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ORIGINAL CONTRIBUTION

J.A. Maroto
F.J. de las Nieves

Theoretical and experimental comparison of the colloid stability of two polystyrene latexes with different sign and value of the surface charge

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J.A. Maroto
Department of Applied Physics
Polytechnique School
University of Jaén
23700 Linares, Jaén
Spain

F.J. de las Nieves (✉)
(Group of Complex Fluids Physics)
Department of Applied Physics
University of Almería
04120 Almería
Spain

Abstract The purpose of this paper is to apply the classical DLVO theory to explain the colloid stability of two model colloids with similar size and different sign and value of the surface charge. For this comparison the hydrodynamic interaction and the presence of hydration forces (extended DLVO theory) have been taken into account. The experimental stability factor and the experimental doublet rate constant in diffusion conditions were compared with those evaluated theoretically. The mathematical treatment permits an easy evaluation and interpretation of the different adjustable parameters such as the Hamaker constant, diffuse layer potential and the hydration layer thickness. The theoretical and experimental comparison shows that the "extended DLVO theory" only permits to explain the stability curves Log[W]/Log[KBr] in a semiquantitative way by using, for the evaluation of the total interaction potential V_T, a value of the Hamaker constant (A) similar to the classical theoretical one for polystyrene particles dispersed in water. In the case of the anionic latex, it was necessary to admit the presence of a hydration layer of a thickness similar to the radius of the hydrated/dehydrated counterion. On the other hand, by using the experimental doublet rate constant in diffusion conditions, we obtain a lower value of the Hamaker constant (A), but within the range of the A values usually found in previous studies.

Key words Colloidal stability – polymer colloids – turbidity – nephelometry

Introduction

The fundamental interpretation of the stability of lyophobic colloids was derived independently by Derjaguin and Landau [1] and Verwey and Overbeek [2] (DLVO theory), who combined the concepts of Langmuir electric double layer [3] with London and van der Waals induced dipoles interactions [4–7]. However, experimental kinetic studies on coagulation [8–11] revealed substantial discrepancies between the theoretically predicted and experimentally determined stability ratios. This fact led to the assumption that other interaction forces exists (in addition to van der Waals and electrostatic forces) which are referred as "solvent structural forces" [12]. These solvent-based interactions include hydration forces [11, 12] and hydrodynamic interactions [11, 13].

Also, it was suggested that one possible explanation for this disagreement may be due to the discreteness of the surface charge [14], but the application of this surface charge segregation (SCS) model did not seem to improve substantially the classical model [15].

In a previous work [16] we determined in a reliable way the kinetic rate constants of two model colloids by

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using two different methods and techniques. In this work we plan to complete the coagulation study from a theoretical point of view, of these latexes with similar size and different sign and value of the surface charge. Thus, the purpose of this paper is to apply the classical DLVO theory by including the hydrodynamic interaction and the presence of hydration forces, the inclusion of these terms is designated as "extended DLVO theory". We have compared the experimental stability factor and the experimental doublet rate constant in diffusion conditions, as obtained in a previous work [16], with those evaluated theoretically. We have carried out a mathematical treatment, partially applied in previous work [17, 18], which permitted an evaluation and interpretation of the different adjustable parameters such as Hamaker constant, diffuse layer potential and hydration layer thickness.

Theory

In order to evaluate the theoretical doublet rate constant in diffusion conditions and the stability coefficients, it is necessary to consider the expressions derived with the "extended DLVO theory". Assuming the validity of the Gouy–Chapman model for the electrical double layer [19, 20], making the Debye–Hückel approximation [21] (valid for low potentials), using the Derjaguin ring method [22] (valid for $\kappa a \gg 1$) and assuming colloidal interaction at constant surface potential, an expression can be obtained for the electrostatic potential V_{DL}:

$$V_{\mathrm{DL}}(H_0) = 2\pi\varepsilon a\psi_{\mathrm{d}}^2 \ln[1 + \exp(-\kappa H_0)] , \qquad (1)$$

where H_0 is the smallest distance between particles, a is the particle radius, ψ_{d} the diffuse layer potential and κ is the inverse of the Debye length.

