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Experimental Study on Viscosity of Colloidal Silica in Aqueous Electrolytic Solutions

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The relative viscosity of colloidal silica dispersion in aqueous electrolytic solutions as the function of volume fraction of dry particles in the solutions has been experimentally determined in this work, in order to study the effects of pH and electrolytes (Na_2SO_4 and $AlCl_3$) on the hydration of the silica surfaces in the solutions. The results have shown that the maximum relative viscosity of the silica dispersion and the strongest hydration of the silica in aqueous solutions appeared at neutral pH, while the stronger the acidity and the alkalinity of the aqueous solution, the weaker the hydration. In the presence of the electrolytes (Na_2SO_4 and $AlCl_3$), the relative viscosity of the silica dispersion reduced and the hydration of the silica in aqueous solutions became weak. The higher the concentration of the electrolytes, the weaker the hydration, indicating that the destabilization of the colloidal silica dispersion in aqueous solutions might be realized through adding the high-valence electrolytes to weaken the hydration of the particle surfaces (hydration forces between the particles). Also, it has been shown that the negative zeta potentials of the colloidal silica in aqueous solutions greatly reduced in the presence of the electrolytes. Therefore, the high-valence electrolytes (Na_2SO_4 and $AlCl_3$) as the coagulant of colloidal silica in aqueous solutions might be originated from that the presence of the electrolytes simultaneously reduces the electrical double layer repulsive force and the hydration repulsive forces between the particles in aqueous solutions.

Keywords Colloidal silica, electrolytes, hydration, viscosity, zeta potential

INTRODUCTION

The stabilization of colloidal particles in aqueous solutions is due to the existence of potential energy barrier between the particles preventing the proximity. It can be categorized into electrostatic stabilization, stabilization by hydration forces and steric stabilization on the basis of the predominant factor for the formation of potential energy barrier.[1] In electrostatic stabilization, the potential energy barrier arises as a result of electrical double layer repulsion, which is dominated by the surface potential or zeta potential of the particles in aqueous solutions;[2–4] in stabilization by hydration forces, hydration repulsion between approaching particles that is originated from hydration layer on hydrophilic particles in aqueous solutions[5] lead to the potential energy barrier. In steric stabilization, steric repulsion between polymer-adsorbed particles predominates the formation of the potential energy barrier.[3] Therefore, in a colloidal aqueous dispersion in the absence of polymers, the electrokinetic property and hydration layers of the particles in the dispersion are the dominant factors for the stabilization.

There are many methods to study hydration layers on hydrophilic surfaces in aqueous solutions, including IR and UV spectroscopes and high-resolution x-ray crystallography for determine the ordering and mobility of the molecules in the layers,[6] SFA and AFM to estimate quantitatively hydration forces between particles in aqueous solutions,[5,7] and AFM and viscosity method to determine the thickness of hydration layers.[8,9] In our previous articles,[10] solvation factor was presented to evaluate the solvation degree of nanoscale particles dispersed in a

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liquid. The solvation factor is correlated to the relative viscosity of the dispersion in the following expression if the nanoscale particles are rigid spheres:

$$\frac{\eta}{\eta_o} = 1 + 2.5(1+f)\phi_p, \quad [1]$$

where η and η_o are the viscosities of the dispersion and the pure liquid, respectively; ϕ_p is the volume fraction of the dry dispersed particles; f is the solvation factor, which is the function of V_l/V_p (V_p and V_l are the volumes of dry particles and solvation layers on the particles, respectively). Allison[11] and Laven and Stein[12] also established a similar formula. A graph of η/η_0 against ϕ_p yields a straight line for a given dispersion with the intercept of 1, and

$$Slope = m = 2.5(1+f). \quad [2]$$

Equation (2) can be rearranged as

$$f = 0.4m - 1. \quad [3]$$

Accordingly, solvation factor can be determined through the measurement of relative viscosity of a colloidal dispersion as a function of volume fraction of the dry particles. For a given solid material that the A_{sp} (specific surface area) is constant, a stronger solvation of a liquid to the solid particles would lead to a larger solvation factor.

The stability of colloidal silica in aqueous solutions has attracted great attentions in scientific and industrial fields. In this study, we shall focus on the viscosity of colloidal silica in aqueous electrolytic solutions. The objective is to obtain more understandings of colloidal silica dispersion in the fundamental aspect for the preparation of a highly stable dispersion of colloidal silica in aqueous electrolytic solutions in the absence of polymer dispersants. Also, the electrokinetic property of the silica particles in aqueous electrolytic solutions is investigated through electrophoretic measurements.

