

# Electrosteric Stabilization of Polymer Colloids with Different Functionality

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The colloidal stability of polymer colloids with different functionality before and after adsorption of Triton X-100 has been studied. Experimental  $\log W$  versus  $\log$  [electrolyte] plots for bare particles were fitted using the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, and values of diffuse potential ( $\psi_d$ ) and the Hamaker constant ( $A$ ) were obtained. In the same way,  $\log W$  versus  $\log$  [electrolyte] plots for some latex–surfactant complexes were fitted using the extended DLVO theory, which considered steric repulsive interaction. Kinetic information was employed in order to reduce the number of fitting parameters of the steric repulsive potentials. In this way, the thickness of the stabilizing layer ( $\delta$ ) was the fitting parameter. We have found that the extended DLVO theory explains directly the results of some of the latex–surfactant complexes. However, in other cases, additional mechanisms had to be considered to explain the results. All these discrepancies could indicate that electrostatic and steric repulsion energies are not completely independent.

## 1. Introduction

Interaction between particles determines the stability, rheology, and many other properties of polymeric colloidal dispersions. Most applications of colloidal systems require the particles to remain dispersed within a relatively large range of electrolyte concentration. One of the main disadvantages of the electrostatic stabilization is its sensitivity to the addition of electrolyte. To avoid this dependence, steric stabilization is frequently used as an alternative. Examples of this improvement in the colloid stability by steric stabilization can be found in food colloids,<sup>1–2</sup> in the petroleum industry,<sup>3–4</sup> and so forth. The addition of polymers to the colloidal dispersions is widely employed to modify the colloidal stability.<sup>5</sup> Once the polymers or surfactants are adsorbed onto the particle surface, three different types of stabilization can be distinguished<sup>6</sup> as a consequence of the relation between the van der Waals attraction energy ( $V_A$ ) and the steric interaction energy ( $V_S$ ). In this paper, we are interested in the situation where  $V_S < |V_A|$  and consequently the colloidal system will be sensitive to the addition of electrolyte, although the steric contribution is not negligible and can play an important role.

In this work, three different polystyrene particles (sulfate, carboxyl, and amidine) have been used as colloidal model systems, to establish the effect of the charge and the type of surface group on the stability results. A complete experimental–theoretical study of the colloidal stability of these particles is overcome with the objective of determining the diffuse potential and Hamaker constant for this type of system. In this way, the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory<sup>7</sup> and the redefined expression by McGown and Parfitt<sup>8</sup> for the stability factor were used. After adsorption of Triton X-100, some latex–surfactant complexes electrosterically stabilized (i.e., electrostatic and steric contributions) were selected in order to quantify the effect of surfactant on the colloidal stability behavior. The well-known interaction potentials proposed by Vincent et al.<sup>9</sup> were used as additional contributions to the DLVO theory. With the objective of minimizing the number of fitting parameters of the modified DLVO theory, a new equation<sup>10</sup> was employed. Globally, the classic and extended DLVO theories can explain the experimental results for bare and covered particles, respectively. However, some complexes presented an anomalous behavior that can be explained on the basis of specific interactions between the ethylene oxide (EO) chains and the carboxyl/amidine groups of the particles.

## 2. Theoretical Background

In aggregating systems, the coagulation rate is usually expressed via the stability factor,  $W$ , which is experimentally defined as the quotient of the rapid kinetic constant,  $k_r$ , divided by the kinetic constant for the

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electrolyte concentration at which the reaction is taking place,  $k_s$ :

$$W_{\text{exp}} = \frac{k_r}{k_s} \quad (1)$$

In rapid coagulation,  $W_{\text{exp}} = 1$ , whereas higher values of  $W_{\text{exp}}$  are obtained for aggregation under conditions of slow coagulation. Fuchs<sup>11</sup> derived theoretically an expression for  $W$ ,

$$W = 2a \int_0^\infty \frac{1}{(H+2a)^2} \exp\{V(H)/k_B T\} dH \quad (2)$$

where  $H$  is the surface to surface distance of two approaching particles of radius  $a$  and  $V(H)$  is the interaction potential.

However, we have used the redefined expression by McGown and Parfitt<sup>8</sup> for the stability factor,  $W$ . This expression takes into consideration the fact that in rapid coagulation, the attractive contribution to the interaction potential still acts. Thus, the new expression for  $W$  is

$$W = \frac{\int_0^\infty \frac{1}{(H+2a)^2} \exp\{V(H)/k_B T\} dH}{\int_0^\infty \frac{1}{(H+2a)^2} \exp\{V_A(H)/k_B T\} dH} \quad (3)$$

Furthermore, the importance of the hydrodynamic interaction was showed in Spielman's work<sup>12</sup> and the approximation by Honig et al.<sup>13</sup> This interaction was incorporated to the stability factor by means of  $\beta(H)$ , which is the quotient of the diffusion coefficients considering that the other particle is at infinite distance and considering that it is at distance  $H$ ,  $\beta(H) = D_\infty/D(H)$ . In this work, we have used the approximation proposed by Honig et al.<sup>13</sup>

$$\beta = \frac{6H^2 + 13Ha + 2a^2}{6H^2 + 4Ha} \quad (4)$$

Therefore, the final expression for the stability factor is

$$W = \frac{\int_0^\infty \frac{\beta(H)}{(H+2a)^2} \exp\{V(H)/k_B T\} dH}{\int_0^\infty \frac{\beta(H)}{(H+2a)^2} \exp\{V_A(H)/k_B T\} dH} \quad (5)$$

where the hydrodynamic friction and McGown's proposal are both taken into account.

