

Preparation of Silica Dispersion and its Phase Stability in the Presence of Salts

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Abstract—In the present study, the phase stability of spherical silica particle dispersion was investigated experimentally. The silica particles were synthesized by the sol-gel method and stabilized by electrostatic and steric stabilization. For a given pH, the silica particles were coagulated at a certain critical salt concentration, which depended on the chemical nature of the added salts. The critical coagulation concentration showed that the particle ζ -potential in the presence of electrolytes, such as NaCl, NaBr, and KCl, had no appreciable influence on the stability of silica dispersion. The aggregate sizes measured by dynamic light scattering gave useful information on the coagulation process in the presence of the electrolytes. The critical coagulation concentration of a salt containing sodium decreased monotonically as pH increased. Meanwhile, the phase stability in the presence of K^+ ions was the worst at the pH 8.5. In addition, the ζ -potential that showed a strong dependence on pH in the presence of Na^+ ions was a very weak function of pH in the presence of K^+ ions.

Key words : Electrostatic and Steric Stabilization, Silica Suspension, ζ -Potential, Critical Coagulation Concentration, Phase Stability

INTRODUCTION

The physical state of colloidal suspensions, such as phase stability, can be altered drastically by subtle changes in composition or by addition of electrolyte or associative polymer. This complicated behavior stems from the different interparticle forces between the neighboring particles [Lee and Yang, 1997, 1998a, b; Lee et al., 1999; Oh et al., 1999]. A colloidal system includes a large number of particles dispersed in a continuous medium, and various attractive and repulsive forces are active between the particles. If the particles are small enough, they will undergo Brownian motion and collisions with one another. In collisions, coagulation can be induced by van der Waals attraction force between the uncharged particles because the attractive van der Waals forces dominate the repulsive forces. Hence, the repulsive force, which is at least comparable to that of the van der Waals attraction, is essential for the stability of colloidal dispersions. However, it is difficult to ascertain that the repulsion extends over the distance required for the neighboring particles to overcome the van der Waals attraction and to escape from the coagulation. Generally, a distance of several nanometers between submicron particles is effective to give phase stability in the colloidal dispersions, and moreover, this can be achieved by electrostatic or steric barriers [Hunter, 1989; Russel et al., 1989; Napper, 1983].

The added salt tends to suppress the repulsion force by screening surface charge and leads to coagulation with a long lifetime. This is because the thermal agitation Brownian force is not

enough to overcome the interparticle attraction force [Hunter, 1989]. Under some conditions, the stability of silica sols is in contradiction to the behavior of typical lyophobic colloidal dispersions [Allen et al., 1969, 1970; Iler, 1979]. In aqueous media, silica particles possess negative charges with nearby cations acting as counterions above the point of zero charge around pH 2. Near the point of zero charge, aggregation occurs due to the negligibly weak electrostatic repulsion. However, the silica sols are permanently stable in the alkaline solution in which the particles acquire negative surface charges owing to the dissociation of the silanol group. Although a number of investigations have been performed on the stability of silica particles in the presence of various salts, there has still been much speculation about the coagulation mechanisms of silica particles [Allen et al., 1969, 1970; Depasse et al., 1970, 1997; Milonjic, 1992]. Recently, the critical sorption behavior of metal ions on the silica surface provided that the amounts of sorbed cations at the critical coagulation concentration were equivalent to the saturated sorption at a given pH.

Monodisperse colloidal silica is of interest in many fields, dealing with ceramic, glass, catalysis, and chromatography. Studies on the surface properties of silica as a function of pH, additives, and salts are relevant to the preparation of silicon-wafer polishing or chemical-mechanical polishing slurries. Specifically, the stability of silica dispersions plays a major role in haze removal and the improvement of roughness and flatness of a wafer. In this study, the silica particles synthesized by sol-gel method are stabilized in an aqueous medium. With the electrostatically stabilized silica suspensions, the critical coagulation concentrations for various electrolytes were measured as a function of pH to examine their phase stability. The present results showed that the particle size from dynamic light scattering was

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sustained at about 90 nm in the presence of KCl at pH 6, at which the silica suspensions formed a very stable sol.

