A comparison of theoretical and experimental aggregation stability of colloidal silica

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Absorbance-vs-time dependences have been determined for well characterized monodisperse colloidal silica spheres of three different diameters, aggregating under the influence of monovalent electrolyte (KCl) at pH 6. Subsequently, absolute aggregation rate constants and corresponding stability ratios were determined from these experimental dependences by using a proper aggregation model. The electrophoretic mobility of the silica spheres was measured as a function of the KCl concentration. This provided the ζ-potential values inserted as the surface electrostatic potentials in the calculation of the stability ratios following the DLVO theory. An essential disagreement was found between the experimentally and theoretically evaluated stability ratios that points toward a systematic underestimation of actual aggregation rate by the theory. Thus, values of theoretical surface potential were calculated in turn for the experimental stability ratios using the same (DLVO) calculus and compared with these of ζ-potential. In this way, an information has been obtained as to the origin of the disagreement.

Key words: *aggregation, silica colloids, DLVO theory, electrophoretic mobility*

Introduction

Aggregation behavior of colloidal particles is controlled by surface forces operating between them during their encounters. There are two main types of the long-range surface forces. The attractive van der Waals and repulsive electrostatic double-layer forces have been incorporated in the DLVO theory and confirmed experimentally, however short-range surface forces such as hydration, hydrophobic and steric have also been found to influence the aggregation process. Their theoretical elaboration and experimental validation is far from complete. The aim of this work is to continue in the previous research on this topic (Škvarla et al., 2001, Škvarla, 2005) and to compare the experimental absolute stability ratio of well characterized colloidal silica particles with the theoretically calculated one, obtained by using physically correct formulas of surface forces with physically accurate and independently determined parameters.

Theoretical section

According to Smoluchowski the kinetics of aggregation is described as diffusion of colloidal particles to each other without interfering (no surface forces are involved during the particles´ encounters). The rate constant of this diffusion-limited aggregation and is given as:

$$k_{\mathrm{Sm}} = \frac{8k_{\mathrm{B}}T}{3\eta} \tag{1}$$

Representing a limiting (fast) aggregation process, its value is ~1,2.10^{-17} m^3.s^{-1} in water and at normal temperature. The “real” or reaction-limited (slow) aggregation of colloids is influenced by their surface forces its rate constant k_{11} is given by the diffusion-limited rate constant which is reduced by the so-called stability ratio. Thus: $W = k_{\mathrm{Sm}}/k_{11}$.

For spherical particles of radius a, the stability ratio can be calculated from the following formulae:

$$W = 2\int_0^\infty \frac{\beta(u)}{(u+2)^2}\exp\frac{V(u)}{k_{\mathrm{B}}T}\,du \tag{2}$$

where $u = h/a$ is the dimensionless distance between the spheres. $\beta(u)$ is the hydrodynamic retardation function due to the viscous forces:

$$\beta(u) = \frac{6u^2+13u+2}{6u^2+4u} \tag{3}$$

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and $V(u)$ is the interaction energy function between the approaching spheres, the latter consisting of two components due to the van der Waals and electrostatic double-layer surface forces (DLVO theory):

$$V(u) = V^{\mathrm{vdW}}(u) + V^{\mathrm{El}}(u) \tag{4}$$

The attractive van der Waals interaction can be exactly expressed by the combined Hamaker and Lifshitz approach as:

$$V^{\mathrm{vdW}}(u) = -\frac{A(\kappa,h)}{6}\left(\frac{2}{u^2+4u} + \frac{2}{(u+2)^2} + \ln\frac{u^2+4u}{(u+2)^2}\right) \tag{5}$$

with $A(\kappa,h)$ being the effective Hamaker constant which is a function of the distance between spheres, h, as well as the Debye screening length of double layers around the spheres in the solution due to electrolyte ions, κ.