This new definition of  $W$  enables direct comparison between theory and experiments and will be used in this work.

Going back to the interaction potential,  $V(H)$ , we have considered a general expression which is separated into three contributions: electrostatic ( $V_R$ ), attractive ( $V_A$ ), and steric ( $V_S$ ):

$$V(H) = V_R(H) + V_A(H) + V_S(H) \quad (6)$$

The classical DLVO expressions for the electrostatic repulsive and attractive potentials have been used:<sup>7</sup>

$$V_R(H) = \frac{64\pi n k_B T}{\kappa^2} \gamma^2 \exp\{-\kappa H\} \quad (7)$$

where  $n$  is the number of ions per unit volume and  $\kappa$  is the Debye reciprocal length. The factor  $\gamma$  is related to the diffuse potential,  $\psi_d$ , through

$$\gamma = \tanh \frac{ze\psi_d}{4k_B T} \approx \frac{ze\psi_d}{4k_B T} \text{ (when } \psi_d \rightarrow 0) \quad (8)$$

and the nonsimplified expression for the attractive Hamaker interaction<sup>14</sup> is

$$V_A(H) = -\frac{A}{6} \left[ \frac{2a^2}{H^2 + 4aH} + \frac{2a^2}{(H+2a)^2} + \ln \frac{H^2 + 4aH}{(H+2a)^2} \right] \quad (9)$$

where  $A$  is the Hamaker constant.

If the Stern layer thickness is considered, eq 7 must be modified by shifting the reference plane for the repulsive energy outward over a distance corresponding to the thickness ( $\Delta$ ) of the Stern layer.<sup>15</sup> The final expression is

$$V_R(H) = \frac{64\pi(a+\Delta)nk_B T}{\kappa^2} \gamma^2 \exp\{-\kappa(H-2\Delta)\} \quad (10)$$

In those cases where the particles have a layer of polymer on their surfaces, an additional repulsive potential has to be taken into account. Vincent et al.<sup>9</sup> carried out a quantitative study of the steric stabilization effect including two contributions: osmotic and elastic.

$$V_S(H) = V_{\text{osm}}(H) + V_{\text{elas}}(H) \quad (11)$$

If there are polymeric chains covering the external surface of a particle, the average thickness of such coils being  $\delta$ , then an osmotic effect will appear when the two particles are closer than a distance equal to  $2\delta$ . The osmotic pressure of the solvent in the overlap zone will be less than that in the regions external to it, leading to a driving force for the spontaneous flow of solvent into the overlap zone, which pushes the particles apart.<sup>16</sup> In that case, the osmotic potential of repulsion ( $V_{\text{osm}}$ ) can be written as

$$V_{\text{osm}}(H) = \frac{4\pi a}{v_1} (\phi_2)^2 \left( \frac{1}{2} - \chi \right) \left( \delta - \frac{H}{2} \right)^2 \quad (12)$$

where  $v_1$  is the molecular volume of the solvent,  $\phi_2$  is the effective volume fraction of segments in the adsorbed layer, and  $\chi$  is the Flory-Huggins solvency parameter.

However, if the two particles are closer than a distance equal to  $\delta$ , at least some of the polymer molecules will be forced to undergo elastic compression. Thermodynamically, this compression corresponds to a net loss in configurational entropy. This effect gives rise to a new repulsion potential ( $V_{\text{elas}}$ ) related to the restriction of movement of the hydrophilic coils extended toward the solvent. This elastic-steric repulsion is given by

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$$V_{\text{elas}}(H) = \left( \frac{2\pi a}{M_w} \phi_2 \delta^2 \rho_2 \right) \left( \frac{H}{\delta} \ln \left[ \frac{H(3 - H/\delta)^2}{2} \right] - 6 \ln \left[ \frac{3 + H/\delta}{2} \right] + 3 \left( 1 + \frac{H}{\delta} \right) \right) \quad (13)$$

where  $\rho_2$  and  $M_w$  are the density and the molecular weight of the adsorbed polymer. This effect modifies the osmotic potential, which is now given by

$$V_{\text{osm}}(H) = \frac{4\pi a}{v_1} (\phi_2)^2 \left( \frac{1}{2} - \chi \right) \delta^2 \left[ \left( \frac{H}{2\delta} \right) - \frac{1}{4} - \ln \left( \frac{H}{\delta} \right) \right] \quad (14)$$

For the electrosteric stabilization mechanism, both effects (electrostatic repulsion and steric stabilization) must be combined. Conventionally, the total interaction energy is assumed to be the sum of all attractive and repulsive potentials (eq 6).