EXPERIMENTAL

1. Preparation of Monodisperse Silica Particles

Chemicals in this study were used as received without further treatment. Silica particles were prepared by sol-gel method proposed by Stöber et al. [1968]. Water was distilled and deionized prior to use. The spherical SiO_2 particles were formed by the hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS, Aldrich) in aqueous ethanol solution, using ammonium hydroxide (28-30 % of NH_3 , Aldrich) as a catalyst. In the particle preparation, the predetermined amounts of ethanol, ammonia, and distilled water were mixed in the vessel and agitated for 1 hr to ensure the well-mixed solution. And then, TEOS was added rapidly. After the reaction was completed, the ethanol was removed via vacuum distillation to obtain aqueous silica suspensions. In the vacuum distillation, the vessel was immersed in the heat bath at a constant temperature, 40 °C. The distillation processes were repeated more than four times by adding the necessary amounts of water to the suspension. The water-based silica sol was concentrated up to 15-20 wt% and its pH was maintained at around 9. The primary particle size and morphology of silica in aqueous media were measured using a transmission electron microscope (TEM, EM912, Car Zeiss) of KBSI (Korea Basic Science Institute) after sampling on a carbon coated copper grid. The particle size was also measured through dynamic lighting scattering (DLS, Brookhaven Instruments). Intensive sonication was re-

quired to prohibit the particle from aggregating and to provide the satisfactory transparency.

2. Stability Test of Colloidal Silica in the Presence of Electrolytes

The stability of colloidal silica in the presence of the alkaline salts such as NaCl, KCl, and NaBr was observed for wide range of pH. The ζ -potentials were measured by using Zeta plus (Brookhaven Instruments). In this experiment, the critical coagulation concentration of salt was estimated from examining the growth rate of the silica particle due to the aggregation. The changes of the particle size were measured by dynamic light scattering as a function of the salt concentration. For the size measurements, 5 wt% silica suspension at predetermined pH was added to the pH-controlled electrolyte solution to adjust the silica concentration at 4.5×10^{-4} g/ml and its pH was rechecked. Then, the aggregate sizes were measured using dynamic light scattering with the sample placed at rest for 12 hrs after mixing.

RESULTS AND DISCUSSION

1. Preparation of Silica Particles

The particle size and its distribution prepared with various compositions are contained in Table 1, where it can be seen that the most influential variables were the water and ammonia contents. The prepared silica particle became large as the water and ammonia contents increased. Meanwhile, both the particle size and polydispersity were increased with the TEOS content. For particle growth by sol-gel method, Bogush suggested that a maximum particle size could be attained by increasing the water