EXPERIMENTALS

Materials

The colloidal silica powder (a fumed silicon dioxide) used in this work was obtained from Sigma-Aldrich Co. (USA), prepared by burning silicon tetrachloride in a flame of hydrogen and oxygen. The purity was of higher than 99%. The particles were molten spheres, which collided and fused with one another to form branched and three-dimensional chain-like aggregates. According to the manufacturer, the density and the BET specific surface area of the colloidal silica powder are $2.3\,g/cm^3$ and $200.25\,m^2/g$, respectively. The mean size of the individual particles was 14 nm, so that the product was commercially named 14 nm silica. Figure 1 shows the transmission electron microscope (TEM) image of the silica particles. It can be observed from the images that the particles were close to spheres, and have a narrow range of size distribution.

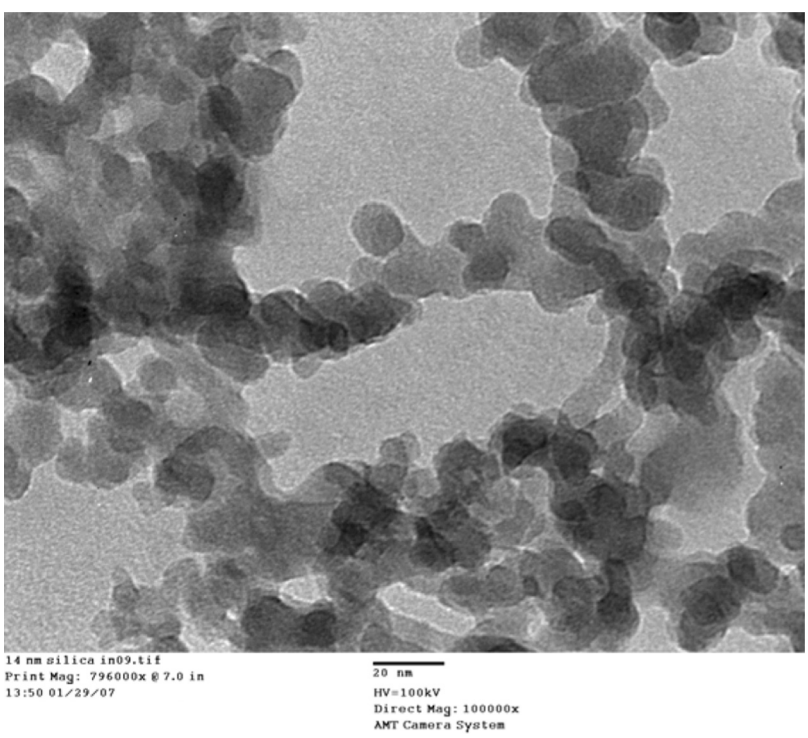

FIG. 1. TEM images of the colloidal silica particles used in this work.

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Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and aluminum chloride ($AlCl_3$) used as electrolytes, chloride acid (HCl), and sodium hydroxide (NaOH) as pH regulating agent in this work were obtained from J. T. Baker (Mexico), all of which were analytical purity. The water used in this work was first distilled and then passed through resin beds and a 0.2 μm filter. The residual conductivity of the water was less than 1 μS/cm.

Measurements

A Physica RHEOLAB MC-1 concentric cylinder rheometer (Physica Messtechnik GmbH, Ostifildern, Germany) was used to determine the viscosity of colloidal silica dispersions. The instrument is a rotational, shear stress and creep rheometer. Samples are positioned in the measuring gap between the stationary measuring cup and the rotating bob (Searle principle). The rheometer employs a highly dynamic system consisting of a measuring drive and an optical encoder without gearing and a mechanical force transducer with which torque is measured without deflection. The torque resolution is 0.01 mN·m. The temperature control system permits viscosity measurement to be performed at a fixed temperature with a precision of ± 0.05°C. In this work, a given weight of dry silica powder was first put into a 100 ml measuring flask. The flask was then filled to the mark with water or aqueous electrolyte solutions. Next, the suspension was mildly stirred with a magnetic agitator (Digital hot plate/stirrer 04644) at 150 rev/minute for 24 hours. Then, the suspension was transferred to the rheometer for viscosity measurements. The measurements were carried out at a shear rate of $1000\,s^{-1}$ and temperature of 20°C. Each measurement was repeated 60 times. Results reported in this paper were the arithmetic average of these 60 measurements. The error estimation has been made for the 60 data. It was found that the standard error of the reported values of measured viscosity was in the range of 0.0013 to 0.0034 mP·s, which depended on the value of measured viscosity.