### 3. Experimental Section

**A. Chemicals.** All chemicals in this study were of analytical grade and were used without further purification. The water in all experiments was ultrapure with specific electrical conductivity lower than 1  $\mu\text{S}/\text{cm}$  (ATAPA S.A., Spain).

The anionic buffers used were acetate at pH 4–5, phosphate at pH 6–7, and borate at pH 10. The cationic buffers used were BIS-TRIS (bis[2-hydroxyethyl]imino-tris[hydroxymethyl]methane) at pH 6, TRIS (tris[hydroxymethyl]aminomethane) at pH 8–9, and AMP (2-amino-2-methyl-1-propanol) at pH 10. The final ionic strength was 2 mM.

**B. Latex Characterization.** The latexes used in this work were synthesized in our laboratories. Styrene (Merk) was previously distilled under low pressure (10 mmHg and 40 °C). All colloidal systems were synthesized using the emulsifier-free method. The first latex, a negatively charged polystyrene latex [PS-S] was prepared, with potassium persulfate as initiator, in a discontinuous reaction, according to Kotera et al.<sup>17</sup> The other two colloidal systems were synthesized using 4,4'-azo-bis(4-cyanopentanoic acid) [PS-C] and *N,N*-azo-bis(dimethyl-isobutylamide hydrochloride) [PS-CAT] as initiators.<sup>18–20</sup> Because of the different chemical functionality of sulfate [PS-S], carboxyl [PS-C], and amidine [PS-CAT] groups, we can dispose of three latexes with different surface properties but prepared with the same material (polystyrene). Table 1 shows the main characteristics of the particles.

**C. Surfactant Characterization.** Triton X-100 (*p*-(1,1,3,3-tetramethylbutyl) phenyl poly(ethylene glycol)), a gas chromatography grade material from Merk, was used without further purification. Surfactant concentrations during adsorption experiments were determined by UV spectrophotometry at 275 nm<sup>21–23</sup> using a Spectronic Genesys 5 spectrophotometer (Milton Roy, USA). The extinction coefficient obtained was equal to  $1.33 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . The critical micelle concentrations (cmc) were determined by the change in slope of the absorbance versus concentration, which indicated the onset of a micellization process. The value of this characteristic magnitude was of  $(5.1 \pm 0.1) \times 10^{-4} \text{ M}$  which is found to be in the range given by other authors.<sup>24–26</sup> To gain more information on the surfactant purity, a mass spectroscopy spectrum was obtained (Centre of Scientific

**Table 1. Characteristics of Colloidal Systems**

latex	functionality	diameter (nm)	PDI	surface charge ( $\mu\text{C}/\text{cm}^2$ )
PS-S	sulfate	$413 \pm 14$	1.0035	$-3.2 \pm 0.5$
PS-C	carboxyl	$303 \pm 9$	1.0029	$-21 \pm 3$ at pH 10 $\approx 0$ at pH 4
PS-CAT	amidine	$192 \pm 10$	1.0066	$9.2 \pm 2.4$ at pH 4 $\approx 4$ at pH 10

**Table 2. Conditions of Aggregation Experiments**

latex	$\lambda_0$ (nm)	$N_p$ (p/m <sup>3</sup> )
PS-S	900	$1.2 \times 10^{16}$
PS-C	800	$2.0 \times 10^{16}$
PS-CAT	600	$5.0 \times 10^{16}$

Instrumentation, University of Granada). The results showed that the surfactant is of good purity, with a polydispersity index ( $\langle M_w \rangle / \langle M_n \rangle$ ) of 1.031(5), where  $\langle M_w \rangle$  and  $\langle M_n \rangle$  are the number average molecular weight and the weight average molecular weight, respectively.

**D. Surfactant Adsorption.** Surfactant adsorption was performed in batteries for 24 h at  $(25.0 \pm 0.1)^\circ\text{C}$  by adding different amounts of surfactant on 0.25 m<sup>2</sup> of latex surface. The surfactant–latex mixtures were gently shaken during and after the addition of the latex suspension. The latex was centrifuged afterward at 13 500 rpm, and the free surfactant solution concentration of the filtered supernatant (100 nm pore PC filter, Millipore) was determined by measuring the optical absorbance at 275 nm. All experiments were repeated at least three times. A previous reproducibility study<sup>27</sup> indicated that the absolute experimental error in the adsorbed surfactant amount was  $\pm 0.05$  and  $\pm 0.11 \mu\text{mol}/\text{m}^2$  before and after the adsorption plateau, respectively. This implies a maximum relative error below 3.6%. A deep study of adsorption–desorption of Triton X-100 onto PS-S, PS-C, and PS-CAT latexes has been published.<sup>28–29</sup>