To calculate the repulsive electrostatic interaction between spheres, the constant surface potential or charge can be assumed, depending on the charge regulation during their interactions:

constant surface potential: $V^{\mathrm{El}}(u) = 2C_2\frac{1+u}{2+u}\ln\left[1+\frac{\exp(-\tau u)}{1+u}\right]$ (6)

constant surface charge: $V^{\mathrm{El}}(u) = -C_2\ln[1-\exp(-\tau u)]$ (7)

with $C_2 = 2\pi\varepsilon_0\varepsilon_r a\psi_0^2$ (8)

In Eq.8, ε_0 is the dielectric constant of free space, ε_r is the relative permitivity of the solution and ψ_0 is the surface potential of the spherical particles. Alternatively, the following expression may be used:

$$V^{\mathrm{El}}(u) = \frac{C_2}{\eta}\ln[1+\eta\exp(-\tau u)] \tag{9}$$

in which $\eta = 1-2p$ is the regulation parameter characterizing the location of the interaction energy between the constant potential (p = 0, η = 1) and the constant charge (p = 1, η = -1). In our case, η = -0.2 was considered.

Materials and methods

Uniform silica micro spheres of three different diameters were obtained as an aqueous stock suspension from the Bangs Laboratories Inc., USA. The spheres were prepared from pure tetra-ethyl orthosilicate $Si(OC_2H_5)_4$ via reaction with water and ammonia. The mean diameter (determined by SEM) is 50, 150 and 320 nm. For experiments, the supplied stock suspension was diluted with doubly distilled water. The initial particle concentration was $1{,}21\pm0{,}32.10^{13}$, $1{,}48\pm0{,}47.10^{11}$, and $3{,}16\pm0{,}3.10^{10}$ for 50, 150 and 320 nm particles, respectively.

Aggregation Tests and Kinetic Constants

The aggregation kinetics was evaluated from the change in the absorbance of initially stable colloidal silica dispersions in the spectrophotometric cell with time, initiated by adding an aliquot amount of KCl solution to achieve various final concentrations, at a given pH and temperature 20 ± 2 °C. The pH value was around 6. The instrument (Spectronic 401 spectrophotometer, Milton Roy, USA) consisted of a visible light source, a grating monochromator, exit slit, sample compartment with cuvette holder, solid state light detector, and a keyboard/display unit and was operated at the wavelength of 380, 540 and 800 nm for 50, 150 and 320 nm particles respectively by using a computer program (Quant software). The argument is that the RGD regime, valid when $4\pi a/\lambda(m-1) << 1$ (λ is the wavelength of light in the liquid medium, a is characteristic length of the particle and m is the relative refractive index), must be fulfilled.

The absorbance-*vs*-time curves recorded experimentally after the addition of KCl were fitted by a Fortran program provided by Dr. Antonio Puertas from the Department of Physics, University of Granada, Spain. This program uses Rayleigh-Gans-Debye (RGD) approximation and the von Smoluchowski kinetic approach to the homo-aggregation process. More detailed description can be found elsewhere (Puertas, 1997). There are several parameters to be launched into the program such as the wavelength of the light, concentration, radius and refraction index of the particles. The kinetic constant k and the initial time are the only fitting parameters. There is a direct relation between the rate constant of dimer formation k_{11} and the experimentally obtained kinetic constant of the whole aggregation process k, that is $k_{11} = 2k$. The value of silica refractive index was set to 1.37 and of KCl solutions to 1.333.

Electrokinetic Measurements and Zeta Potentials

The electrophoretic light scattering method was engaged to determine the electrokinetic mobility of colloidal silica particles under the same conditions as the aggregation tests were carried out. For this purpose, the fully automated Zeta Plus instrument (Brookhaven Instruments Corporation, USA) was used. It was operated in the heterodyne mode with a wavelength of the laser source of 670 nm, the sampling time of 256 μs, modulation frequency of 250 Hz and the scattering angle 15^o. Since moderate KCl concentrations and small particles sizes were used, the parameter κa varied in the range from 0.82 to 26 for 50 nm particles, from 2.46 to 78.04 for 150 nm particles and 5.23 to 234 for 320 nm particles. It means that for most samples it was neither within the Hückel ($\kappa a < 0.1$) nor the Smoluchowski limit ($\kappa a > 100$) entirely. For this reason, the electrophoretic mobilities were converted to zeta potentials using the Zeta program (by Kosmulski) taking into account both the retardation and relaxation effect. The data input in the program was the molar conductivity of ions (0.00735 and 0.00764 $m^2\Omega^{-1}mol^{-1}$ for K^+ and Cl^-, respectively), dielectric constant, ionic strength, temperature and viscosity of aqueous solutions and the particle radius.