Hamaker [23] developed the next equation for the attractive potential V_{A} between two identical particles, considering that the London interaction is dominant for colloidal systems:

$$V_{\mathrm{A}}(H_0) = -\frac{A}{6}\left[\frac{2}{4u + u^2} + \frac{2}{(2 + u)^2} + \ln\frac{4u + u^2}{(2 + u)^2}\right] , \qquad (2)$$

where $u = H_0/a$ and A is the Hamaker constant, which for polystyrene particles dispersed in water has a value of 1.37×10^{-20} J [24].

On the other hand, we must consider the possibility of a hydration layer with a thickness Δ, owing to the adsorption on the particle surface of a monolayer of hydrated counterions. This parameter only influences the electrostatic potential [17] modifying the interaction distance to a new distance of $(H - 2\Delta)$.

Now, we can evaluate the total interaction potential $V_{\mathrm{T}}(H_0)$ by adding the two conforming potentials (electrostatic and repulsive).

Finally, it is necessary to consider the notion of stability factor relating the fast and slow doublet rate constant:

$$W = \frac{K_{\mathrm{D,F}}}{K_{\mathrm{D,S}}} . \qquad (3)$$

The relationship between the doublet rate constant and the total interaction potential was obtained by Fuchs [25]. The retardation in the motion of two approaching colloidal particles owing to the "hydrodynamic interaction" can be incorporated to the stability factor by means of the function $\beta(u)$ [26, 27]:

$$K_{\mathrm{D}} = \frac{\frac{4}{3}kT/\eta}{2\int_0^\infty \frac{\beta(u)}{(u+2)^2} \exp\frac{V_{\mathrm{T}}(u)}{kT}\,\mathrm{d}u} . \qquad (4)$$

Therefore, the relationship between the stability factor W and the total interaction potential V_{T} is given by

$$W = \frac{2\int_0^\infty \frac{\beta(u)}{(u+2)^2} \exp\frac{V_{\mathrm{T}}(u)}{kT}\,\mathrm{d}u}{2\int_2^\infty \frac{\beta(u)}{(u+2)^2} \exp\left(\frac{V_{\mathrm{A}}(u)}{KT}\right)\mathrm{d}u} = \frac{F_1(\psi_\delta, A, [BrK])}{F_2(A)} . \qquad (5)$$

Honing [26] proposed the next approximate expression for the function $\beta(u)$:

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

As can be seen, Eq. (5) expresses the stability factor W as the ratio of two functions F_1 and F_2, in which appears the mathematical dependences (we assume to work with KBr as electrolyte). The particle radius (182 nm) and the temperature ($T = 293$ K) do not appear in these functions, because these are fixed parameters. These functions will be useful to clarify the mathematical treatment.

Experimental

Two polymer colloids one having sulfonate and the other amidine surface groups with dissimilar surface charge densities (-3.6 and $+16.4\ \mu\mathrm{C\,cm^{-2}}$, respectively) but almost equal particle sizes (370 ± 9 and 361 ± 5 nm) were used [16, 28] in the homocoagulation measurements. The anionic and cationic latex are named SN4 and M9, respectively. More details about the latex characterization can be found in a previous paper [16].

The turbidity and nephelometry techniques were also described in the previous paper [16], where the experimental results were discussed. We would like only to note that for both experimental methods two different data analyses were used based on the drawing of initial slopes and fitting the whole $A(t)/I_\theta(t)$ curve. Similar results were obtained for the doublet rate constant in diffusion conditions (an average value of 2.75×10^{-18} particle m^3/s for both latices) using turbidimetric initial slopes/fitting curve and nephelometric initial slopes/fitting curve methods.

Also, the stability factor W versus the electrolyte concentration was obtained for the two systems. The CCC was 1.75 M for the anionic SN4 latex and 0.100 M for the cationic M9 latex. These data are very important because they permited us to establish the diffusion conditions for the coagulation experiments.