**E. Colloidal Stability.** The stability of the dispersions was evaluated with a Spectronic Genesys 5 spectrophotometer by measuring the absorbance as a function of time for different electrolyte concentrations. In a typical coagulation experiment, 2.4 mL of a buffered latex solution was put into the spectrophotometer cell and the optical absorbance was measured. Then, 0.6 mL of a sodium chloride solution at a given concentration was quickly added and mixed.<sup>30</sup> The optical absorbance was measured immediately and recorded continuously via computer for a period of 30 s. The initial slope of these curves,  $(dA/dt)_0$ , is directly proportional to the initial coagulation rate. Table 2 shows the main characteristics of colloidal stability experiments.

### 4. Results and Discussion

**Stability of Bare Latexes.** Stability curves for the sulfate latex (PS-S) are presented in Figure 1, showing that the colloidal stability is not pH dependent because of the strong character of the surface group. On the other hand, stability curves for carboxyl and amidine latexes (PS-C and PS-CAT, respectively) are shown in Figures 2 and 3. It is clearly seen for PS-C that as the pH decreases, the stability of this latex also decreases, according to the discharging process of the carboxyl groups. In relation with PS-CAT, a reverse phenomenon is observed because of a charging process. However, it can be observed that for the PS-C latex the colloidal stability showed a higher pH dependency than that for the PS-CAT latex. This fact can be explained by the change in the repulsive electrostatic energy for both systems, because the surface charge

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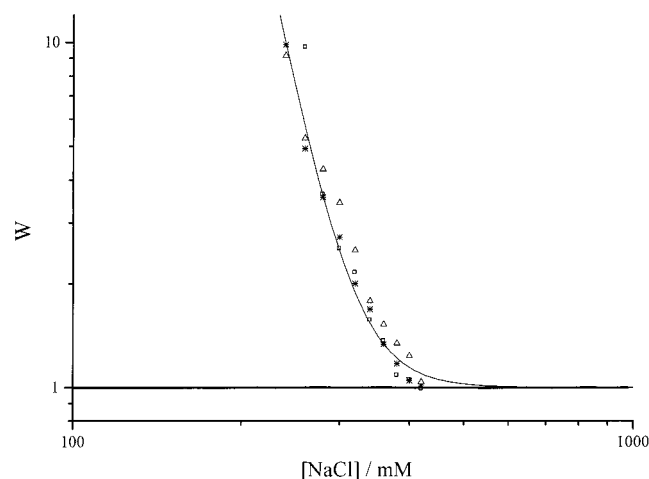
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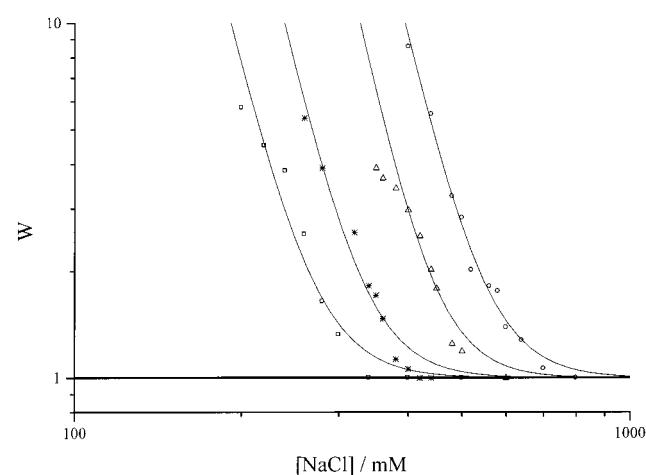
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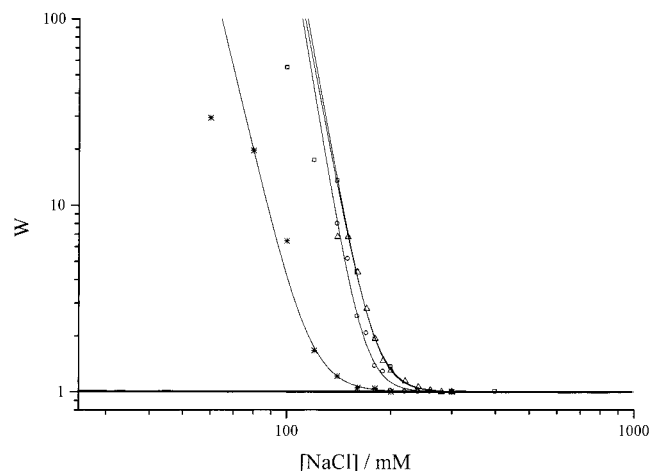




**Figure 1.** Stability of sulfate latex PS-S at pH 4 ( $\square$ ), 7 ( $\Delta$ ), and 10 (\*). The line represents the fitting theoretical curve using eq 5.