Results

Fig. 1 represents an example of the absorbance-*vs*-time dependences (see the marks) recorded in the aggregation experiments with 150 nm particles of silica spheres at pH around 6 and three KCl concentrations. As can be seen, the adopted model describes the aggregation kinetics of silica dispersions quite well, as documented by the best fits in Fig. 1 with $R^2 = 0.999$ and better (see the lines), at least for the higher KCl concentrations presented. Fig. 2 shows complete relationships between the rate constant of dimer formation k_{11} obtained by doubling the fitted kinetic constant k and the KCl concentration for 50, 150 and 320 nm particles, revealing some maxima ($9.48.10^{-20}$, $3.22.10^{-18}$ and $9.17.10^{-18}$ $m^3.s^{-1}$) at 0.3, 0.25 and 0.1 M KCl, respectively.

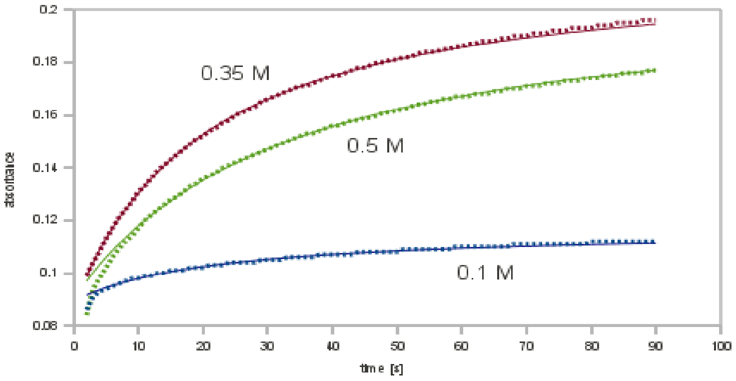


Fig. 1. Absorbance-vs-time records for 150 nm silica particles at pH 6 for three different KCl concentrations (marks). The full lines are the best fits of the records obtained by using the aggregation model.

