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Kinetics of Heterocoagulation

Part. 2—The Effect of the Discreteness of Surface Charge†

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Coagulation rates in dispersions of uniform spherical particles of surfactant-free sulfate latices, silica and cerium (hydrous) oxide were measured as a function of the ionic strength by a low-angle scattering technique. The results were used to interpret the significant discrepancies between theoretical predictions and experimental results of slow coagulation kinetics. The variations in values of all usual parameters in the accepted theoretical models were tested in order to eliminate the disagreements, but the task proved unsuccessful. However, the assumption of the segregated surface charge on the smooth spherical particles has led to the concordance between the measured and calculated stability ratios. In the model employed, the heterocoagulation theory is required even though one deals with systems of identical particles.

1. Introduction

The fundamental understanding of coagulation kinetics stems from a classic concept developed independently by Derjaguin and Landau, and Verwey and Overbeek (DLVO), in which the van der Waals and the double-layer interactions[1–14] are combined. This model was later extended to account for the heterocoagulation case.[15–27] Combining the derived expressions with the classic Smoluchowski[28] and the modified Fuchs formulations,[29,30] makes it possible to calculate the expected rates of coagulation. These data can then be compared with the experimental results, obtained by properly designed techniques, such as light scattering,[31–37] using well defined dispersions. Useful information can also be obtained from particle deposition (adhesion) phenomena on solid surfaces from dispersions in solutions of known compositions.[38–42]

Numerous studies have revealed significant discrepancies between the calculated and measured (hetero)coagulation rates, especially when the process was slow.[31–37,42] Reerink and Overbeek[33] reported such disagreements in homocoagulation of silver iodide sols. Since the latter dispersions consisted of irregular particles, Ottewill and Shaw[34] used monodispersed spherical latices of various sizes, and concluded that the predicted dependence of the coagulation rate on the particle diameter could not be confirmed experimentally. Similar problems were encountered in the kinetics of adhesion, such as in a recent study by Elimelech and O'Melia,[39,42] in which they compared the experimental results with the calculations based on the Hogg, Healy and Fuerstenau (HHF) approximation for interactions of unlike particles.[17] Even the recently published more advanced non-linear heterocoagulation treatment by Overbeek,[18] could not account for the observed disagreements.[26]

This work describes the homocoagulation experiments with dispersions of uniform spherical latex, silica and cerium (hydrous) oxide particles and compares the results with the Overbeek model. It is shown that the discrepancies in the coagulation rates can be accounted for if the discreteness of the surface charge is taken into consideration.

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2. Theoretical

Stability Ratio

The coagulation kinetics are usually expressed in terms of the stability ratio, W, which is defined by

$$W = k_r/k_s \tag{1}$$

where k_r and k_s are the rate constants for the rapid and slow processes, respectively. This parameter can be theoretically evaluated from interaction energy curves, using the modified Fuchs treatment:[9,24,28–30]

$$W = \frac{\int_0^\infty \frac{\beta(a_1 + a_2)}{(a_1 + a_2 + H_0)^2} \exp\left(\frac{V_{tot}}{k_B T}\right) dH_0}{\int_0^\infty \frac{\beta(a_1 + a_2)}{(a_1 + a_2 + H_0)^2} \exp\left(\frac{V_A}{k_B T}\right) dH_0} \tag{2}$$

where a_1 and a_2 are the radii of spherical particles, V_{tot} and V_A are the total and London van der Waals interaction energies, H_0 is the distance of closest approach between two spheres, and k_B and T are the Boltzmann constant and absolute temperature. Parameter β is the hydrodynamic correction factor,[43–45] as modified assuming that the radii of the two spheres do not differ much:[37]

$$\beta = \frac{6\left(\frac{2H_0}{a_1 + a_2}\right)^2 + 13\left(\frac{2H_0}{a_1 + a_2}\right) + 2}{6\left(\frac{2H_0}{a_1 + a_2}\right)^2 + 4\left(\frac{2H_0}{a_1 + a_2}\right)} \tag{3}$$

When the hydrodynamic correction is unnecessary, $\beta = 1$. The computation scheme and its precision were described elsewhere.[25,26,46]

Interaction Energy Curves

Interaction energies for the double layers, V_{OV}, and London–van der Waals, V_A, are calculated by the use of Overbeek's full non-linear treatment[18,25,26] and Hamaker's equation,[3,4] respectively. The total energy, V_{tot}, is obtained by $V_{tot} = V_{OV} + V_A + V_H$, where V_H is the hydrophobic interaction energy, which will be included as necessary [eqn. (11), later].

3. Experimental

Materials

All solutions and dispersions were stored in polypropylene containers to avoid contamination by silicates. Cerium (hydrous) oxide suspensions were kept at pH 11.0 ± 0.1 (KOH) to prevent possible dissolution of the particles.[47,48] The pH of latices and of the silica sol was 5.7 ± 0.1, which was due to the presence of a minor amount of carbonate ions. However, the concentration of the latter was too small to affect the ionic strength of the studied range. All solutions were filtered through Nuclepore membranes to remove possible particulate contaminants.

The ultraclean hydrophobic surfactant-free sulfate polystyrene microspheres, as specified by the lot numbers 10-141-91 (sample a), 10-67-60 (b) and 2-94-35 (c), were purchased from Interfacial Dynamic Corporation.

Silica dispersions were prepared by hydrolysing alcoholic solutions of tetraethylorthosilicate (TEOS) with ammonia.[49] In order to remove any residual ammonia from silica surfaces, the particles were boiled in pure ethanol for 3 h, and then washed 20 times with doubly distilled water.

