for 9 wt.% (b) and 13 wt.% (b) silica dispersion in solution of 0.1 M LiCl

The thixotropic properties can be estimated from a hysteresis loop shape (Fig. 8a). If the rate of recovery interparticle bonds is low the hysteresis loop is open. At silica concentrations more than 9 wt.% in the presence of electrolytes, the rheopexy is observed. The effective viscosity is not reduced due to destruction of the structure during measurements, but it increases due to the formation of a larger number of coagulation contacts between the particles (Fig. 8b).

For nanosilica dispersions prepared in distilled water without electrolytes, the critical gelling concentration is 9 wt. %. Therefore, below this concentration, the gel is not formed and the systems remain free-dispersed. For nanosilica dispersions in the presence of electrolyte, gelling realized at a concentration of 5 wt.% The critical concentration is reduced in the presence of all investigated electrolytes. Gelling time essentially depends on the concentration of dispersion (Fig. 9).

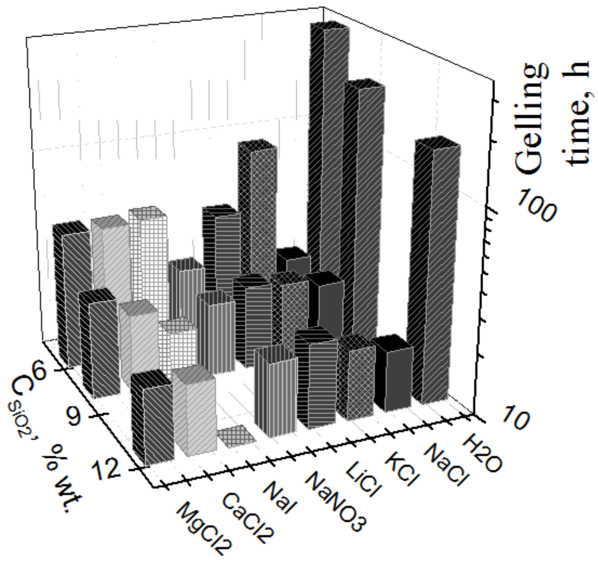

Figure 9. Gelling time vs. silica content and electrolyte type.

Thus, for 13 wt.% dispersion of silica in distilled water, the structure formation is quite slow and gelling time is of 170 hours. However, as can be seen from Fig. 9, in the presence of all investigated electrolytes, the gelling proceeds significantly faster, and at silica concentration of 13 wt.%, the structure formation takes within 10-20 hours.

Conclusions

Thus, the effects of indifferent electrolytes on the processes of coagulative structuring were investigated for nanosilica dispersions. The studied electrolytes have different effects on the structure and properties of water since LiCl, NaCl, and $NaNO_3$ increase the solution viscosity, but NaI and KCl reduced it. All investigated electrolytes lead to an increase in the size of aggregates in the silica dispersions. The double-charged cations Ca^{2+} and Mg^{2+} have the strongest effect. The critical concentration of gelation and gelling time decrease in the presence of indifferent electrolytes, but the effective viscosity of the dispersions and the average size of aggregates increase in the series of $Li^+ < Na^+ < K^+ < Ca^{2+} < Mg^{2+}$. This corresponds to an increase in the cation radius and a reduction of its hydration shell, and anions series $I^- < NO_3^- < Cl^-$ corresponds to an increase in the hydrate shell. The processes of structure formation are affected by both cations and anions, but the mechanism of their effects is different. The presence of electrolytes in the silica dispersions results in an increase in their thixotropic properties (the ability to reconstruct the destroyed structure), and at a concentration over 9 wt.% the rheopexy effect is observed.

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