**Figure 2.** Stability of carboxyl latex PS-C at pH 5 ( $\square$ ), 6 (\*), 7 ( $\Delta$ ), and 10 ( $\circ$ ). The line represents the fitting theoretical curve using eq 5.



**Figure 3.** Stability of cationic latex PS-CAT at pH 6 ( $\square$ ), 8 ( $\Delta$ ), 9 ( $\circ$ ), and 10 (\*). The line represents the fitting theoretical curve using eq 5.

densities change, in the pH range studied, between  $-3$  and  $-21 \mu\text{C}/\text{cm}^2$  for PS-C latex and between  $+8.5$  and  $+4 \mu\text{C}/\text{cm}^2$  for PS-CAT latex.

According to Reerink and Overbeek,<sup>31</sup> the  $\log W$  versus  $\log [\text{electrolyte}]$  curves can be approximated by a straight line, with a slope depending on the valency of the ions, the

radius of the particle, and the diffuse potential through  $\gamma$ . From the CCC, defined as the cross point of this line and the line  $\log W = 0$ , the value of the Hamaker constant can be obtained,<sup>31,32</sup> once the diffuse potential is known. In Table 3, the values for the CCC, the diffuse potential, and the Hamaker constant for the latexes PS-S, PS-C, and PS-CAT are presented. It can be observed that as the particle charge decreases, a decrease in the CCC is obtained, as expected.

On the other hand,  $\psi_d$  and  $A$  can also be calculated using eq 5 without the Reerink and Overbeek approximation. Obviously, for bare particles, the interaction potential is given by the DLVO theory that only considers an electrostatic repulsive and attractive interaction potential. The fitting process was performed by minimizing the statistical parameter  $\chi^2$ , using standard numerical methods.<sup>33</sup> In Figures 1–3, the fittings for the experimental stability curves are presented. The fitted values obtained for diffuse potentials and Hamaker constants with and without hydrodynamic effects are presented in Table 3. In all cases, a similar trend can be observed, as found using the Reerink and Overbeek approximation.

However, although all colloidal systems were prepared with the same material (polystyrene), the Hamaker constant presents an anomalous behavior. The theoretical nonretarded Hamaker constant value obtained by Prieve and Russel<sup>34</sup> using the Lifshitz theory was  $1.37 \times 10^{-20}$  J. They showed, in addition, that  $A$  is not constant. Its value decreases with the distance between the surfaces, being  $0.9 \times 10^{-20}$  J at a separation of 1 nm. According to Visser,<sup>35</sup> a comparison of the experimental results shows that, in a large number of cases, the value from colloidal stability studies deviates substantially from the theoretical ones. The difference between both values is a consequence of the use of incomplete theories. Puertas and de las Nieves<sup>36</sup> explained this fact as being due to the presence of ion layers with different thicknesses surrounding the particles. Including the size of the ions of the Stern layer ( $\Delta$  in eq 10), the Hamaker constant values were more similar to the theoretical ones (i.e., for PS-S latex including the hydrodynamic effect, Hamaker constant values were  $3.24 \times 10^{-21}$  and  $15.13 \times 10^{-21}$  J when  $\Delta$  values were equal to 0.096 nm (nonhydrated) and 0.372 nm (hydrated)). Similar results have been obtained by other authors.<sup>4,37–39</sup>

**Stability of Surfactant–Latex Complexes.** Before beginning with the analysis of the  $W$  versus [electrolyte] plots of the latex–surfactant complexes, we would like to remark on some important aspects concerning the effects of nonionic surfactant adsorption over the colloidal stability of latex particles. In previous work,<sup>6,27,40</sup> we studied the effect of Triton X-100 coverage on the colloidal stability of PS-S, PS-C, and PS-CAT latexes. In these papers, two regions were distinguished in the colloidal stability of the

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**Table 3. Diffuse Potential and Hamaker Constant Using the Reerink and Overbeek Approximation and the DLVO Theory**