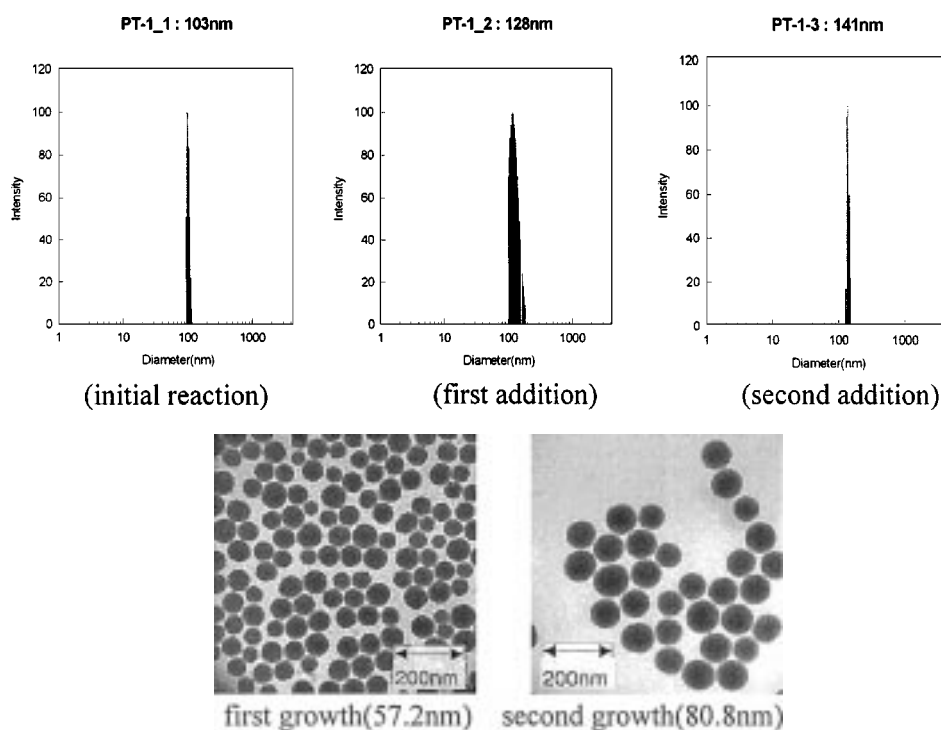


Fig. 1. Stepwise growth of the particles with addition of TEOS. The first reaction proceeded with $[\text{TEOS}] = 0.1$ M and the same amounts were added in the subsequent growth processes. 2 M H_2O and 0.17 M NH_3 were added in the first reaction.

Table 1. Effects of H₂O, NH₄OH, and TEOS contents on the particle size at room temperature. The particle sizes and standard deviations were obtained from dynamic light scattering at 25 °C

| H ₂ O [M] | NH ₄ OH [M] | TEOS [M] | Diameter [nm] | Polydispersity |
|----------------------|------------------------|----------|---------------|----------------|
| 2 | 0.13 | 0.2 | 138 | 0.005 |
| 4 | 0.13 | 0.2 | 141 | 0.043 |
| 5 | 0.13 | 0.2 | 280 | 0.018 |
| 5 | 0.1 | 0.2 | 113 | 0.036 |
| 5 | 0.2 | 0.2 | 279 | 0.038 |
| 5 | 0.4 | 0.2 | 404 | 0.026 |
| 5 | 0.2 | 0.1 | 186 | 0.018 |
| 5 | 0.2 | 0.2 | 181 | 0.097 |
| 5 | 0.2 | 0.4 | 259 | 0.168 |

Table 2. Stepwise growth of the particles with addition of TEOS. After the first step reaction, 0.1 M of TEOS was added in the second and third reaction steps. The concentrations of H₂O and NH₃ in the first reaction were 2.0 and 0.17 M, respectively

| Initial TEOS concentration (M) | 0.1 | | | 0.2 | | | 0.3 | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Growth step | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Particle size (nm, DLS) | 103 | 128 | 141 | 157 | 164 | 181 | 112 | 125 | 129 |

and ammonia contents at a fixed TEOS content, and that the particle sizes were not reproducible and the size distributions became broad at high TEOS contents. As noted from Table 1, the present results are consistent with Bogush's observations [Bogush et al., 1988].

For an illustrative purpose, the particle size change in the stepwise growth procedure was reproduced in Table 2. The stepwise growth of the silica particle was carried out by the stepwise addition of TEOS, in which the initial water and ammonia contents were kept at 2.0 and 0.17 M, respectively. The results of DLS and TEM measurements are presented in Fig. 1. The stepwise growth technique can be used not only for the modification of size distribution but also for the preparation of suspensions with higher solid contents. Recently, considerable research efforts have focused on interpreting the growth mechanism. However, only empirical suggestions are available for modeling the particle size and the solid content due to the complicated reactions between various reagents [Bogush et al., 1988; Matsoukas et al., 1988, 1989, 1991; van Blaaderen, 1992]. In the present study, we used three different contents of TEOS (i.e., 0.1, 0.2 and 0.3 M) in the first growth step. Then, in the second and third steps, 0.1 M of TEOS was added to each suspension prepared in the preceding step. As far as the first growth step was concerned, a particle size of 157 nm for 0.2 M of TEOS was the largest among the particles prepared with three different TEOS contents. The result implies that for the size of particle there exists an optimal TEOS content, which is consistent with the previous result [Lindberg et al., 1997]. The existence of the optimal concentration of TEOS arises from the fact that hydrolysis

and condensation reactions in the sol-gel process are fast at low concentrations of TEOS in ammonia-catalyzed systems of ethanol media. Thus, to make large particles with the narrow size distribution, the particles should be grown below a certain concentration. Meanwhile, above the optimal concentration, the particle size distribution becomes broad with considerable number density of very tiny particles [Lindberg et al., 1997].