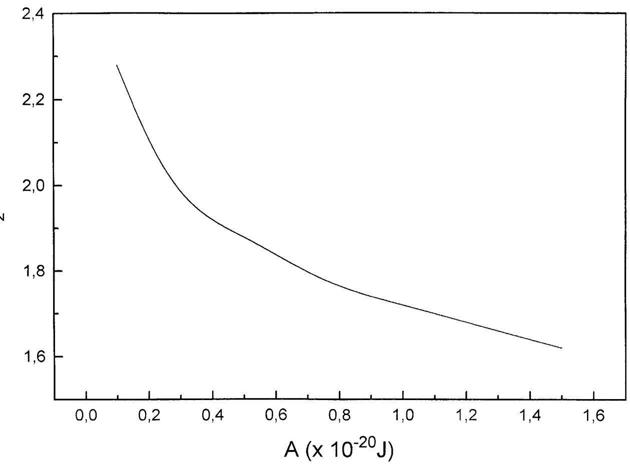
Theoretical and experimental comparison

In order to compare theory and experimental data we have evaluated the stability factor W and, in a second step, the doublet rate constant in diffusion conditions. This methodology has the advantage of working with the whole curve log[W]/log[KBr] and not with only one point $K_{\mathrm{D,F}}$, which permit us an inambiguous interpretation of data [17, 18, 29, 30].

First of all, we evaluated the F_2 function in Eq. (5) by developing some computer programs. Basically, this function characterizes the doublet rate constants in diffusion conditions and it will be treated at the end of this work. Figure 1 shows the F_2 values versus the Hamaker constant A.

In relation with the F_1 function, the CCC values are known for both SN4 and M9 latexes. Now, we check a pair of values (ψ_d, A) that fit the experimental log[W]/log[KBr] curve. By using a graphical method [18] we determine (within a reasonable range of Hamaker constant values) the pair of values (ψ_d, A) that fulfil this condition. That implies that the maximum of the total potential of interaction has a zero value. Figure 2 shows the appearance of this curve for the M9 latex. It can be seen as an energy barrier that prevent the coagulation process. However, for a fixed A value, the energy barrier can disappear by decreasing the diffuse potential.

Fig. 1 F_2 function versus the Hamaker constant A. In the evaluation we assume a particle radius of 182 nm and a temperature of 293 K



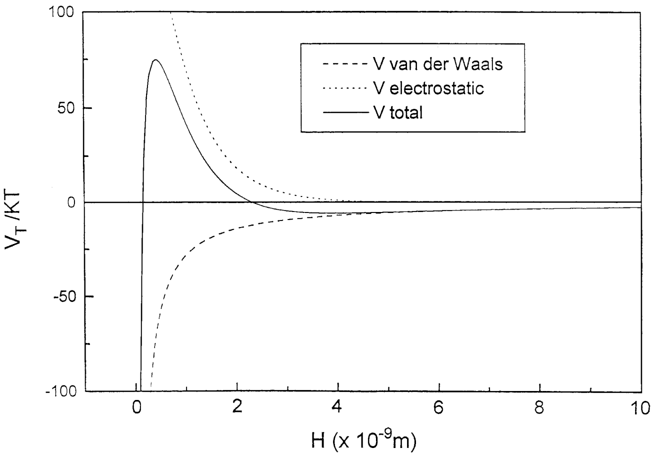


Fig. 2 Total interaction potential, repulsive potential and attractive potential versus the smaller distance between particles. In this figure $A = 7.5 \times 10^{-21}$ J, [KBr] = 175 mM and $\psi_\mathrm{d} = 65$ mV

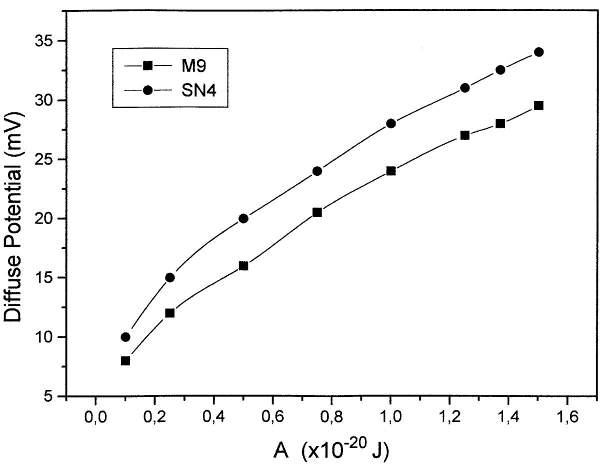


Fig. 3 Diffuse potential ψ_d in the CCC conditions of SN4 (●) and M9 (■) latexes versus the Hamaker constant (A)

Figure 3 shows the diffuse potential values obtained with this graphical method for both latexes. The diffuse potential ψ_d, increases as the Hamaker constant (A) does, owing to the opposite effects of the two parameters (ψ_d affects the repulsive potential and A affects the attractive one).