Cerium (hydrous) oxide particles were synthesized as described elsewhere.[50] An aqueous solution of 1.2×10^{-3} mol dm^{-3} $Ce(SO_4)_2$ and 8×10^{-3} mol dm^{-3} H_2SO_4 was aged at 90 °C for 67 h, and the particles so obtained were separated and washed 10 times with 1×10^{-3} mol dm^{-3} NaOH and 20 times with 1×10^{-3} mol dm^{-3} KOH aqueous solutions. Although it is recognized that the composition of the particles is that of a hydrous oxide, $Ce(OH)_xO_y$, for simplicity it will be designated CeO_2 in this paper.

The size distributions of the above dispersions were assayed either by transmission electron microscopy (TEM) or by light scattering (LS) using the polarization ratio technique.[51,52] The values obtained by the non-destructive optical technique were considered more reliable, since the electron beam irradiation caused the shrinkage of particles of 5–15% as was also reported earlier.[53] The radius of latex particles designated as sample a was too small to be determined by the employed LS technique; instead, the size was evaluated by counting *ca.* 500 particles on transmission electron micrographs.

The modal radii and the standard deviations (in parentheses) of the particles used in this study are as follows: latex a: 65.5 nm (5.45%, TEM), latex b: 159 nm (9.4%, LS), latex c: 260 nm (2.3%, LS), SiO_2: 210 nm (3.8%, LS), and CeO_2: 110 nm (10%, LS). As expected, the surfaces of all latex particles were smooth and so were those of silica [Fig. 1(*a*)]. In contrast, cerium (hydrous) oxide spheres showed a certain degree of surface roughness [Fig. 1(*b*)].

Stern Potential Estimation

The Stern potential, ψ_s, which is an indispensable parameter in the computation of the interaction energies, cannot be obtained directly. Instead, the electrokinetic potential, ζ, is commonly used, as evaluated from electrophoretic mobilities by a proper computation scheme, such as the MOBILITY program,[54,55] in which the retardation and relaxation effects are taken into account.[56]

In order to assess the Stern potential from the ζ-potential, it is necessary to assume a value for the distance of the slipping plane, l. For the purpose of this study, the qualitative estimate of the latter was carried out as follows. Electrophoretic mobilities were measured using the Coulter DELSA 440 instrument at various ionic strengths. The Stern potentials, ψ_s, were then calculated from experimentally obtained ζ-potentials for different l values by means of the Gouy and Chapman relationship:[57–60]

$$\psi_s = \frac{2k_B T}{e} \ln\left[\frac{\exp(-\kappa l) + \tanh(e\zeta/4k_B T)}{\exp(-\kappa l) - \tanh(e\zeta/4k_B T)}\right] \quad (4)$$

The results for the latex c at pH 5.7 indicate that the l value should be $\lesssim 3$ Å, because an increase of the ionic strength, and hence of the specific adsorption, should result in the lowering of the Stern potential (Fig. 2). The same critical values were obtained for other latices and the cerium (hydrous) oxide. Such a short distance l justifies equating the

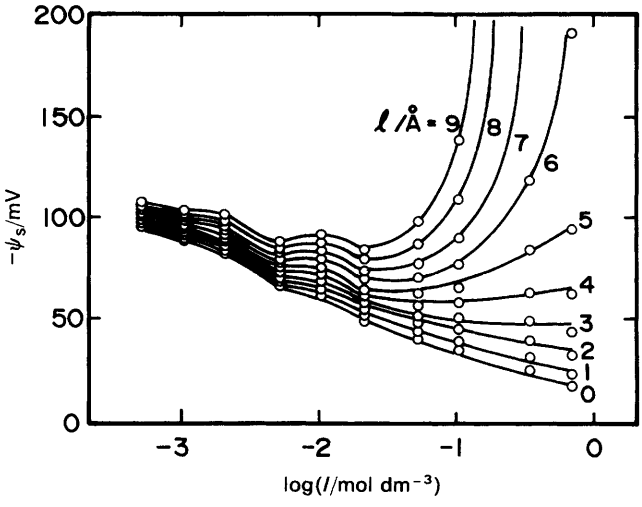

Fig. 2 Estimated Stern potentials, ψ_s, as a function of the ionic strength, I, of aqueous KNO_3 solutions at pH 5.7 and various values of assumed separation between the slipping plane and the Stern plane, l, for polystyrene latex of 260 nm in radius

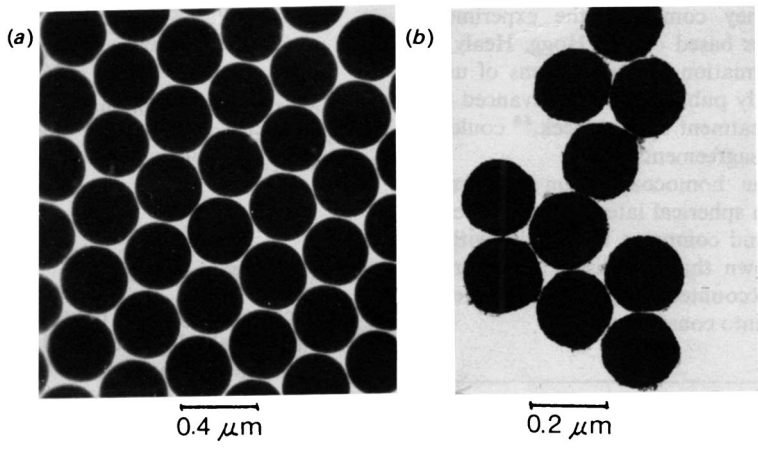

Fig. 1 Morphologies of the particles synthesized for the present work. (*a*) Silica, (*b*) cerium (hydrous) oxide

Stern potential with the ζ-potential for the purpose of this study.