latex	pH	linear approximation			$\beta = 1$		$\beta = \text{eq 4}$	
		CCC (mM)	$\psi_d$ (mV)	$A \times 10^{21}$ (J)	$\psi_d$ (mV)	$A \times 10^{21}$ (J)	$\psi_d$ (mV)	$A \times 10^{21}$ (J)
PS-S	4, 7, 10	390 $\pm$ 30	9.6 $\pm$ 0.3	1.23 $\pm$ 0.13	14.60	1.41	14.55	1.90
PS-C	5	330 $\pm$ 80	11.1 $\pm$ 0.7	1.8 $\pm$ 0.4	15.95	1.76	15.74	2.36
	6	400 $\pm$ 30	11.3 $\pm$ 0.4	1.69 $\pm$ 0.17	16.39	1.71	16.11	2.24
	7	520 $\pm$ 40	11.7 $\pm$ 0.5	1.6 $\pm$ 0.3	16.86	1.59	16.70	2.10
	10	650 $\pm$ 50	11.6 $\pm$ 0.6	1.40 $\pm$ 0.23	16.14	1.24	16.10	1.74
PS-CAT	6	195 $\pm$ 30	20.2 $\pm$ 1.0	7.7 $\pm$ 1.6	24.57	6.06	24.39	7.16
	8	200 $\pm$ 24	18.5 $\pm$ 0.8	6.4 $\pm$ 0.6	24.06	5.74	23.88	6.84
	9	190 $\pm$ 70	18.1 $\pm$ 1.4	6.2 $\pm$ 2.0	25.54	6.92	25.37	8.07
	10	130 $\pm$ 60	17.8 $\pm$ 1.5	7.2 $\pm$ 2.1	21.59	5.47	21.43	6.75

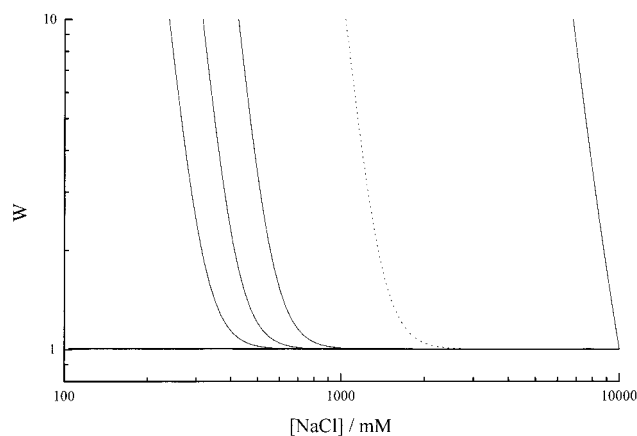
latex-surfactant complexes. When the surfactant coverage was maximum, the complexes were insensitive to electrolyte addition. In this situation, it is not possible to study the system from a kinetic point of view ( $W$ - $C$  plots). However, when latex-surfactant complexes had medium coverage, the colloidal systems showed sensitive electrolyte aggregation behavior. Then, some adequate complexes were selected for a quantitative study: PS-S/TX100 with  $1.7 \mu\text{mol}/\text{m}^2$ , PS-C/TX100 with 1.0 and  $1.5 \mu\text{mol}/\text{m}^2$ , and PS-CAT/TX100 with  $2.0 \mu\text{mol}/\text{m}^2$ .

When the particles have a layer of polymer on their surfaces, an additional repulsive potential has to be taken into account. In this case, there are four fitting parameters ( $\psi_d$ ,  $A$ ,  $\delta$ ,  $\phi_2$ ) involved in the total interaction potential ( $V$ ) (see eqs 9, 10, and 12–14). Other parameters such as  $\chi$ ,  $\rho_2$ , and  $M_w$  are well-known for Triton X-100.<sup>27</sup> In a first step, we have decided to keep two of them constant. The use of well-characterized latexes permits us to have an estimation of the  $\psi_d$  and  $A$  values. Thus, we have assumed for the latex-surfactant complexes the  $\psi_d$  and  $A$  values that appear in Table 3 when the hydrodynamic effect is considered.

Additionally, the parameters  $\delta$  and  $\phi_2$  are related and dependent on the amount of surfactant adsorbed onto the surface and its conformation. In a recent work,<sup>10</sup> we have proposed a relation between these two parameters through the kinetic constants of bare particles ( $k_{11,\text{bare}}$ ) and latex-surfactant complexes ( $k_{11}$ ):

$$k_{11} = \frac{\int_0^\infty \frac{\beta(H)}{(H+2a)^2} \exp\{V_A(H)/k_B T\} dH}{k_{11,\text{bare}} \int_0^\infty \frac{\beta(H)}{(H+2a)^2} \exp\{(V_A(H) + V_S(H))/k_B T\} dH} \quad (15)$$

In that way, it is possible to know the thickness of an adsorbed layer of Triton X-100 when the complex has maximum coverage. Through different studies,<sup>41–43</sup> we can conclude that the thickness ( $\delta$ ) of a latex/TX100 complex with maximum coverage is around 2 nm. In these papers, Tadokoro et al.<sup>41</sup> established the crystalline structure of ethylene oxide chains which predicts a maximum length of 2.68 nm for 10 units of EO. Then, Kimura et al.<sup>42</sup> concluded that the structure of EO in an aqueous medium is similar to that in the crystalline state. Additionally, Johnson<sup>43</sup> found an experimental thickness of 2 nm by dynamic light scattering (DLS) for a monolayer of Triton X-100 adsorbed onto polystyrene latex. In our



**Figure 4.** Theoretical dependence of  $W$  on  $[\text{NaCl}]$  at different values of  $\delta$  for the PS-S/TX100 complex: (from left to right) 0.1, 1.0, 1.2, 1.5, and 2.0 nm.