2. Effects of Metal Ions on the Stabilization of Colloidal Silica

The silica sol in basic media can be coagulated by alkaline cations due to either the reduction of repulsion or the interparticle bridging [Iler, 1979]. The silica suspension in basic media exhibits the different phase stability behavior with the types of cations dissociated from the salts and experimental methods. In acidic media, however, the silica sol sustains its stability owing to the adsorption of water on the silica surface. Further, it is noteworthy that the dissociation of silanol groups of the silica surface forms the surface charge. With increasing pH, progressive dissociation of the silanol groups led to surface dehydration, and consequently to thickening electric double layer [Iler, 1979] in the absence of the counterions. Under these circumstances, the silica suspensions become stabilized at high pH's. However, the stability trend is quite different in the presence of the counterions since the electrostatic potential of colloidal silica varies also with the concentration of the electrolyte. In Figs. 2-4, the variations of zeta potential as a function of NaCl, NaBr, and KCl concentrations are plotted for various pH's. The magnitude of zeta potential was decreased either by adding the electrolytes at a given pH or by decreasing pH at a given concentration of the electrolyte. As shown in Fig. 2, the zeta potential that remained unchanged at about -6 mV for the entire concentration range of NaCl at pH 3.0 showed a relatively strong dependence on the NaCl concentration at higher pH's. This is due to the fact that the sodium ions acting as counterions reduced the electrical double layer of silica surface and thereby decreased the ζ -potential via the screening effect. Since the silica surface

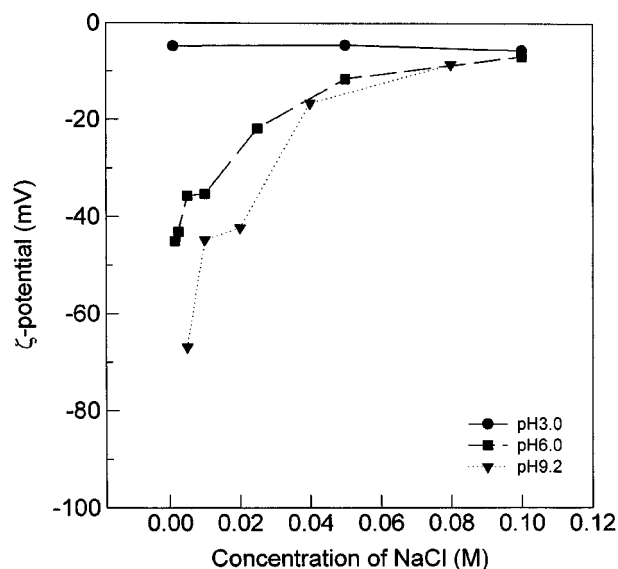


Fig. 2. ζ -potential as a function of NaCl concentration at various pHs.

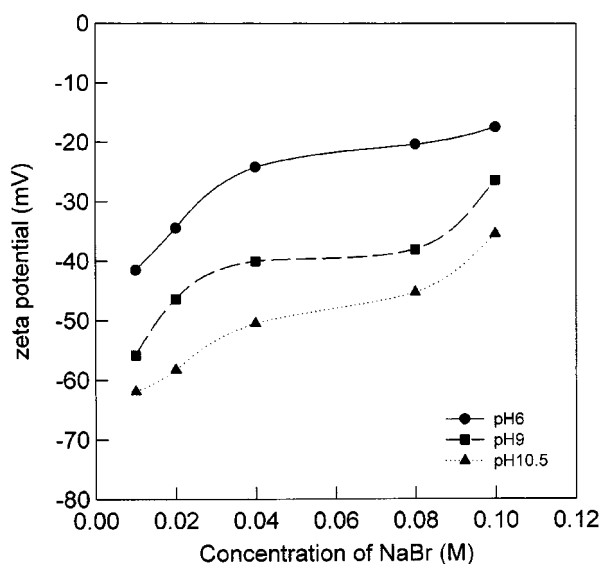


Fig. 3. ζ -potential as a function of NaBr concentration at various pHs.