Low-angle Light Scattering Technique

The low-angle light scattering technique for the measurement of the coagulation rates, originally developed by Lips, Smart and Willis (LSW),[61,62] is based on the combination of the Mie and the Rayleigh–Gans–Debye (RGD) theories for the calculation of the interfered scattered light from aggregated particles. While the Mie theory is applicable to spheres of all sizes and refractive indices, the RGD approximation holds only when the relative refractive indices are close to unity or when the sizes of particles are relatively small.[51,52,63] Since all dispersions used in the present work are out of the RGD applicability limit, it is necessary to assess the suitability of the LS technique for the coagulation rate evaluation.

Recently, the relationship between the intensities of scattered light observed at a low angle and the sizes of aggregates was determined by the so-called 'single particle optical sizing' (SPOS),[64,65] and similar techniques.[66–69] An empirical rule, $i = cv^{\omega}$, was established where i is the scattering intensity from an aggregate of the total volume v, while c and ω are constants. ω ranges between 1.7 and 2.0, depending on the size of the primary particles and the angle of observation.[64–69] For convenience, this empirical rule is rewritten as:

$$i_j = i_1 j^{\omega} \tag{5}$$

where j indicates the number of primary particles in an aggregate.

According to the Smoluchowski theory,[28,61,62,64] the number concentration of j-mer aggregates, N_j, as a function of time is given by:

$$N_j = N_0 \frac{\tau^{j-1}}{(1+\tau)^{j+1}} \tag{6}$$

where N_0 is the initial particle number concentration, $\tau = kN_0 t$, k being the rate constant, and t is time. When the change in the scattering intensity with time is measured at a low observation angle, the total intensity from a scattering volume, v_s, can be expressed as:

$$i_T(\tau) = v_s \sum_{j=1}^{\infty} i_j N_j = v_s i_1 N_0 \sum_{j=1}^{\infty} j^{\omega} \frac{\tau^{j-1}}{(1+\tau)^{j+1}} \tag{7}$$

Fig. 3 shows the scattering intensity ratio, R, defined as:

$$R = \frac{i_T(\tau)}{i_T(0)} = \sum_{j=1}^{\infty} j^{\omega} \frac{\tau^{j-1}}{(1+\tau)^{j+1}} \tag{8}$$

for various values of ω. It is obvious that at the early stages of coagulation ($t \rightarrow 0$), the linear relationship is justified:

$$R \approx \alpha\tau + 1 = \alpha k N_0 t + 1 \tag{9}$$

with α being a proportionality constant.

Accordingly, the classical low-angle LS technique for the evaluation of coagulation rates should be applicable to spherical particles of larger sizes of any refractive indices. The comparison of the initial slopes in the plots of the scattering intensity as a function of time for rapid and slow coagulations generates the experimental value of the stability ratio:

$$W = \frac{k_r}{k_s} = \frac{(dR_r/dt)_{t\rightarrow 0}}{(dR_s/dt)_{t\rightarrow 0}} \tag{10}$$

For scattering measurements at the low angle, a modified DAWN model B Laser Scattering Photometer (Wyatt Technology)[70] was used. The light source was a vertically polarized 5 mW He–Ne laser, and a photovoltaic detector with an extended collimator was located at a horizontal angle of 10° with respect to the beam path. The latter was tilted vertically at 5° in order to reduce any disturbance caused by the stray light reflected from the optical cell wall. The effect of the tilting of the incident beam of the parallel polarized component on the measured scattering intensities was shown to be negligible.[70] The initial slopes of the experimentally obtained time evolution curves were obtained by a polynomial fit using more than 500 points acquired through an analogue-to-digital converter.

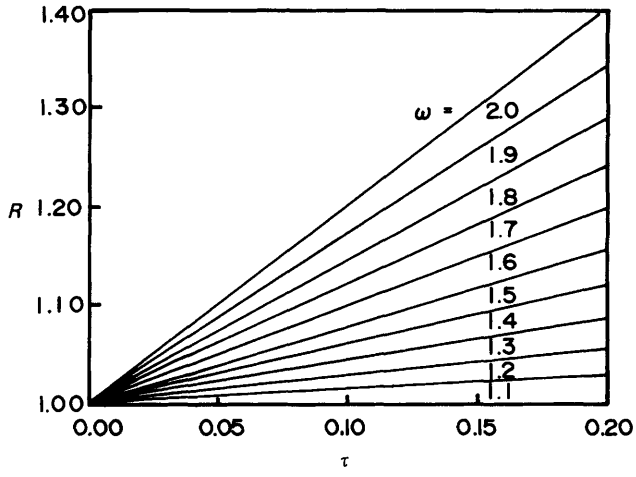

Fig. 3 Computation results of eqn. (8) as a function of various values of ω

To prepare samples for measurements, an aliquot of the stock colloid dispersion was injected into the solution of a desired composition in an optical glass cell in an ultrasonic bath. The recording of light scattering intensities was started within 120 s of mixing. Depending on the particle sizes, the typical initial number concentration of the singlet particles was kept in the range 5×10^6 to 5×10^8 cm^{-3} to prevent the secondary scattering effects.

Applicability of the Materials Prepared

In order to assure the applicability of the low-angle LS technique to the dispersions investigated, it is necessary to confirm that eqn. (5) indeed holds.