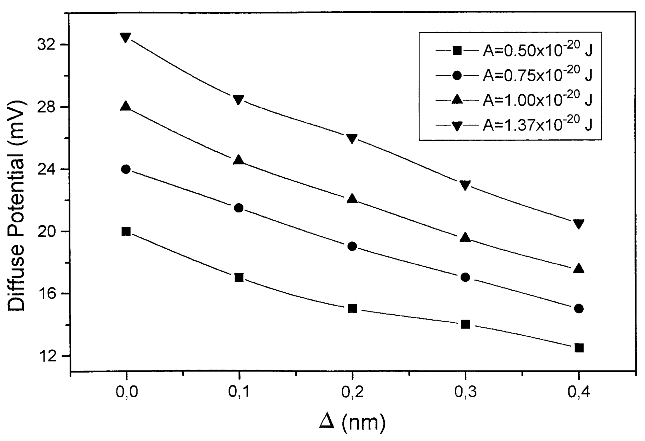


Fig. 4 Diffuse potential ψ_d of the SN4 latex in the CCC conditions versus the thickness of the hydration layer (Δ), for different A values

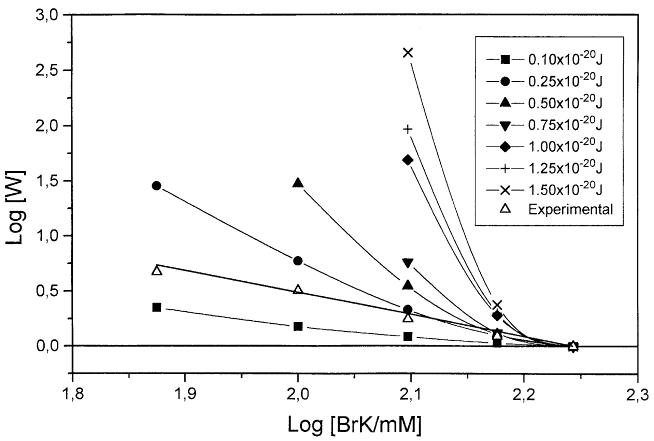


Fig. 5 Theoretical and experimental W values of the SN4 latex. The theoretical W values are evaluated for a variety of Hamaker constant (A) values

Also, we assumed the presence of a hydration layer (Δ) in the SN4 latex surface for future convenience. The presence of this layer was successfully considered in a previous work [17] for a sulfonate latex with low surface charge and synthesized by a similar procedure to that used for the SN4 latex. Thus, we have used the same method to obtain another group of pairs (ψ_d, A) but now considering Δ. We varied the thickness of the hydration layer with a step of 0.1 until 0.4 nm, that is, the same order of magnitude of the ionic diameter of the hydrated and dehydrated K^+ counterion (0.37 and 0.26 nm, respectively). Figure 4 shows the ψ_d versus Δ values for several Hamaker constants, showing a similar behaviour to that found in Fig. 3.

Once the pairs of (ψ_d, A) are obtained, we plot the theoretical log[W]/log[KBr] curve, in a first step with the assumption of no hydration, that is, without the inclusion of Δ to evaluate ψ_d and A. Figures 5 and 6 show the calculated stability factor versus the electrolyte concentration for SN4 and M9 latex, respectively. These figures show the theoretical W values for different Hamaker constants and, for comparison, the experimental one. As can be seen, the extended DLVO theory does not predict a linear dependence of the log[W]/log[KBr] plot for any of both latexes. This theory only permits us to explain the stability curves in a semiquantitative way; similar behaviour has been found for both latexes. These curves indicate an increasing stability of the systems when the ionic strength decreased below the CCC. The disagreement between the theoretical and experimental stability factor values have been obtained for a variety of authors [15, 31–36], justifying several efforts to clarify the electrostatic potential [37], that seems to provoke a failure in the explanation of the experimental data [38, 39].