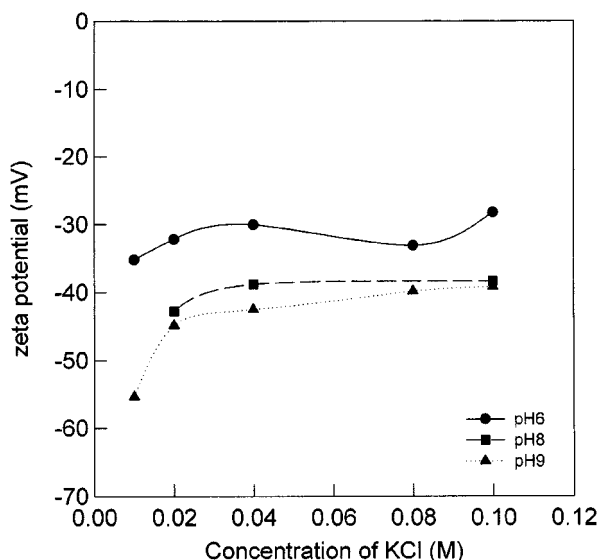


Fig. 4. ζ -potential as a function of KCl concentration at various pHs.

has a higher negative surface charge density at higher pH's, the surface charges of the silica particle may be screened by sodium counter ions more effectively. This could be confirmed by monitoring the changes of ζ -potential as a function of the NaCl concentration as shown in Fig. 2.

As noted from Figs. 3 and 4, although the general features of ζ -potential were preserved in the presence of NaBr, it showed a relatively weak dependence of KCl concentration compared to the cases of NaCl and NaBr. Similar trends were observed by Zukoski et al. for the ζ -potential of polystyrene particles in the presence of NaBr or KCl [Zukoski IV et al., 1985, 1986a, b]. According to their reports, the presence of mobile counterions in the Stern layer lowers the ζ -potential. Since the potassium ion adsorbs less strongly on the silica surface than the sodium ion, it displaces the hydrogen ions of the silanol group less effectively

during adsorption. As KCl concentration is increased, more potassium ions adsorb neutralizing the negative adsorption sites, and decreasing the charge density. Of course, at the same time, the bulk concentration of chloride ions increases, and more chloride ions adsorb at neutral sites. Therefore, the particle charge density decreases at a slower rate than that would be expected without chloride ions adsorbed. Overall, the surface of silica in the presence of KCl below a certain concentration possesses low charge density compared with the case with NaCl or NaBr. However, at even higher KCl concentrations, the Stern layer is almost saturated with potassium ions that neutralize the covalently bound negative charges, and adsorbed chloride ions keep negative charges in the layer.

The silica sols exhibit a different stability with types of cations in acidic or basic media. In Figs. 5-7, the aggregate sizes were

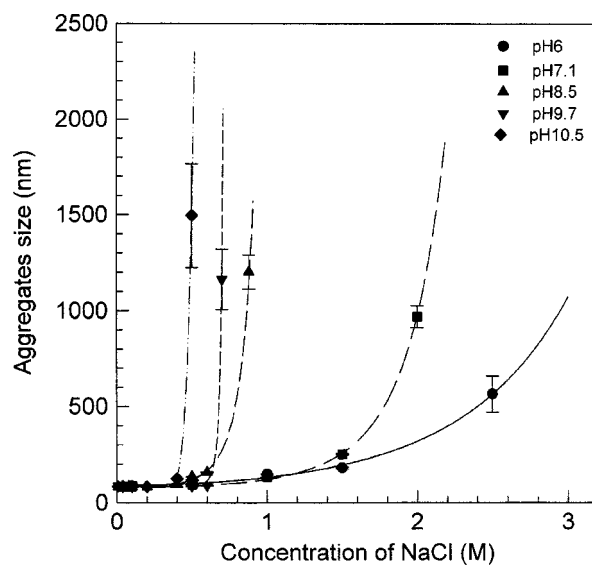


Fig. 5. Aggregate size measured by dynamic light scattering as a function of NaCl concentration at various pHs.

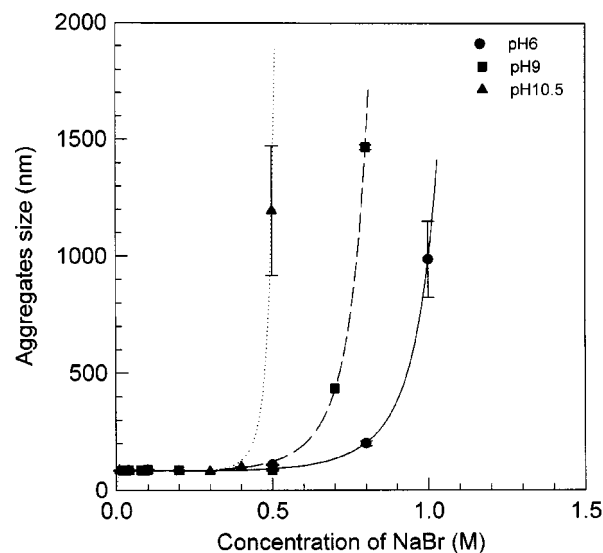


Fig. 6. Aggregate size measured by dynamic light scattering as a function of NaBr concentration at various pHs.