The theoretically computed relationship between the logarithms of the intensity function, i_1, at 10° and particle radii for refractive indices corresponding to cerium (hydrous) oxide, polystyrene latex, and silica are given by solid lines 1, 2 and 3, respectively, in Fig. 4. Open symbols, representing the calculated i_1 values for the prepared materials using their measured radii, are located on the straight portion of these lines with the slope of 6; since $a^6 \propto v^2$, the applicablity of eqn. (5) to the system studied is confirmed. The aggregated particles should also obey the same relationship according to the SPOS studies.[64–69]

4. Results

The stability ratios, W, and ζ-potentials were plotted as a function of the ionic strengths, I, for the three latices in Fig. 5–7, for silica in Fig. 8, and for cerium (hydrous) oxide in Fig. 9, along with the theoretically calculated curves for the expected values of W. The effective Hamaker constant for polystyrene latex in the aqueous solution was estimated from the Lifshitz theory[7] to be $A_{131} = (1.94 \pm 0.44) \times 10^{-21}$ J.

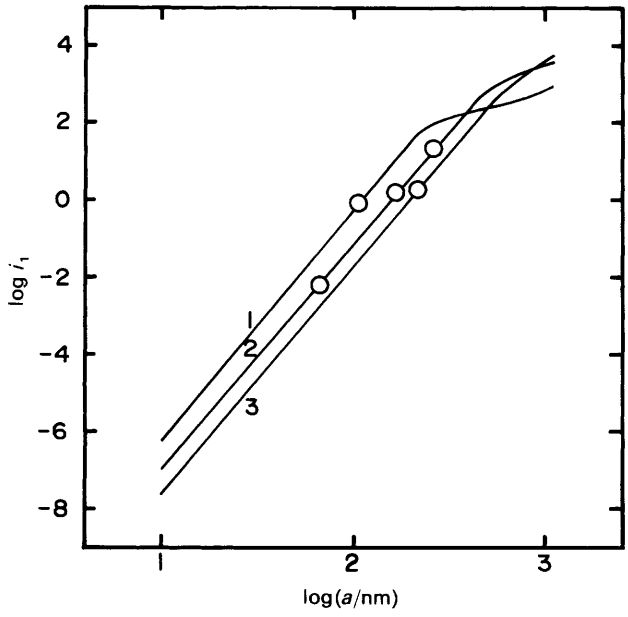

Fig. 4 Scattering intensity function, i_1, caused by a laser beam ($\lambda = 632.8$ nm) polarized perpendicular to the observation plane as a function of particle radii, a. Lines 1, 2 and 3 are theoretical curves at the observation angle of 10° obtained by the Mie expression for cerium (hydrous) oxide (refractive index: $2.04 + 0.013i$), polystyrene latex (1.59), and silica (1.45), respectively. The open symbols show calculated i_1 values for these systems using the parameters cited

The corresponding parameters for the silica/water and the cerium (hydrous) oxide/water systems, as detemined experimentally from the critical coagulation concentrations, were $A_{131}(SiO_2) = 3.0 \times 10^{-20}$ J, $A_{131}(CeO_2) = 1.0 \times 10^{-20}$ J.

These results show that despite the application of the advanced Overbeek model[18] to dispersions of uniform spherical particles, significant discrepancies are observed in slow coagulation regions between the calculated and measured

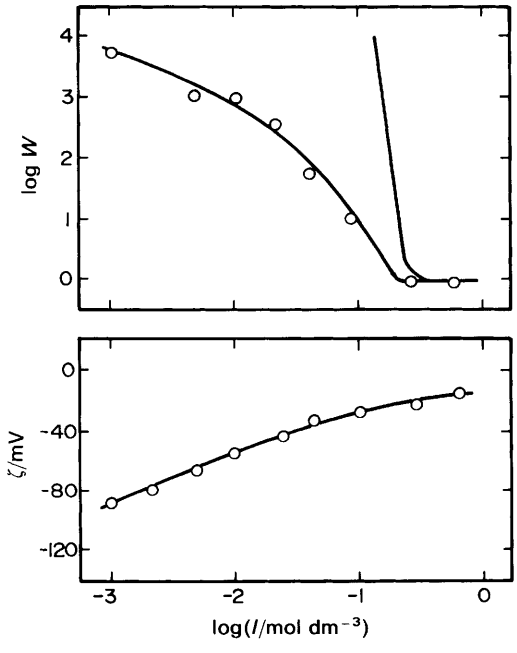

Fig. 5 Experimental (○) and theoretical (——) stability ratios, W, and ζ-potentials as a function of the ionic strength, I (KNO_3), at pH 5.7 for aqueous dispersions of uniform spherical particles of polystyrene latex a of 65.5 nm in radius. The theoretical curve was obtained by the use of Overbeek's expression with $A_{131} = 1.94 \times 10^{-21}$ J and $\psi_s = \zeta$

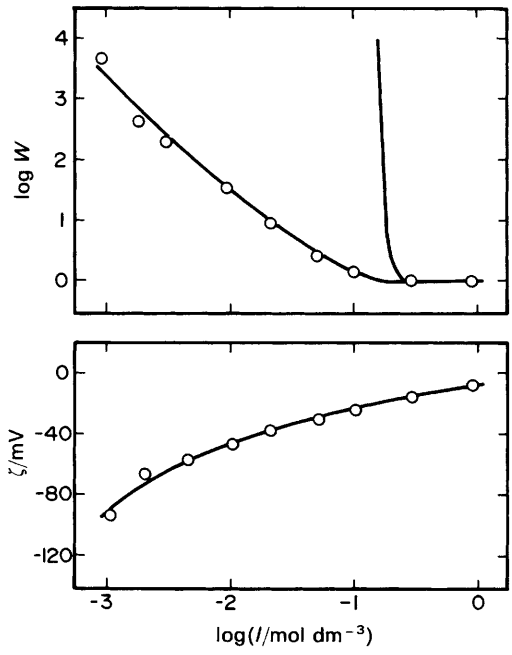

Fig. 6 As for Fig. 5 for uniform spherical particles of polystyrene latex b of radius 159 nm