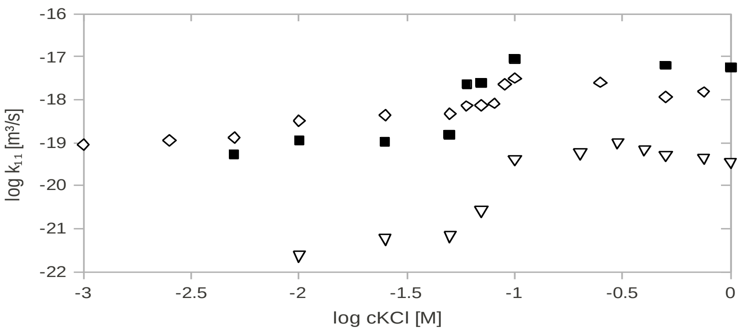
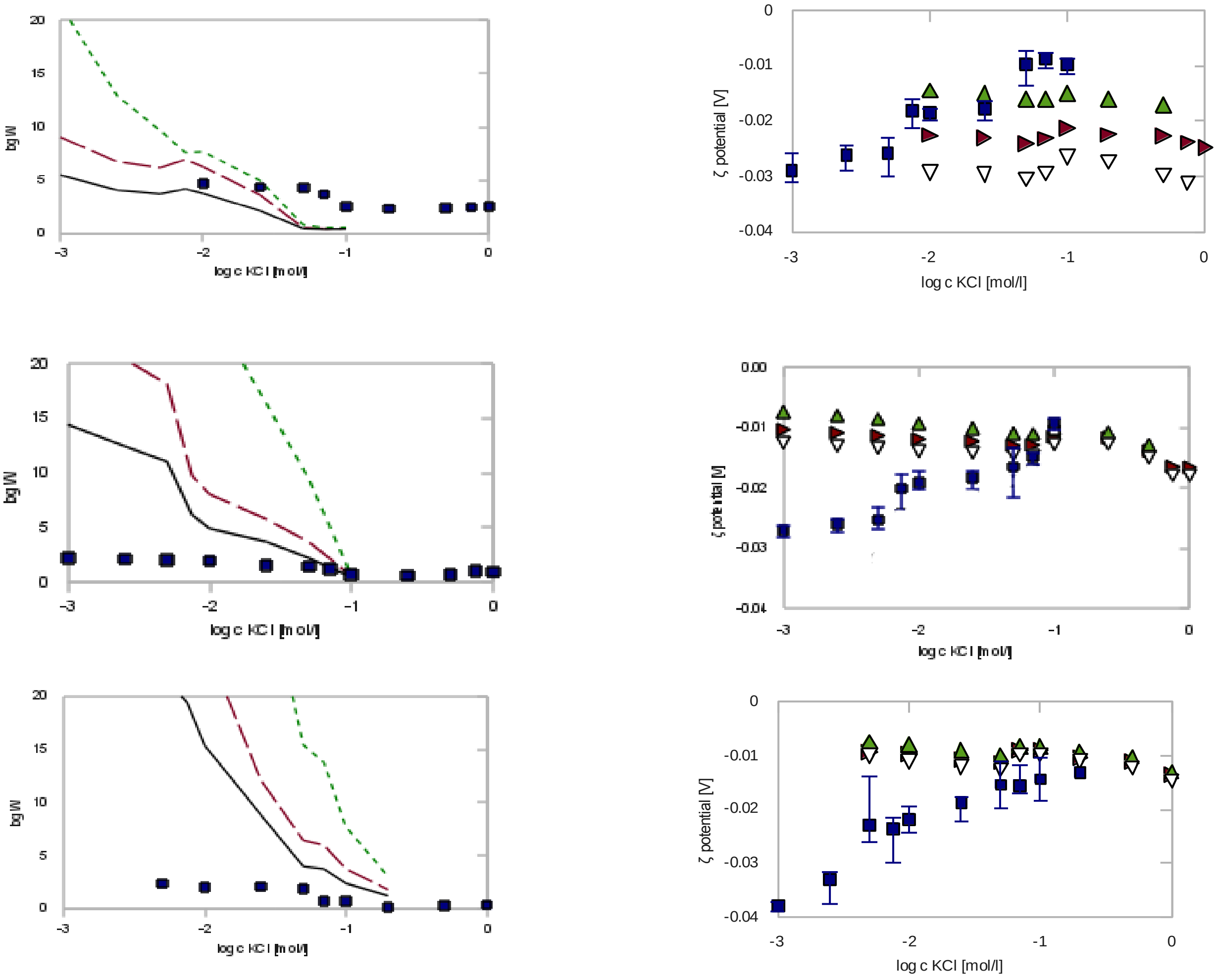


Fig. 2. Aggregation rate constant of the colloidal dispersion of 320 (■), 150 (◊) and 50 (Δ) nm silica spheres as a function of KCl concentration at pH 6.

These maximal values, attributable to pseudofast rate constants, lie within the range of values reported by other authors for silica (except for the biggest particles where the observed rate constant is significantly higher) even though the aggregation is influenced by the preparation technique, particle size and concentration of silica colloids.

Tab.1.Values of maximum aggregation rates for colloidal silica particles reported by other authors

Author	Particle size	Method of determination	Aggregation rate constant [m^3.s^{-1}]
Ludwig P. et.al (1988)	45 – 515 nm	PCS	1,7.10^{-24} - 3,2.10^{-18} m^3.s^{-1}
Higashitani et. al. (1991)	5 - 120 nm	LALS	5.10^{-21} m^3.s$^-$1 - 5.10^{-18} m^3.s^{-1}
Killmann E. et. al (1995)	138 nm	PCS	3 – 6.10^{-18} m^3.s^{-1}
Barany S. et. al (1996)	530 nm	SPOS	1,75.10^{-18} m^3.s^{-1}
Axford S.D.T. et. al (1997)	12 nm	PCS	3.10^{-24} m^3.s^{-1} - 2.10^{-21} m^3.s^{-1} (0.4-0.7 M KCl)
Kobayashi et. al. (2005)	50, 80 nm	DLS, SSDLS	2.10^{-18} m^3.s^{-1}



(a) (b)

Fig. 3. (a) Experimental and theoretical stability ratios for 50, 150 and 320 nm silica particles (from top to bottom) as a function of KCl concentration at pH 6. The full squares represent experimental data. The blue, green and red lines represent the theoretical stability ratio calculated with the assumption of the electrostatic repulsion in the constant potential (Eq. 6) and the constant charge limit (Eq. 7), and of the regulation between these limits (Eq. 9), respectively, and considering the experimental zeta potential as the surface electrostatic potential. (b) Experimental zeta potentials (blue squares) and theoretical surface potentials predicted from the experimentally obtained stability ratios assuming the constant potential limit (white triangles), the constant charge limit (green triangles), and the regulation between these limits (brown triangles) for the electrostatic repulsion.