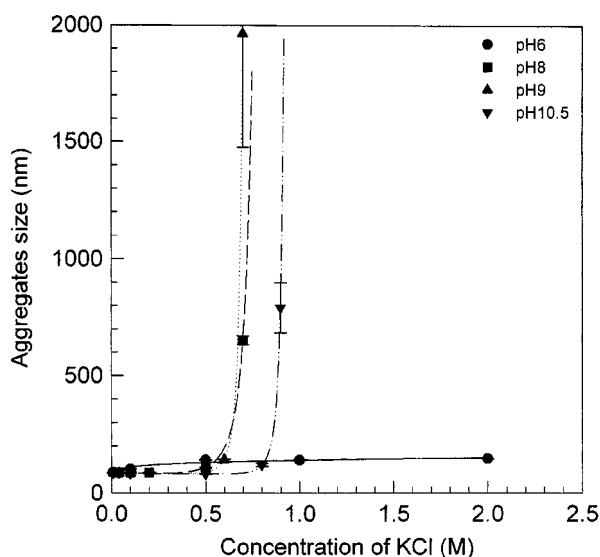


Fig. 7. Aggregate size measured by dynamic light scattering as a function of KCl concentration at various pHs.

plotted as a function of NaCl, NaBr and KCl concentrations at various pHs, respectively. In this plot, we used the silica particles with a primary size of 81 nm. As noted earlier, the sizes were measured from dynamic light scattering and thus reflected the effective hydrodynamic diameters. Considering that the primary particle size was about 81 nm, the particle aggregation proceeded considerably as the salt concentration exceeded a certain critical value at high pHs. In the presence of NaCl or NaBr, the stability of silica particles became deteriorated especially above pH 6 with the electrostatic repulsion between particles diminishing at high ionic strengths. It can be seen from Figs. 5-7 that the destabilizing effect induced by the added salts became significant in the order of KCl, NaBr and NaCl. This is consistent with the changes of zeta potential in the presence of these salts. One of the most interesting trends observed here is the phase stability at around pH 6 in the case of KCl. As shown in Fig. 7, the silica suspension sustained its phase stability up to 2 M of KCl at pH 6, which was quite different from the results in the presence of NaCl or NaBr. This can be explained as follows. Since the silanol groups are less dissociated at pH 6, the silica particle possesses still plenty of $-OH$ groups. Furthermore, K^+ ions do not substitute the hydrogen ions on the silica surface at low pHs and the suspensions are stable at high KCl concentrations around pH 6.

The hydrodynamic size of silica particles in the aqueous media decreases with the addition of electrolyte up to the critical coagulation concentration. The hydrophilic nature of silanol groups causes the surface hydration. The dipole-dipole interaction and hydrogen bonding between the silanol groups and water molecules are responsible for the formation of hydration layer [Sasaki et al., 1994]. The existence of viscous vicinal water near a charged silica surface is an important factor for the hydrodynamic properties. The water molecules are immobilized due to the electrostatic double layer surrounding a charged surface. In general, the double layer becomes thin either as the ionic strength is enhanced or pH is lowered, and the decrease in the

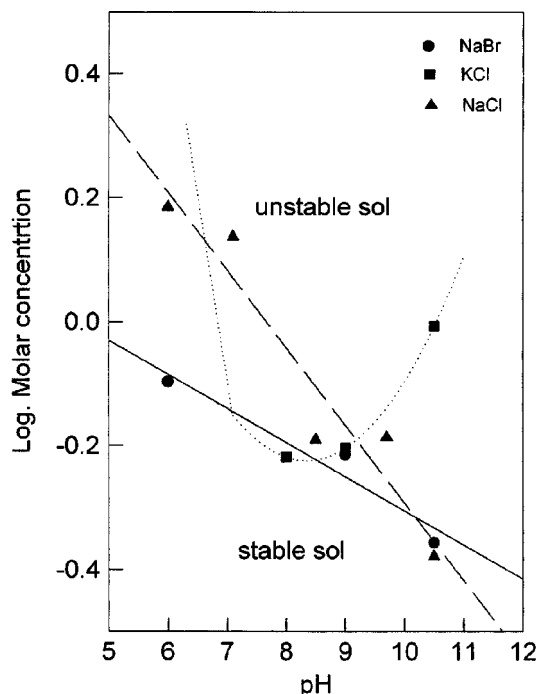


Fig. 8. Critical coagulation concentration as a function of pH for various electrolytes.