Anyway, we selected the pair of (ψ_d, A) values that fit the experimental data in a semiquantitative way. For the anionic SN4 latex, we found a reasonable fitting between the pairs (10 mV, 0.10 × 10^{-20} J) and (15 mV, 0.25 × 10^{-20} J), while for the cationic M9 latex we found a reasonable fitting between the pairs (24 mV, 1.00 × 10^{-20} J) and (27 mV, 1.25 × 10^{-20} J). Obviously, the Hamaker constant value obtained for the M9 latex is similar to the theoretical value (1.37 × 10^{-20}), while for the latex SN4 the Hamaker constant value obtained is one order of magnitude lower than the theoretical one. A possible explanation for the disagreement with this latex, can be the use in the synthesis process of the comonomer sodium styrene sulfonate that could provokes a mechanism of additional stabilization [17, 40]. Furthermore, the sulfonate latex has a more hydrophilic character than other conventional latexes, which could justify the presence of a thicker hydration layer. So, we included in the theoretical treatment the possibility of

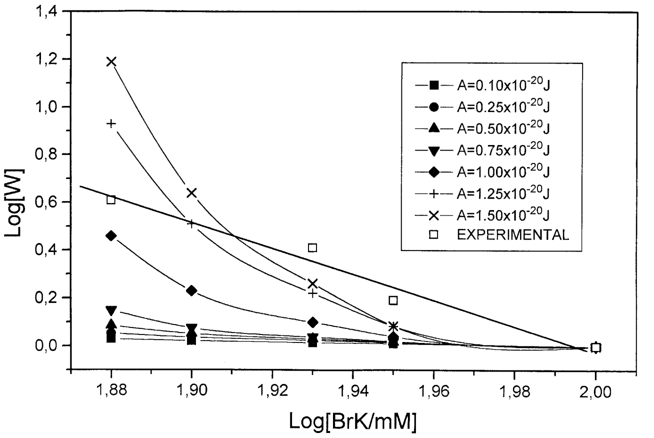


Fig. 6 Theoretical and experimental W values of the M9 latex. The theoretical W values are evaluated for a variety of Hamaker constant (A) values

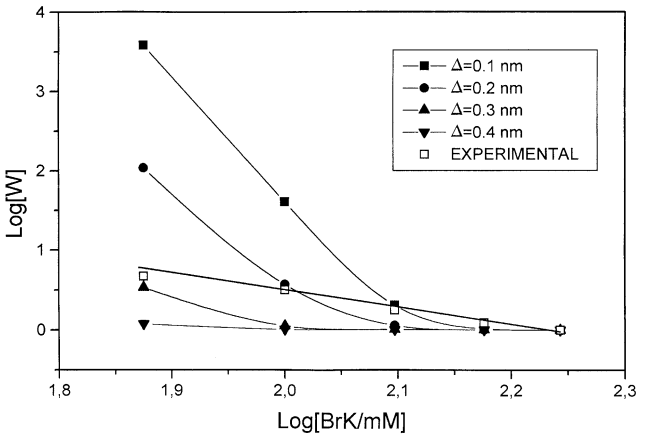


Fig. 7 Theoretical and experimental W values of SN4 latex for a value of the Hamaker constant of 10^{-20} J and different Δ values