Fig. 3a (left column) presents the experimentally determined stability ratio $W = k_{\mathrm{Sm}}/k_{11}$ (squares) with the theoretical W (lines) calculated by using Eq. 2 to Eq. 4 with the van der Waals attraction (Eq. 5), three different electrostatic repulsion modes (Eq. 6 to Eq. 9) and the surface electrostatic potential identified with experimentally estimated values of zeta potential as a function of KCl concentration, c_{KCL}. Apparently, the constant potential mode provides the relatively lowest (blue line) values and the constant charge mode (green line) the relatively highest values of stability ratio, with the regulation mode (red line) in between them. For smallest, i.e. 50 nm silica spheres, the DLVO theory with V^{El} based on the experimental zeta potentials overestimates the experimental aggregation kinetics for c_{KCL} above ca. 30 mM, irrespective of the mode of electrostatic repulsion applied in the calculation. On the opposite side, the DLVO calculation underestimates the actual aggregation kinetics for largest 320 nm silica spheres, again regardless of the repulsive mode but in the whole c_{KCL} scale. The agreement is better for 150 nm spheres of silica at $c_{\mathrm{KCL}} > 50$ mM, considering the constant potential. Altogether, there is a dramatic underestimation of the aggregation kinetics, as documented by the overestimation of the stability ratio for all silica particles.

To evaluate the possible contribution of identifying the surface electrostatic potentials with experimental zeta potentials to the given disagreement, the former were calculated in turn from the same formulas used above for the values of experimental stability ratio, see Fig. 3b. It can be seen that, in analogy with the theoretical stability ratio, the theoretically predicted potentials attain highest and lowest values for the constant potential and charge mode of electrostatic repulsion, respectively, and middle values for the regulation case. Moreover, the difference in the values provided by the three modes is highest (around 15 mV) for the 50 nm spheres and lowest (a few mV) for the 320 nm spheres, with a middle value (ca. 6 mV) for the medium, 150 nm spheres. More importantly, the predicted surface potentials are higher and lower than the experimental zeta potentials of 50 and 320 nm spheres, with an error in both cases on the level of up to 20 mV. With 150 nm spheres, the situation is similar to that with 320 nm spheres, except for $c_{\mathrm{KCL}} > 50$ mM, as expected. Interestingly, all the predicted values of the surface potential vary in much lesser extent than the experimental zeta potentials when the KCl concentration increases but there is a shift in such a “constant” value from (very roughly) – 30 mV to – 12 mV and – 10 mV for, respectively, 50, 150 and 320 nm particles, when for example the constant potential limit is followed. The above facts seem to be of crucial importance for understanding the reason of the disagreement between the absolute values of aggregation rate constant calculated according to the DLVO theory and that determined experimentally.

Conclusion

There is a simple yet reasonably accurate method to determine the absolute aggregation rates of monodisperse spherical colloidal silica particles from the development of their aggregates after addition of monovalent electrolyte (KCl). The experimental values of aggregation rates were obtained from the absorbance-*vs*-time curves by fitting them with an aggregation model using constant kinetic kernel. It has been discovered that the experimental absolute rate constants are steadily lower than these predicted by the theory with proper DLVO expressions of surface forces and electrostatic potentials at the (ideal) surfaces of colloids equaled to their experimentally measured zeta potentials. This is in qualitative agreement with the observations of other authors who based their conclusions on relative aggregation rate constants. Interestingly, the electrostatic surface potential, as predicted in turn from the aggregation experiments by the DLVO theory, was found to be almost constant or vary much less than the experimental zeta potential. This fact indicates that the interface between the silica colloids and the aqueous electrolyte solution in which they are dispersed is not “ideal”, leading possibly to an incorrect selection of expressions for calculating their surface forces and/or zeta potential.

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