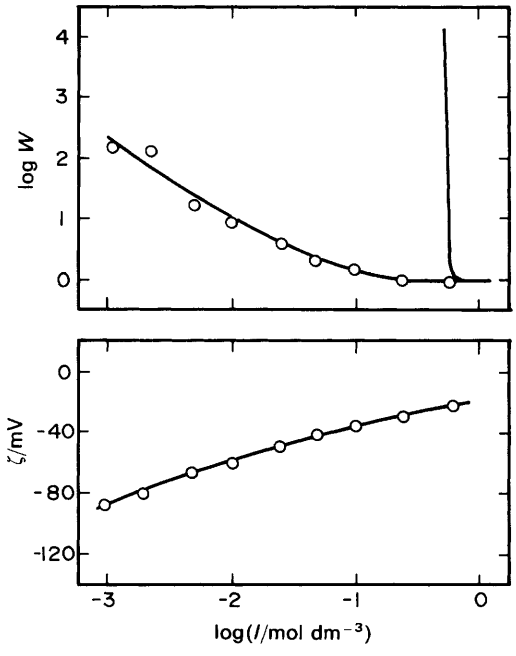

Fig. 7 As for Fig. 5 for uniform spherical particles of polystyrene latex c of radius 260 nm

stability ratios. It is also noteworthy that the disagreements in the c.c.c. values become larger with increasing size of latex particles.

5. Discussion

Heterocoagulation Theory and Additional Factors

In order to account for the observed discrepancies between the experimentally obtained and theoretically calculated results on coagulation kinetics, several factors must be considered, as discussed below.

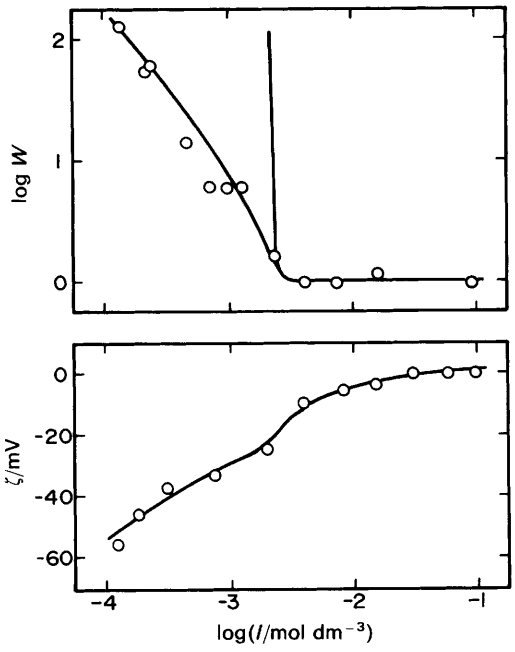

Fig. 8 As for Fig. 5 for uniform spherical particles of silica, of radius 210 nm with $A_{131} = 3.0 \times 10^{-20}$ J

Hydrodynamic Retardation

On particle collision the fluid between them is squeezed out, resulting in the so-called hydrodynamic retardation effect. The theoretical solutions available in the literature[37,44,45] were used to assess the effect of the retardation on the computations of stability ratios for the systems studied according to eqn. (2) and (3). It was established that this correction caused only a parallel shift in the log W *vs.* log I plots, as reported by others.[42,43,45] Thus, the hydrodynamic effect could not explain the significant differences in the slopes as shown in Fig. 5–9.

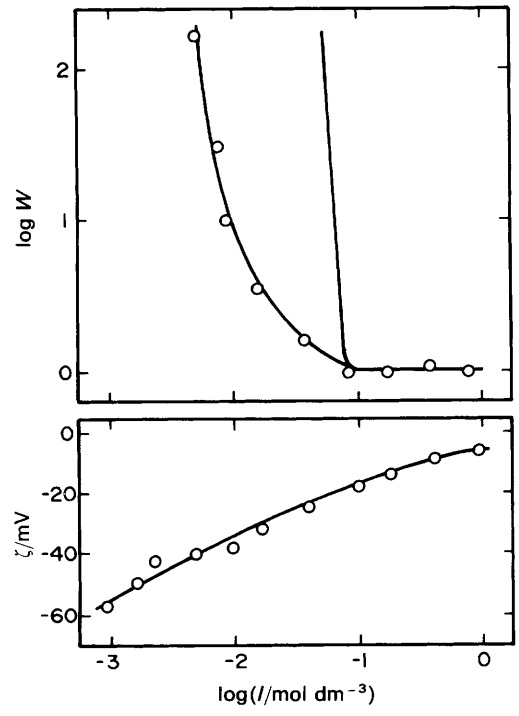

Fig. 9 As for Fig. 5 for uniform spherical particles of cerium (hydrous) oxide, of radius 110 nm with $A_{131} = 1.0 \times 10^{-20}$ J at pH 11 (KNO_3/KOH)

Recently, it was demonstrated that the introduction of a correction of the electro-viscous force could not alter these slopes.[71]