number of immobilized water molecules reduces the effective hydrodynamic size. Thus, the hydration layer, which is affected by the ionic strength, becomes thick with the increase in pH. Indeed, as shown in Figs. 5-7, the hydrodynamic radius of silica particle at high pHs was larger than that at low pHs for a given ionic strength below the critical coagulation concentration. In addition, the hydrodynamic diameter of silica particles with the primary size of 81 nm was decreased slightly with the addition of salts in the limit of weak ionic strengths, although the size reductions could not be clearly seen from Figs. 5-7 due to the scale of the axes. Obviously, as the ionic strength approached the critical value at a given pH, the hydrodynamic size increased due to the doublet or multiplet formation.

In Fig. 8, the critical coagulation concentrations were plotted as a function of pH for NaCl, NaBr and KCl. The critical concentration was determined as the concentration of electrolyte at which the hydrodynamic diameter was doubled from the primary size 82 nm to 165 nm. As noted, the critical concentration of Na^+ ions decreased linearly with pH above 6, but for K^+ , the critical concentration exhibited a nonlinear dependence on pH. Specifically, the critical concentration of K^+ reached a minimum at pH 8.5, and at even higher pHs, the enhanced ionic strength was required for coagulation. Similar behavior has been also observed in a silica suspension in the presence of CsCl and the required ionic strength had a minimum near pH 9 [Allen, 1969]. In addition, infinite stability was also noted in the presence of K^+ [Depasse, 1970]. Indeed, as shown in Fig. 8, the required ionic strength became considerably high as pH approach either 6 or 12. As mentioned earlier, this different coagulation behavior in the presence of cations Na^+ and K^+ arises from their capabilities in hydration or dehydration of the silica surface. Since the silica

surface loses at least one site for hydrogen bonding by cation exchange, one or more adsorbed water molecules are removed from the surface with ion exchange. Therefore, dehydration of the silica surface accompanied by ion exchange is responsible for the enhanced coagulation of colloidal silica. On the other hand, the effects of the anions Cl^- and Br^- were not so significant as the cations. However, the present results clearly showed that the stability of the colloidal silica could not be explained fully by the surface potential behavior alone. Otherwise, the affinity of cations or anions to the particle surface and interactions with the solvent phase were also the important factors.

CONCLUSION

In the present study, spherical silica particles were prepared by a stepwise growth procedure using the sol-gel method. The results showed that there exists an optimal TEOS content for preparation of the large particles with a narrow size distribution. Above the optimal concentration, the particle size distribution becomes broad with considerable number density of very tiny particles. The prepared silica particles were dispersed in aqueous media and the stability of the silica dispersion was examined for various added electrolytes. In the presence of Na^+ ions, the critical coagulation concentration was decreased monotonically by increasing pH. On the other hand, in the presence of K^+ ions, the worst stability was observed at pH 8.5, with an infinite stability at pH around 6.0. The ζ -potential that was decreased abruptly in the presence of Na^+ ions by lowering pH showed little difference with K^+ ions. Finally, the stability of silica suspensions with the added salts was not controlled solely by the surface charge density but depended also on their capabilities in hydration or dehydration of the silica surface.