case, it was not possible to detect the thickness of the adsorbed layer by DLS because the differences obtained in bare and covered particle diameters are within the experimental error. Moreover, we know the kinetic constants for PS-S bare latex particles and PS-S/TX100 complexes with maximum coverage:  $(1.90 \pm 0.18) \times 10^{-18}$  and  $(5.7 \pm 0.7) \times 10^{-20} \text{ m}^3/\text{s}$ , respectively. If these values of  $k_{11,\text{bare}}$  and  $k_{11}$  are introduced in the above equation, an effective volume fraction ( $\phi_2$ ) of 0.012 is obtained. We have decided to use this value as a constant using the thickness  $\delta$  as the unique fitting parameter. To consider the effective volume fraction ( $\phi_2$ ) as a constant for all latex-surfactant complexes is in agreement with our previous adsorption theoretical study.<sup>28</sup> In this work, Kronberg's model showed that the number of contacts  $q$  between Triton X-100 molecules and the particle surfaces, that are directly related with  $\phi_2$ , did not depend on the latex particles. With this consideration, in a later work,<sup>10</sup> comparison of Brownian dynamic simulations and experiments for the PS-S/TX100 system leads to a good agreement.

In Figure 4, theoretical stability curves for PS-S/TX100 systems are shown as a function of surfactant layer thickness. It can be observed that a thickness of 2.0 nm causes total stabilization. Moreover, an increase in  $\delta$  causes only a displacement of the curves to higher stability regions, leaving the slopes of the lines unaltered.

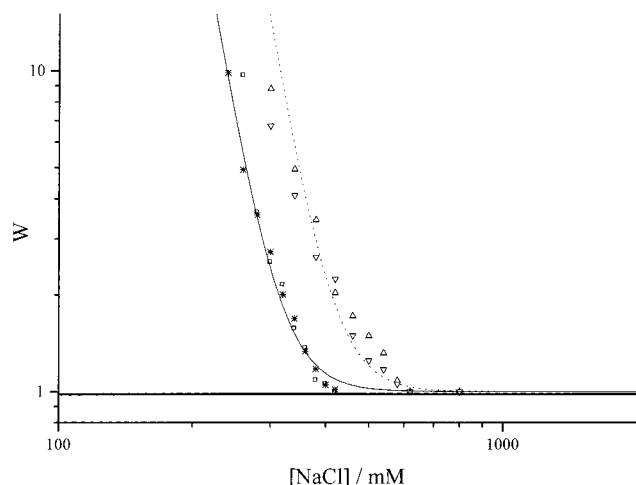
Figures 5–8 show the  $W$  values versus the electrolyte concentration for all latex-surfactant complexes. It is possible to distinguish two different behaviors for the latex-surfactant complexes: some of them have the same slope as bare particles and can be explained by the extended DLVO theory, whereas others do not and consequently cannot be explained directly by this theory.

In Figure 5, a comparison between the colloidal stability of PS-S bare particles and a complex of PS-S/TX100 with a coverage of  $1.7 \mu\text{mol}/\text{m}^2$  at two pHs is shown. As expected,

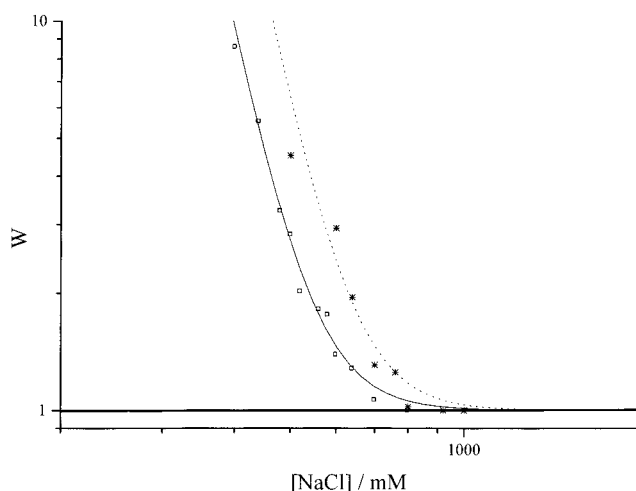
(41) Tadokoro, H.; Chatani, Y.; Yoshihara, T.; Tahara, S.; Murahashi, S. *Makromol. Chem.* **1964**, *73*, 109.

(42) Kimura, N.; Umemura, J.; Hayashi, S. *J. Colloid Interface Sci.* **1996**, *182*, 356.