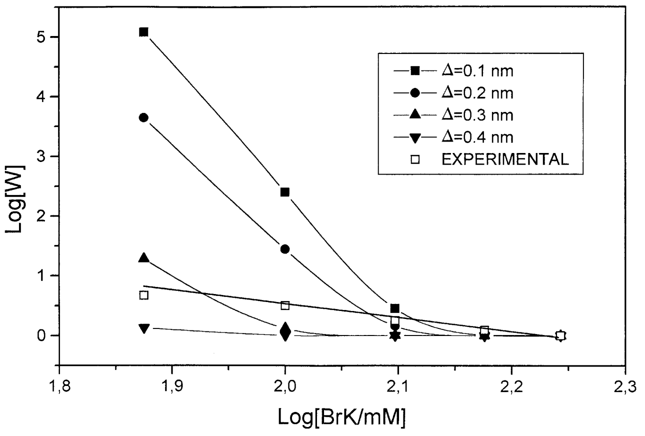


Fig. 8 Theoretical and experimental W values of the SN4 latex for a value of the Hamaker constant of 1.37×10^{-20} J and different Δ values

a hydration layer on the surface of this latex. To consider this influence, we evaluated the theoretical log[W]/log[KBr] curves with the data from Fig. 4. Figures 7 and 8 show that for a value of $\Delta = 0.3$ nm (between the ionic diameter of the hydrated and dehydrated K^+ counterion), we found a reasonable fitting between the pairs (19.5 mV, 1.00×10^{-20} J) and (23 mV, 1.37×10^{-20} J) reproducing the theoretical Hamaker constant for polystyrene particles in water. We must note the semiquantitative character of the fitting, that is not usually shown in the majority of theoretical works [17] that only offers the final data. In short, we find that the "extended DLVO theory" does not predict a linear dependence of the stability curves, so we can only obtain approximative ψ_d and A values from the fitting procedure.

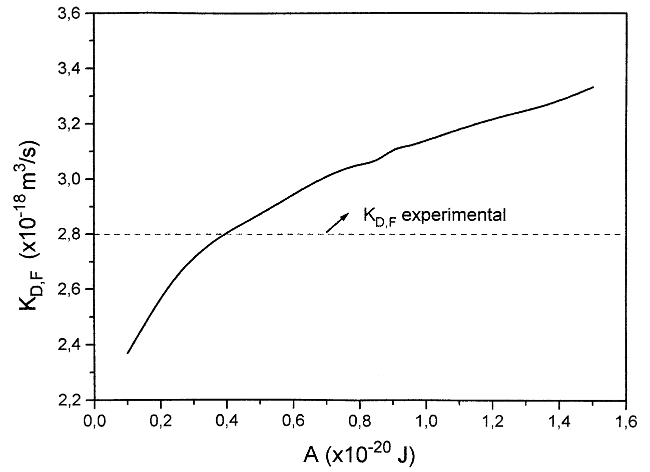


Fig. 9 Theoretical rate constant in diffusion conditions versus the Hamaker constant (A). By comparing with the experimental value of 2.75×10^{-18} J m^3/s, we find a value of the Hamaker constant of 0.4×10^{-20} J in the cutting point

On the other hand, by using Eq. (4) and the data from Fig. 1, we have obtained the evolution of the doublet rate constant in diffusion conditions with the Hamaker constant A. The advantage of this evolution is that we do not use the repulsive potential (and ψ_d, obviously), that seems to provoke the failure in the theory. Figure 9 shows this theoretical curve and the experimental rate constant value in diffusion conditions of 2.75×10^{-18} particles m^3/s, previously obtained with a variety of experimental methods [16]. We found a value of the Hamaker constant of 0.4×10^{-20} J in the cutting point, lower than the theoretical value proposed by Prieve and Russel [24]. However, recent studies [40, 41] proposed a value for the Hamaker constant for polystyrene dispersed in water in a range between 0.4 and 0.9×10^{-20} J.

Conclusions

The "extended DLVO theory" only provides an explanation of the stability curves (log[W]/log[KBr]) in a semiquantitative way by using, for the evaluation of the total interaction potential V_T, a value of the Hamaker constant (A) similar to the classical theoretical one for polystyrene particles dispersed in water. In the case of the anionic SN4 latex it is necessary to admit the presence of a hydration layer of a thickness similar to the radius of the hydrated/dehydrated counterion.

However, by using the experimental doublet rate constant in diffusion conditions we obtain a lower value of the Hamaker constant A, but within the range of the A values found by several recent studies. This second method of comparison has the advantage of avoiding the use of the repulsive potential (so we eliminate two fitting parameters, ψ_d and Δ), but has the disadvantage of working with only one point for the comparison.

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