Kinetics and Cluster Morphology Evolution of Shear-Driven Aggregation of Well Stabilized Colloids

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Supporting Information

Part A: Applications of the generalized stability model to quantify the interaction energy barrier.

The colloidal systems used for this study were aqueous dispersions of polystyrene particles produced by emulsion polymerization with SDS (sodium dodecyl sulfate) as surfactant and KPS (potassium persulfate) as initiator. The radius of the particles is 21.5 nm by DLS measurements. The particle volume fraction (ϕ) of the original latex is 0.15. The aggregation systems with different ϕ were prepared by direct dilution of the original latex with deionized water. This leads to changes in the SDS adsorption isotherm and the ionic strength at different ϕ values and consequently to the changes in the interaction energy barrier (U_m), which should be estimated. To this aim, the generalized stability model developed previously[1] has been applied, which accounts simultaneously for the interplays among three important physicochemical processes: adsorption equilibrium of surfactants, association equilibria of the ionic surfactants with counterions, and colloidal interactions. The following describes briefly the quantities that we considered in the generalized stability model:

   1. The DLVO interactions.

   According to the DLVO theory, the interaction energy between two colloidal particles, *U,* is the sum of the van der Waals attractive interaction (U_A) and the electrostatic repulsive

interaction (U_R)

$$U = U_A + U_R \tag{1}$$

According to the Hamaker relationship, the expression for U_A is given by

$$U_A = -\frac{A_H}{6}\left[\frac{2}{l^2-4}+\frac{2}{l^2}+\ln\left(1-\frac{4}{l^2}\right)\right] \tag{2}$$

where A_H is the Hamaker constant, and $l = x/a$. The modified Hogg-Healy-Fuersteneau expression is commonly used to describe the electrostatic repulsion [2]:

$$U_R = \frac{4\pi\varepsilon_r\varepsilon_0 a\psi^2}{l}\ln\left\{1+\exp\left[-\kappa a(l-2)\right]\right\} \tag{3}$$

where ε_r is the permittivity constant of the dispersion medium, ε_0 is the permittivity of vacuum, ψ is the surface potential which is obtained from zeta potential measurement[3] and κ is the reciprocal Debye length, which is defined as:

$$\kappa \equiv \left(N_A e^2 \sum_i c_i^b z_i^2 \,/\, \varepsilon_r\varepsilon_0 k_B T\right)^{1/2} \tag{4}$$

where N_A is the Avogadro constant, e is the electron charge, and c_i^b and z_i are the bulk concentration and charge valency of the ith ion, respectively. The constants used in calculating U is listed below:

A_H	J	1.37×10^{-204}
N_A	1/mol	6.022×10^{23}
k_B	J/K	1.381×10^{23}
F	C/mol	9.65×10^{4}
e	C	1.602×10^{-19}
T	K	298
$\varepsilon_r\varepsilon_0$	C/V/m	6.950×10^{-10}

Where A_H value was estimated from the Lifshitz theory and taken from the literature.[4] In order

to estimate the DLVO interaction of the colloidal systems, several parameters has to be described:

2. Charges on the particle surface

The colloidal systems of this work contain the SDS surfactant, which adsorbs on the particle surfaces based on the adsorption isotherm and their dissociation leads to the formation of negative charges on the surface. Since the adsorption is reversible, the charges deriving from the surfactant molecules are referred to as mobile charges (E^-). Besides, the polymer end group which comes from the initiator KPS contribute to the fixed charge (L^-) on the particle surface.
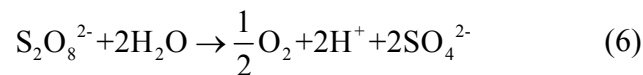
3. Ionic strength

Since the colloidal systems which are used in the experiment are directly diluted from the original latex, the change of ionic species in the bulk liquid phase causes the redistribution of the ionic species, which in turn changes the association equilibria between the ionic surfactant adsorbed on the particle surface and the counter-ions in the bulk phase. Specifically, two sets of ionic specious SDS and KPS are considered in this calculation. The dissolved SDS in the bulk can be calculated according to the Langmuir-type adsorption isotherm of SDS on polystyrene nanoparticles:[5]
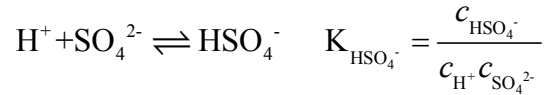
$$Vc_{SDS} + \frac{Kc_{SDS}}{1+Kc_{SDS}}\Gamma_\infty S = Vc_0 \tag{5}$$

where $K = 1.208 \times 10^5$ cm^3/mol; $\Gamma_\infty = 7.257 \times 10^{-10}$ mol/cm^2; c_{SDS} is the SDS concentration in the bulk, c_0 is the total SDS concentration, S is the total surface area of the polystyrene particles in the latex, and V is the total volume.