Hydrophobic/Hydrophilic and Born Interactions

Expelling water spontaneously between approaching particles, due to the hydrophobic interaction, causes additional attraction. A quantitative analysis of this phenomenon based on the direct surface force measurements was made by Israelachvili and Pashley,[72] who derived an empirical equation for two unlike spherical particles:

$$V_H^{SP} = -\Lambda C_H \frac{a_1 a_2}{a_1 + a_2} \exp\left(\frac{-H_0}{\Lambda}\right) \qquad (11)$$

where Λ is a decay constant and C_H is the force constant for hydrophobic interaction. The corresponding values for mica surfaces coated with a monolayer of the cationic surfactant hexadecyltrimethylammonium bromide were reported as $\Lambda = 1.0 \times 10^{-9}$ m and $C_H = 0.14$ N m^{-1}. C_H should vary with the hydrophobicity of the surface, and even a negative value of C_H may result for a short-range repulsive force in a solution of relatively high ionic strength.[73,74] The computations, using several values for C_H, showed that this factor just causes a parallel shift in the plots used in Fig. 5–9. The incorporation of the Born repulsion,[40,75,76] could not explain the discrepancy in the slopes either.

Stern Potential

All theoretically calculated slopes are much steeper than the experimental ones (Fig. 5–9), which contradicts the theory and leads to the impossible conclusion that Stern potentials, evaluated from the coagulation data, should be much lower than ζ-potentials. Similar findings were reported by Reerink and Overbeek[33] and Dumont *et al.*[77]

Hamaker Constant

Owing to the remaining ambiguities in the induced dipole interactions,[4–13] the Hamaker constant is often regarded as an adjustable parameter. Again, it could be shown that altering this parameter caused only a parallel shift in the log W *vs.* log I plot, in agreement with the results by Lips and Willis.[62]

Particle Size Effect

Theoretically, spheres of larger size should yield steeper slopes of the log W *vs.* log I plots. However, even though the ζ-potentials of the three latices studied did not differ much, the experiments showed a reverse order in slopes (Fig. 5–7), which cannot be explained even by the recently developed theoretical approach by Dukhin and Lyklema.[78] It should also be noted that a negligible influence of the latex particle size on the stability ratio was reported by Ottewill and Shaw.[34]

Applicability of the Constant Charge Model

In the constant charge model,[2,20] the Stern charge instead of the potential, is taken to be independent of the separation, resulting in a higher osmotic pressure when the particles approach each other.[25] The latter should cause a stronger repulsion than when the constant potential is assumed, leading to an even larger discrepancy in the stability ratios. The inapplicability of the constant charge model was also demonstrated in the particle detachment experiments.[41]

Possible Reasons for Discrepancies

Discreteness of the Surface Charge

The above discussion has shown that the observed discrepancies between the theoretical and experimental coagulation rates could not be explained by the consideration of a number of different parameters. In contrast, direct surface force measurements with perfectly smooth surfaces showed excellent agreement with the DLVO theory.[72–74]

In all previous theoretical treatments smoothed out surface charges were assumed, although such a condition is not necessarily met in reality, even on apparently perfectly smooth spherical particles. The charges of the studied solids are of discrete ionic nature and need not be uniformly distributed, as was considered earlier.[79] As a consequence, it is worthwhile investigating the effect of the surface charge segregation on the colloid stability.

When two particles with unevenly distributed charges approach each other, the repulsion between sections of the lower potential is less pronounced. With this condition in mind, the overall collision probablity, which is the inverse of the stability ratio, $1/W_T$, normalized by the diffusion-limiting case (*i.e.* the absence of the double-layer interaction), can be obtained by:

$$\frac{1}{W_T} = \int\int_{-\infty}^{\infty} f_A(\psi_{S1}, \psi_{S2}, \gamma_{S1}, \gamma_{S2}) \frac{1}{W(\psi_{S1}, \psi_{S2})} d\psi_{S1}\, d\psi_{S2} \quad (12)$$

where the function $W(\psi_{S1}, \psi_{S2})$ yields the W value for the interacting surfaces having Stern potentials ψ_{S1} and ψ_{S2} and $f_A(\psi_{S1}, \psi_{S2}, \gamma_{S1}, \gamma_{S2})$ describes the probability for the portions of surfaces of ψ_{S1} to face those of ψ_{S2}. The γ_{S1} and γ_{S2} parameters describe the extent of the surface charge segregation.

As a first approximation, f_A was substituted by a Gaussian distribution function:

$$f_A(\psi_{S1}, \psi_{S2}, \gamma_{S1}, \gamma_{S2}) = \frac{1}{\gamma_{S1}\sqrt{2\pi}} \exp\left[\frac{-(\psi_{S1} - \bar{\psi}_{S1})^2}{2\gamma_{S1}^2}\right] \times \frac{1}{\gamma_{S2}\sqrt{2\pi}} \exp\left[\frac{-(\psi_{S2} - \bar{\psi}_{S2})^2}{2\gamma_{S2}^2}\right] \quad (13)$$

in which the standard deviation was given as $\gamma_{S1} = \gamma_{S2} = \gamma_S$ for homocoagulation systems, and average Stern potentials, $\bar{\psi}_{S1}$ and $\bar{\psi}_{S2}$ were designated $\bar{\psi}_{S1} = \bar{\psi}_{S2} = \zeta$. A larger change in the potential is expected at the site of densely segregated functional groups when the ionization is pronounced; thus, it was assumed that γ_S was proportional to the measured ζ-potential. In calculations, the proportionality constant was varied to establish its effect on the slope of the log W *vs.* log I plots. Although this analysis was applied to dispersions of identical particles, the fact that their surface charges were considered to be inhomogeneous, requires that the heterocoagulation theory be used.