The TEM images were obtained by using a Jeol JEM-1230 transmission electron microscope. The silica particles were first dispersed in alcohol with 0.01% solid concentration. Next, a 3 mm grill was immersed into the dispersion for a while, and then taken out for drying in air. The silica particles were adhered on the grills. After that, the grill was moved to the TEM for observation and analysis.

Electrophoretic mobility of the colloidal silica particles in aqueous electrolytic solutions were determined using a Coulter DELSA 440SX instrument, which is based on the electrophoretic light scattering (ELS) technique to directly measure the velocity of particles moving in an electric field. In this work, silica dispersion in aqueous electrolytic solutions with 0.01% solids was first conditioned for 5 minutes together with pH regulating reagents. The suspensions were then transferred to the rectangular capillary cell of the instrument. The measurement was performed using an electric field of 16–19 V/cm and the frequency range of 500 Hz with a duration time of 100 seconds (using a 2-seconds-on and 1-second-off sequence alternating the electric field polarity) at the upper stationary layers of the cell. Four-angle electrophoretic light scattering were simultaneously utilized. The average value of zeta potential from the four angles was reported as final result. The temperature through the whole measurement was kept at 20 ± 0.1°C.

The pH value of the silica dispersions were determined by using a Thermo Orion pH meter at room temperature.

RESULTS AND DISCUSSIONS

The viscosities of colloidal silica dispersion in aqueous solutions were determined as a function of volume fraction of dry particles at various pH values in this study. Some results are illustrated in Figure 2 in the form of the relative viscosity of the colloidal silica dispersions versus volume fraction of dry particles. As it can be seen, the relative viscosities increased almost linearly with increasing volume fraction of the dry particles. Linear regression for the data led to the five straight lines with the intercept of 1 and the slopes of 25.86 for pH 3.02, 51.58 for pH 5.5, 57.70 for pH 6.3, 43.07 for pH 9.0, and 38.1 for pH 10.6, respectively. Obviously, the relative viscosity of the colloidal silica dispersion strongly changed on pH value of the dispersion.

The values of the slopes from the experimental results of the viscosity measurements have been used to obtain the solvation factors of the colloidal silica in aqueous solutions

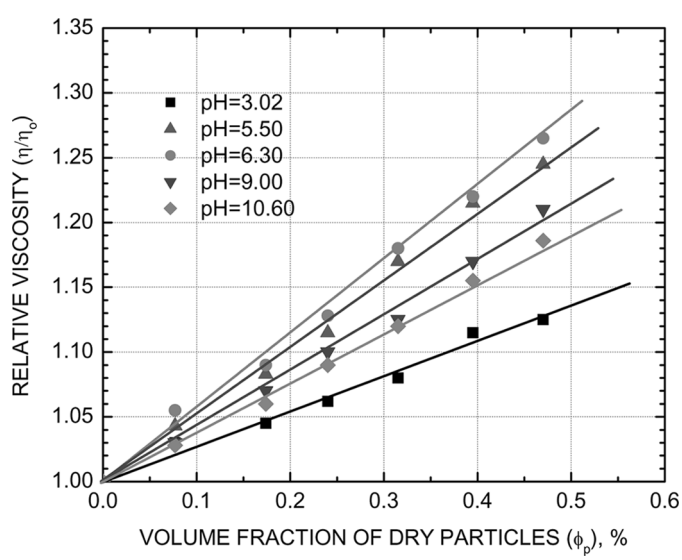

FIG. 2. Relative viscosity of the colloidal silica dispersion in aqueous solutions as the function of volume fraction of dry particle at various pH values.