During the emulsion polymerization, besides the part which initiates the free radical polymerization, KPS will also be hydrolysed according to the following reaction:

$$S_2O_8^{2-} + 2H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2SO_4^{2-} \tag{6}$$

Consequently, H^+ and SO_4^{2-} will be generated and contribute to the ionic strength.

Since the H^+ concentration is significant in our system (pH= 2-3), in order to simplify the calculation, we only consider the association of H^+ with SO_4^{2-} in the bulk and the -SO_4^- groups (L^- for fixed charge) on the polystyrene particle surface. The association of ions such as Na^+ and K^+ with anions is neglected.

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \qquad K_{HSO_4^-} = \frac{c_{HSO_4^-}}{c_{H^+} c_{SO_4^{2-}}}$$

$$H^+ + L^- \rightleftharpoons LH \qquad K_{LH} = \frac{c_{LH}}{c_{H^+} c_{L^-}}$$

4. Surface charge density and surface potential

As discussed above, two species contribute to the surface charge: the mobile charge from adsorbed surfactant (E^-) and the fixed charge from polymer end group (L^-). The total surface charge density:

$$\sigma_0 = \sigma_{0,E} + \sigma_{0,L}$$

Where $\sigma_{0,E} = F c_E^S$ and $\sigma_{0,L} = F c_L^S$. c_E^S and c_L^S are the concentration of surfactant and the fixed end group on the particle surface (mol/m^2), respectively. The surface potential of the particle is related to the surface charge by eq 7.[6]

$$\sigma_0 = -\{R_0 \sum_j c_j^{\,b} [\exp(-\frac{z_j e \psi_0}{k_B T}) - 1]\} \qquad (7)$$

where $R_0 = 2F\varepsilon_0 \varepsilon_r k_B T / e$, ψ_0 is the surface potential and $c_j^{\,b}$ is the concentration of the jth ion in the bulk.

In order to estimate the fixed charge density, we have mixed part of the original latex with a mixture of cationic and anionic exchange resins (Dowex MR-3, Sigma-Aldrich), according to a procedure described elsewhere.[7] This procedure can clean up all the SDS (adsorbed and dissolved), as well as all the other possible ions, leaving only the counterions (H^+) of the surface

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fixed charges. Then, we dilute this cleaned latex to $\phi = 1.0 \times 10^{-4}$ with water in the presence of NaCl, $c_{NaCl} = 0.01$ mol/L, which is considered as the model system. The ζ-potential of the model system was measured using Zetasizer Nano instrument (Malvern, UK), equal to -45 mV, which is computed from the measured mobility using the Smoluchowski theory. Then, from the generalized stability model, we estimated the fixed charge of the polystyrene particles, whose value is 0.012 C/m^2. Sample No. 1 in Table S1 corresponds to the model system.

With this model system together with the above descriptions of all the quantities, we are able to describe well the colloidal interactions of all the systems used for the shear-driven aggregation, which are listed in Table S1.

Table S1 Properties and colloidal interaction quantities of all the dispersions used in this work

Sample No.	ϕ	a nm	ψ_0 mV	s C/m^2	Total I mol/m^3	$1/k$ nm	U_m k_BT	a_{cr} nm
1	10^{-4}	21.5	−45.0	0.012	20.0	3.04	21	31.2
2	0.02	21.5	−158.8	0.083	8.2	4.77	348	79.7
3	0.03	21.5	−152.2	0.091	13.3	3.73	325	77.9
4	0.05	21.5	−143.1	0.098	21.5	2.93	280	74.2
5	0.15	21.5	−120.7	0.107	57.2	1.78	218	68.2
6*	0.02	21.5	−54.0	0.012	1.3×10^{-4}	1202	42.2	39.5

Sample No.	ϕ	c_{SDS} mol/m^3	c_{H^+} mol/m^3	c_{Na^+} mol/m^3	c_{Cl^-} mol/m^3	$c_{HSO_4^-}$ mol/m^3	$c_{SO_4^{2-}}$ mol/m^3
1	10^{-4}	0.0	1.3×10^{-4}	10.0	10.0	0.0	0.0
2	0.02	0.94	0.57	3.6	0.0	0.041	0.75
3	0.03	1.0	0.99	5.4	0.0	1.5	1.1
4	0.05	1.2	1.6	9.1	0.0	2.4	1.8
5	0.15	1.3	3.8	27.0	0.0	6.7	4.6
6*	0.02	0.0	1.3×10^{-4}	0.0	0.0	0.0	0.0

* is the latex after cleaning with ionic exchange resins.