Note that a similar treatment was proposed by Cooper[80] in 1972, and later on by Prieve and Ruckenstein[81] and Prieve and Lin[82] under the assumption that otherwise identical particles bore uniform potentials but different in magnitude. The same studies also showed that the effect of the particle size distribution on calculated stability ratios was not significant. Elimelech and O'Melia,[39,42] observed analogous discrepancies in particle adhesion, which could not be eliminated by Cooper's correction, assuming $\gamma_S/|\zeta|$ to be as high as 0.20. The charge segregation on an individual particle surface thus seems to be a reasonable consideration, because it allows to assign much larger $\gamma_S/|\zeta|$ values. The present model assumes macroscopic inhomogeneity of the surface charge in contrast to a theoretical attempt made by Kuin,[83] in which the effect of the microscopic uneven charge distribution on the interactions of parallel plates was considered. The latter is not discussed in this work.

Test of the Model

Polystyrene Latices

The computational results for three polystyrene latices using eqn. (12) and assuming different extents of the surface charge segregation are shown in Fig. 10–12. It is clearly demonstrated that taking into consideration the discreteness of surface charges indeed alters the slope of the log W *vs.* log I curves in the right direction. By proper choice of γ_S it is possible to bring the experimental data and theoretical curves into a reasonable agreement. The $\gamma_S/|\zeta|$ values that fit the data can be as high as 0.40.

The shifts in the c.c.c. as a function of the particle size can also be explained by the discreteness-of-charge effect. To fit the experimental c.c.c. values, the parameter C_H was varied

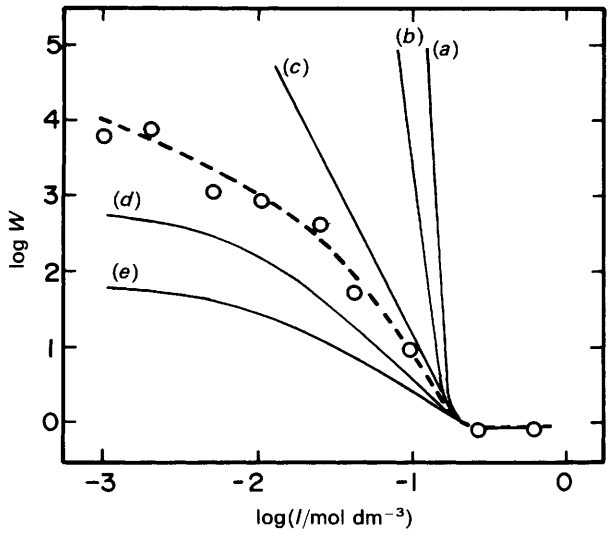

Fig. 10 Effect of the surface charge segregation and hydrophobic interaction on the stability of latex a at conditions corresponding to Fig. 5. Solid lines (a)–(e) are obtained theoretically assuming $\gamma_S/|\zeta| = 0$, 0.1, 0.2, 0.3 and 0.4, respectively, given $C_H = 1.0$ mN m^{-1}. Experimentally determined values are shown by open symbols and the dashed line

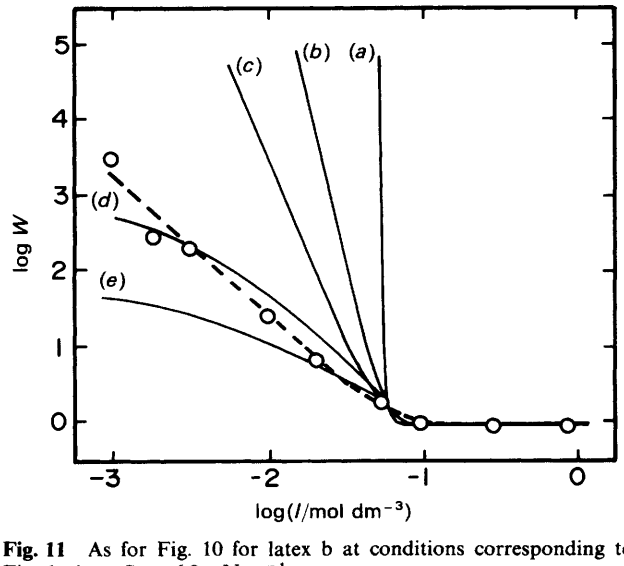

Fig. 11 As for Fig. 10 for latex b at conditions corresponding to Fig. 6, given $C_H = 6.0$ mN m^{-1}

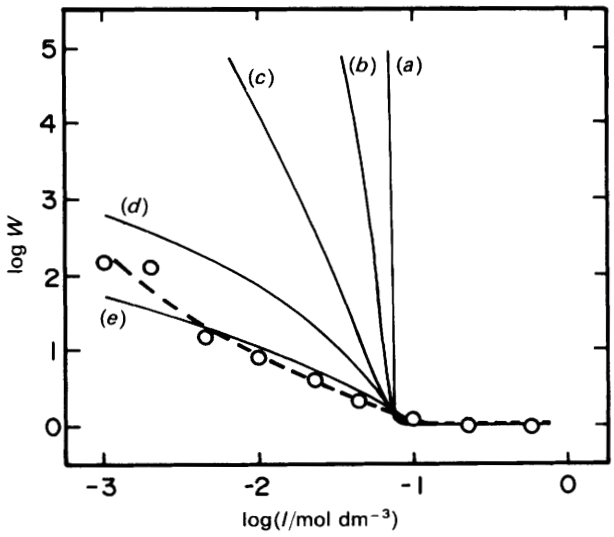

Fig. 12 As for Fig. 10 for latex c at conditions corresponding to Fig. 7, given $C_H = 10.0$ mN m^{-1}

and the results in Fig. 13 indicate enhanced hydrophobicity of larger particles, caused by a more extended surface charge segregation. This suggestion is supported by the fact that an increase in the particle size resulted in greater values of $\gamma_S/|\zeta|$, as seen in Fig. 10–12.