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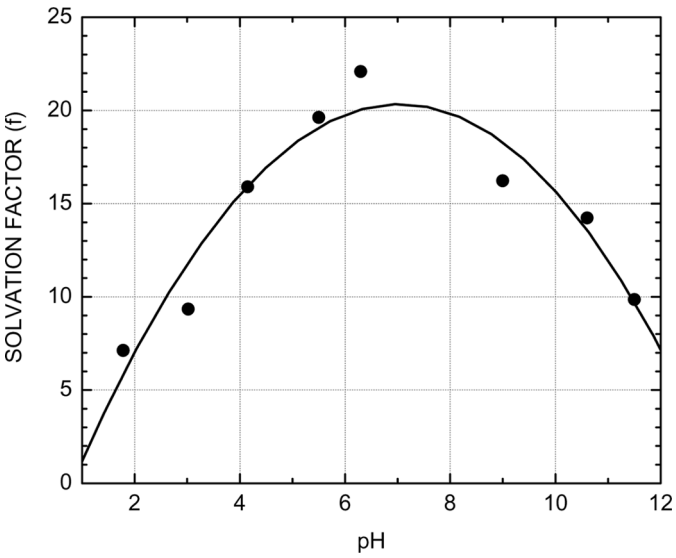

FIG. 3. Effect of pH on the solvation factor of the colloidal silica dispersed in aqueous solutions.

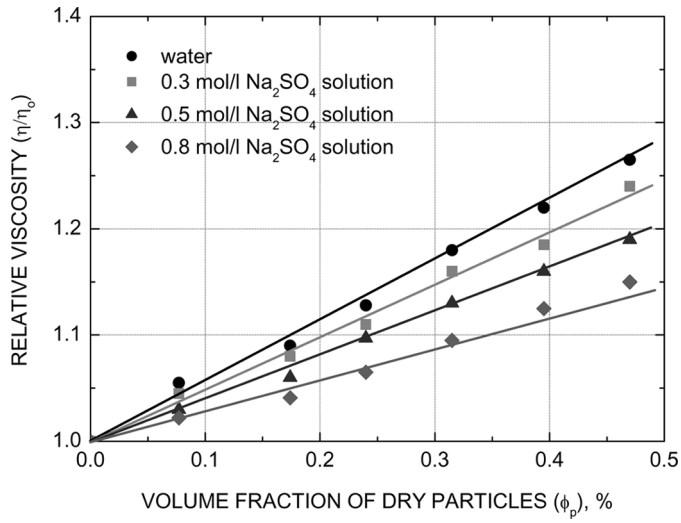

FIG. 4. Relative viscosity of the colloidal silica dispersion in aqueous electrolytic solutions as the function of volume fraction of dry particle at various Na_2SO_4 concentrations.

at various pH values on the basis of the Equation (3). The calculation results are shown in Figure 3. In this graph, a bell can be observed, indicating that there was a maximum solvation factor for the colloidal silica in aqueous solutions around the neutral medium. In acidic medium, the lower the pH value, the smaller the solvation factor of the colloidal silica in aqueous dispersions; in alkaline medium, the higher the pH value, the smaller the solvation factor. The result suggests that the strongest hydration of the silica surfaces and thus the strongest hydration force between the silica particles in aqueous solutions is in neutral aqueous solution. Therefore, the stabilization of the colloidal silica dispersion in aqueous solutions is recommended to be realized in a neutral medium.

The viscosities of colloidal silica dispersion in aqueous electrolytic (Na_2SO_4 and $AlCl_3$) solutions also were determined in this study, in order to understand the effect of electrolyte on the viscosity of the dispersion and the solvation factor of the colloidal silica in aqueous solutions. Figure 4 shows the relative viscosity of colloidal silica dispersion as a function of volume fraction of dry particles in aqueous solutions at various Na_2SO_4 concentrations. Similarly, the experimental data almost located on the corresponding straight line with the intercept of 1 for each Na_2SO_4 concentration. Linear regression for the data led to the slopes for each case: 57.7, 49.3, 41.2, and 29.05 for the colloidal silica dispersion in pure water, 0.3, 0.5, and 0.8 mol/l Na_2SO_4 aqueous solutions, respectively. Compared with the dispersion in pure water, the presence of Na_2SO_4 reduced the slope. The higher the Na_2SO_4 concentration in the aqueous solution, the smaller the slope. The results indicate that the effect of Na_2SO_4 addition on the relative viscosity of the colloidal silica dispersion is negative.