Part B: Scaling of the characteristic time

In shear-driven aggregation, the characteristic time may be represented by the inverse of the rate constant of the doublet formation:[8]

$$\frac{1}{k_{1,1}} \sim \frac{1}{\sqrt{(3\pi\alpha\mu\dot{\gamma}a^3 - U_m'')/k_B T}} e^{(U_m - 6\pi\alpha\mu\dot{\gamma}a^3)/k_B T} \qquad (8)$$

where U_m'' is the second derivative of the interaction energy at U_m. Now we estimate the U_m'' value in order to further simplify the rate constant equation.

Consider the case of the DLVO interactions described above. The first derivative of U from eqs 2 and 3 reads:

$$U' = -\frac{A_H}{6}\left[-\frac{4a^2 r}{(r^2 - 4a^2)^2} - \frac{4a^2}{r^3} + \frac{8a^2}{r^3 - 4a^2 r}\right] - \frac{4\pi\varepsilon_r\varepsilon_0 a^2\psi^2}{r^2}\ln\{1 + \exp[-\kappa(r - 2a)]\}$$

$$-\frac{4\pi\varepsilon_r\varepsilon_0 a^2\psi^2\kappa}{r^2}\frac{1}{1 + \exp[\kappa(r - 2a)]} \qquad (9)$$

At $r = r_m$, $U' = 0$ and $U = U_m$. The second derivative reads:

$$U'' = -\frac{A_H}{6}\left[\frac{4a^2}{(r^3 - 8a^2 r + 16a^4/r)^2}(3r^2 - 8a^2 - 16a^4/r^2)\right. \qquad (10)$$

$$\left. + \frac{12a^2}{r^4} - \frac{8a^2}{(r^3 - 4a^2 r)^2}(3r^2 - 4a^2)\right] + \frac{8\pi\varepsilon_r\varepsilon_0 a^2\psi^2}{r^3}\ln\{1 + \exp[-\kappa(r - 2a)]\}$$

$$+ \frac{8\pi\varepsilon_r\varepsilon_0 a^2\psi^2\kappa}{r^2}\frac{1}{1 + \exp[\kappa(r - 2a)]} + \frac{4\pi\varepsilon_r\varepsilon_0 a^2\psi^2\kappa^2}{r}\frac{\exp[\kappa(r - 2a)]}{\{1 + \exp[\kappa(r - 2a)]\}^2}$$

For the colloidal system used in this work, we have $a = 23$ nm, $\varepsilon_r\varepsilon_0 = 6.950\times10^{-10}$ C/V/m, $1/\kappa = 9.62\times10^{-9}$ m, and $A_H = 1.30\times10^{-20}$ J. With these values, considering the surface potential in the range of $\psi \in [0.005, 0.1]$ V, we obtain from eq 10 that at $r = r_m$, $U_m'' \in [-2.07\times10^{-4}, -1.79]$.

Instead, for the term, $3\pi\alpha\mu\dot{\gamma}a^3$, with the values, $\alpha = 1/(3\pi)$, $\mu = 0.001$ Pa·s and $\dot{\gamma} = 10^6$ s^{-1}, we have $3\pi\alpha\mu\dot{\gamma}a^3 = 1.22\times10^{-20}$. Therefore, it can be concluded that in general, we have $3\pi\alpha\mu\dot{\gamma}a^3 \ll -U_m''$, and for given colloidal interactions, the rate constant, eq 8, can be simplified as follows:

$$\frac{1}{k_{1,1}} \sim \frac{e^{U_m/k_BT}}{\sqrt{U_m^{''}/k_BT}} e^{-6\pi\alpha\mu\dot{\gamma}a^3/k_BT} \sim e^{-6\pi\alpha\mu\dot{\gamma}a^3/k_BT} = e^{-\alpha(2Pe)} \qquad (11)$$

where Pe $[= 3\pi\mu\dot{\gamma}a^3/k_BT]$ is the Peclet number.

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