Recently, it was suggested that the surfaces of polymer latices are more or less 'hairy',[84,85] which might cause a decrease in the stability ratio. However, since an analogous discrepancy was observed with the silica dispersion, such surface structure of latex particles could not be solely responsible for the behaviour described.

Silica Particles

The discreteness-of-charge model also satisfactorily explains the coagulation of silica particles. Using $\gamma_S/|\zeta| \approx 0.4$ the theoretical calculations fit the experimental results (Fig. 14). The density of *ca.* 8000 Å^2 per Stern charge, as calculated from the ζ-potential at $I = 1 \times 10^{-4}$ mol dm^{-3}, is rather low; consequently, it is likely that the charge segregation under these conditions should be more pronounced.

Cerium (Hydrous) Oxide Particles

The analogous approach to the cerium (hydrous) oxide dispersion did not produce satisfactory fits between the experiment and theory, which was probably due to the surface

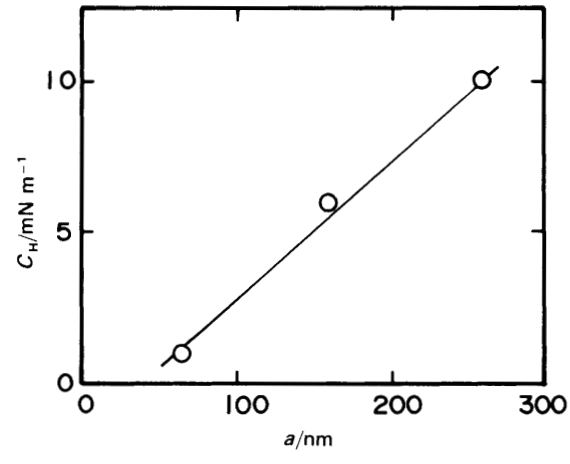

Fig. 13 Hydrophobic force constant, C_H, as a function of the particle radius of polystyrene latices at pH 5.7 (KNO_3)

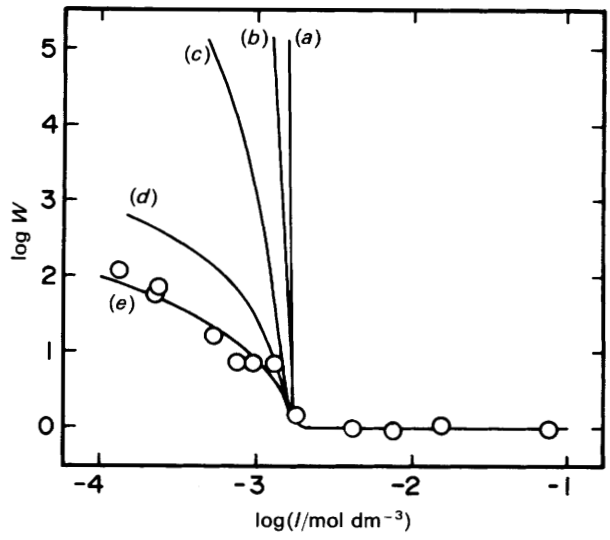

Fig. 14 As for Fig. 10 for silica particles at conditions corresponding to Fig. 8. Experimentally determined stability ratios are shown by open symbols

roughness as shown in Fig. 1(*b*). The overall repulsion between two such particles was expected to be weaker. Assuming uniform distribution of the Stern potential, a computation of the double-layer interaction energies was made by varying the radius of curvature (a') of protruded segments, and the results were used to estimate the values of W. Fig. 15 shows that the best fit was obtained with $a' = 6$ nm. Although this analysis is merely an approximation, the results indicate that the surface roughness affects the slope of the log W *vs.* log I curves, as mentioned by several investigators.[33–36]

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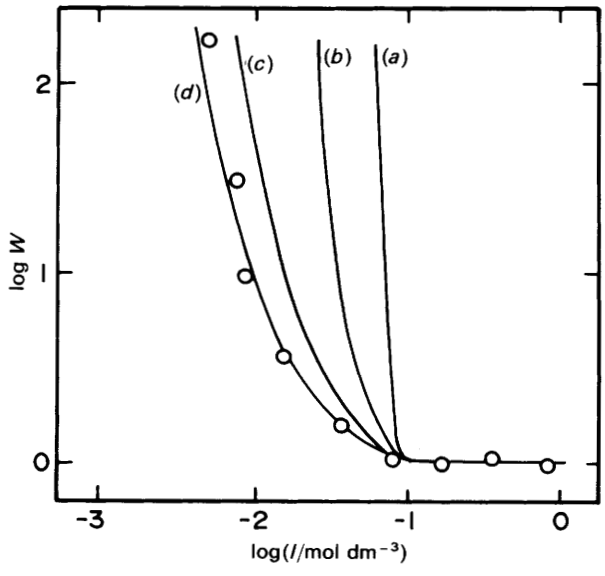

Fig. 15 Effect of the surface roughness of the cerium (hydrous) oxide particles on the same plot as for Fig. 9. Solid lines, (*a*)–(*d*) are calculated with assumed radii of surface curvature of 110, 30, 7 and 6 nm, respectively. Experimentally determined stability ratios are shown by open symbols

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