Figure 5 illustrates the relative viscosity of the colloidal silica aqueous dispersion as a function of volume fraction of dry particles at various $AlCl_3$ concentrations. Similarly, we made a linear regression for the experimental data and obtained the slopes of 48.4, 43.6, and 35.65 for the dispersions in 0.2, 0.5, and 0.8 mol/l $AlCl_3$ aqueous solutions, respectively. It indicates that the relative viscosity of the colloidal silica aqueous dispersion was also reduced by the addition of $AlCl_3$, as shown in the case of Na_2SO_4 solution.

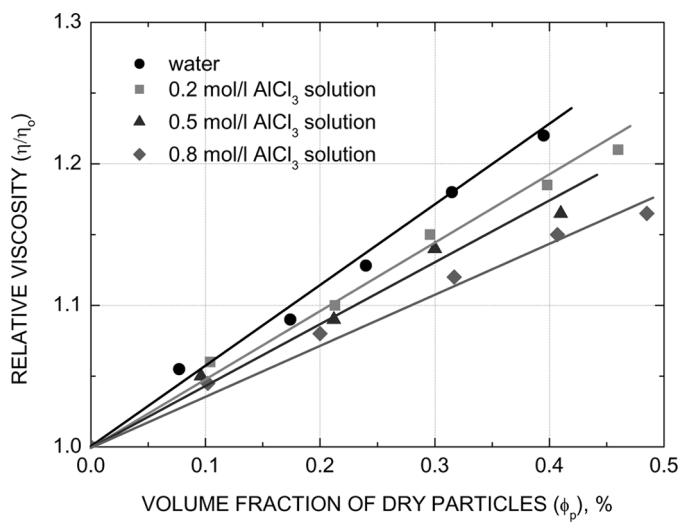

FIG. 5. Relative viscosity of the colloidal silica dispersion in aqueous electrolytic solutions as the function of volume fraction of dry particle at various $AlCl_3$ concentrations.

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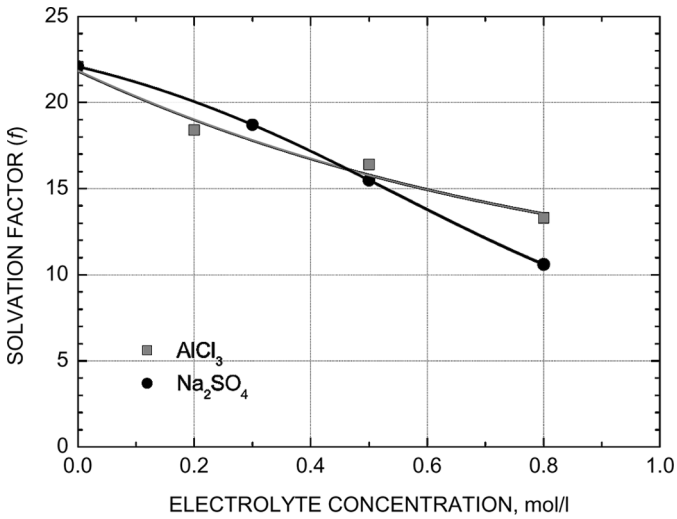

FIG. 6. Effect of electrolyte (Na_2SO_4 and $AlCl_3$) concentration on the solvation factor of the colloidal silica dispersed in aqueous solutions.

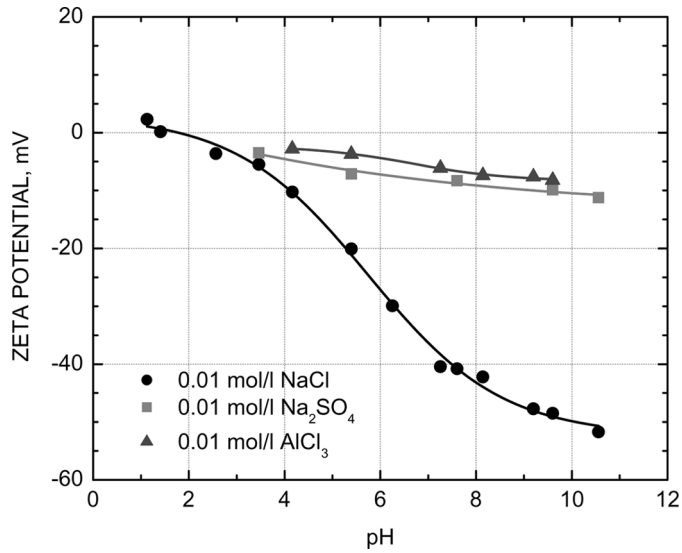

FIG. 7. Zeta potential of the colloidal silica in aqueous solutions as the function of pH value in the presence of electrolytes.