REFERENCES

- Allen, L. H. and Matijevic, E., "Stability of Colloidal Silica: I. Effect of Simple Electrolytes," *J. Colloid Interface Sci.*, **31**, 287 (1969).
- Allen, L. H. and Matijevic, E., "Stability of Colloidal Silica: II. Ion Exchange," *J. Colloid Interface Sci.*, **33**, 420 (1970).
- Bogush, G. H., Tracy, M. A. and Zukoski IV, C. F., "Preparation of Monodisperse Silica Particles: Control of Size and Mass Fraction," *J. Non-Cryst. Solids*, **104**, 95 (1988).
- Depasse, J. and Watillon, A., "The Stability of Amorphous Colloidal Silica," *J. Colloid Interface Sci.*, **33**, 430 (1970).
- Depasse, J., "Coagulation of Colloidal Silica by Alkaline Cations: Surface Dehydration or Interparticle Bridging?," *J. Colloid Interface Sci.*, **194**, 260 (1997).
- Hunter, R. J., "Foundations of Colloid Science," Oxford Univ. Press, New York (1989).
- Iler, R. K., "The Chemistry of Silica," Wiley, New York (1979).
- Lee, J.-D. and Yang, S.-M., "Rheo-optical Behavior and Microstructural Changes in Silica Particle Dispersions," *HWAHAK KONGHAK*, **35**, 782 (1997).
- Lee, J.-D. and Yang, S.-M., "Rheo-optical Behavior and Stability of a Silica Particle Suspension Coated with Silane Coupling Agents," *J. Colloid Interface Sci.*, **205**, 397 (1998b).
- Lee, J.-D. and Yang, S.-M., "Rheological Behavior of Concentrated Silica Particle Suspensions Prepared by Sol-gel Method," *Korean J. Rheol.*, **15**, 136 (1998a).
- Lee, J.-D., So, J.-H. and Yang, S.-M., "Rheological Behavior of Concentrated Silica Suspensions Stabilized with γ -Methacryloxypropyl Triethoxy Silane," *J. Rheol.*, **43**(5) (1999).
- Lindberg, R., Sundholm, G., Pettersen, B., Sjöblom, J. and Friberg, S. E., "Multivariate Analysis of the Size Dependence of Monodisperse Silica Particles Prepared According to the Sol-gel Technique," *Colloids Surfaces*, **123-124**, 549 (1997).
- Matsoukas, T. and Gulari, E., "Dynamics of Growth of Silica Particles from Ammonia-Catalyzed Hydrolysis of Tetra-ethyl-orthosilicate," *J. Colloid Interface Sci.*, **124**, 252 (1988).
- Matsoukas, T. and Gulari, E., "Monomer-addition Growth with a Slow Initiation Step: A Growth Model for Silica Particles from Alkoxides," *J. Colloid Interface Sci.*, **132**, 13 (1989).
- Matsoukas, T. and Gulari, E., "Self-sharpening Distributions Revisited: Polydispersity in Growth by Monomer Addition," *J. Colloid Interface Sci.*, **145**, 557 (1991).
- Milonjic, S. K., "A Relation between the Amounts of Sorbed Alkali Cations and the Stability of Colloidal Silica," *Colloids Surfaces*, **63**, 113 (1992).
- Napper, D. H., "Polymeric Stabilization of Colloidal Dispersions," Academic Press, London (1983).
- Oh, M.-H., So, J.-H. and Yang, S.-M., "Rheological Evidence of the Silica-mediated Gelation of Xanthan Gum," *J. Colloid Interface Sci.*, **216**, 320 (1999).
- Russel, W. B., Saville, D. A. and Schowalter, W. R., "Colloidal Dispersions," Cambridge Univ. Press, New York (1989).
- Sasaki, S. and Maeda, H., "Electrostatic Effect on the Hydration Layer of Colloidal Silica Particles," *J. Colloid Interface Sci.*, **167**, 146 (1994).
- Stöber, W. and Fink, A., "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," *J. Colloid Interface Sci.*, **26**, 62 (1968).
- Zukoski IV, C. F. and Saville, D. A., "Electrokinetic Properties of Particles in Concentrated Suspensions," *J. Colloid Interface Sci.*, **107**, 322 (1985).
- Zukoski IV, C. F. and Saville, D. A., "The Interpretation of Electrokinetic Measurements using a Dynamic Model of the Stern Layer: I. The Dynamic Model," *J. Colloid Interface Sci.*, **114**, 32 (1986a).
- Zukoski IV, C. F. and Saville, D. A., "The Interpretation of Electrokinetic Measurements using a Dynamic Model of the Stern Layer: II. Comparison between Theory and Experiment," *J. Colloid Interface Sci.*, **114**, 45 (1986b).
- van Blaaderen, A. and Kentgens, A. P. M., "Monodisperse Colloidal Silica Spheres from Tetraalkoxysilanes: Particle Formation and Growth Mechanism," *J. Non-Cryst. Solids*, **149**, 161 (1992).