From the slopes of the straight lines as shown in Figures 4 and 5, the solvation factors of the colloidal silica in the aqueous solutions of Na_2SO_4 and $AlCl_3$ have been calculated according to Equation (3). The calculated results were illustrated in Figure 6 in the form of solvation factor as a function of electrolyte concentration. It can be noted in this graph that the solvation factor decreased markedly as the increase of the electrolyte (Na_2SO_4 and $AlCl_3$) concentration. The decreases were almost linear, and were sharper for Na_2SO_4 than for $AlCl_3$, revealing that Na_2SO_4 was stronger than $AlCl_3$ to weaken the hydration of the colloidal silica in aqueous solutions. These results are contrary to those as shown in our previous article,[10] in which NaCl enhanced the hydration of silica particles dispersed in aqueous electrolytic solutions.

It is clear that the high-valence electrolytes (Na_2SO_4 and $AlCl_3$) can markedly weaken the hydration of the silica surfaces and thus the hydration forces between the silica particles in aqueous solutions. Therefore, the colloidal silica dispersion in aqueous solution would be more unstable due to the presence of the electrolytes (Na_2SO_4 or $AlCl_3$). In other words, the high-valence electrolytes play a role of coagulant in the stabilization of the aqueous colloidal silica dispersion.

Figure 7 illustrates the zeta potentials of the colloidal silica in aqueous electrolytic (0.01 mol/l NaCl, Na_2SO_4 and $AlCl_3$) solutions as the function of pH value. The addition of NaCl was to increase the ionic strength in the suspension in order to determine the electrophoretic mobility of the silica particles. As it is known, the presence of NaCl only compresses the electrical double layer of silica particles in aqueous solutions, leading to the decrease of the absolute value of the zeta potential, but not changes the IEP (isoelectric point). Therefore, the zeta potential versus pH curve of the colloidal silica in absence of electrolyte has the same tendency as that in the 0.01 mol/l NaCl, except for much larger absolute values of zeta potential. As it is noted from the curve in 0.01 mol/l NaCl solution, the IEP of the colloidal silica in an aqueous solution was at pH 1.8, which is coincident with the result from the measurements for silica and quartz as reported elsewhere.[13] After the IEP, the negative zeta potential greatly increased as the increase of pH value. In the presence of 0.01 mol/l Na_2SO_4 and $AlCl_3$, the negative zeta potential of the colloidal silica in the range of $pH > 3$ considerably reduced. The two curves are very close to the line of zero zeta potential, indicating that the two electrolytes strongly compressed the electric double layer of the colloidal silica in aqueous solutions and thus leaded to the low zeta potentials.

It has been shown that there was a correlation between the hydration of the colloidal silica in aqueous solutions and the zeta potential of the particles in the presence of the high-valence electrolytes (Na_2SO_4 and $AlCl_3$). As the increase of the addition of the electrolytes, the solvation factor of the colloidal silica in the solutions reduced, and also the negative zeta potential of the silica particles decreased. The first fact would weaken the hydration force between the colloidal silica particles, and the second fact would reduce the electrical double layer repulsive force between the particles. Both of them would lead to the decrease of the potential energy barrier between the silica particles in aqueous solutions, indicating a coagulation. Accordingly, Na_2SO_4 and $AlCl_3$ simultaneously reduce the repulsive forces of electrical double layer and hydration between silica particles in aqueous solutions, which might be attributed

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to the coagulation of colloidal silica particles in an aqueous solution.

CONCLUSIONS

1. The hydration of colloidal silica surfaces dispersed in the aqueous electrolyte (Na_2SO_4 and $AlCl_3$) solutions reduced as the increase of the concentration of the electrolytes in the solutions. Accordingly, colloidal silica dispersion in aqueous solutions of (Na_2SO_4 and $AlCl_3$) might be unstable because of the weak hydration forces between the particles.
2. The maximum hydration of the colloidal silica in aqueous solutions appeared in the neutral medium. The stronger the acidity and the alkalinity of the aqueous solutions, the weaker the hydration.
3. The coagulation of colloidal silica particles in aqueous electrolyte (Na_2SO_4 and $AlCl_3$) solutions might be originated from the simultaneous reduction of the repulsive forces of electrical double layer and hydration between the particles due to the presence of the electrolytes.

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