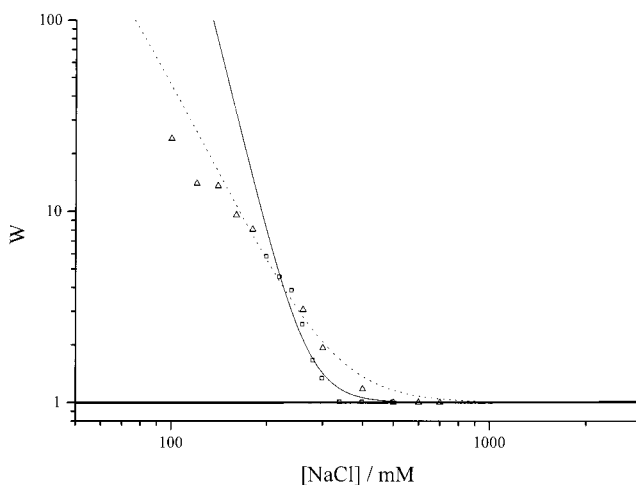
(43) Johnson, P. *Langmuir* **1993**, *9*, 2318.



**Figure 5.** Theoretical dependence of  $W$  on  $[\text{NaCl}]$ : experimental data for PS-S bare particles at pH 4 ( $\square$ ) and 10 ( $*$ ) and a  $1.7 \mu\text{mol}/\text{m}^2$  PS-S/TX100 complex at pH 4 ( $\triangle$ ) and 10 ( $\nabla$ ).

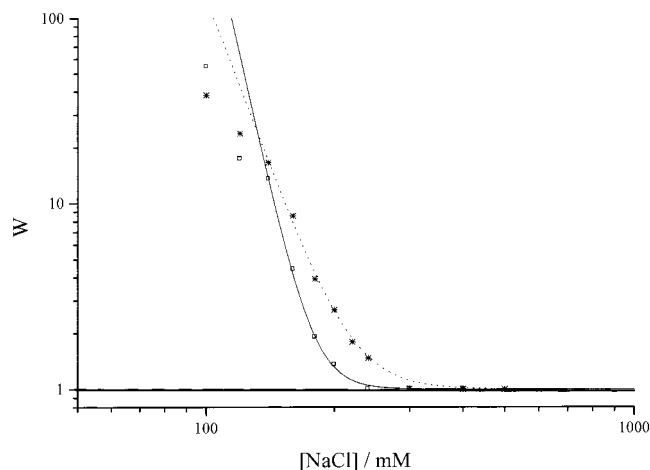


**Figure 6.** Theoretical dependence of  $W$  on  $[\text{NaCl}]$ : experimental data for PS-C bare particles ( $\square$ ) and a  $1.0 \mu\text{mol}/\text{m}^2$  PS-S/TX100 complex ( $*$ ) at pH 10.



**Figure 7.** Theoretical dependence of  $W$  on  $[\text{NaCl}]$ : experimental data for PS-C bare particles ( $\square$ ) and a  $1.5 \mu\text{mol}/\text{m}^2$  PS-C/TX100 complex ( $\triangle$ ) at pH 5.

no pH dependence was found. An increase in CCC from  $(390 \pm 30)$  to  $(530 \pm 50)$  mM was observed as a consequence of a steric repulsive barrier caused by the EO chains that are extended into the solution. In this case, the extended DLVO theory gives a good description of the latex-



**Figure 8.** Theoretical dependence of  $W$  on  $[\text{NaCl}]$ : experimental data for PS-CAT bare particles ( $\square$ ) and a  $2.0 \mu\text{mol}/\text{m}^2$  PS-CAT/TX100 complex ( $*$ ) at pH 6.

surfactant complex stability when the thickness of the surfactant layer is 1.0 nm. Obviously, at medium coverage the thickness of the stabilizer layer is lower than at maximum coverage because of an increase in the flexibility of the EO chains.

Figures 6 and 7 show the  $W$  values versus electrolyte concentration for a  $1.0 \mu\text{mol}/\text{m}^2$  PS-C/TX100 complex at pH 10 and a  $1.5 \mu\text{mol}/\text{m}^2$  PS-C/TX100 complex at pH 5 compared with bare particles at the same pH conditions. The first system (pH 10) showed a similar behavior to PS-S/TX100, with an increase in CCC from  $(650 \pm 50)$  to  $(770 \pm 40)$  mM. The best theoretical fit is obtained when  $\delta$  was 0.8 nm. However, at pH 5 for PS-C/TX100 an unexpected behavior is observed, corresponding to a different slope in the  $W$ - $C$  curves, meaning that a change in the diffuse potential has taken place, although Triton X-100 molecules are not charged. At the same time, the CCC increased from  $(330 \pm 80)$  to  $(410 \pm 40)$  mM. To fit these experimental results, it was necessary to include a layer of ions of thickness ( $\Delta$ ) equal to 0.25 nm, the layer of surfactant being  $\delta = 0.8$  nm. In the latter situation and although the diffuse potential is considered to be equal to that of bare particles, the Hamaker constant must be changed to more attractive values. However, the presence of more hydrophilic material on the surface of polystyrene particles causes an inverse effect.<sup>44-45</sup> Thus, we can conclude that this fitting procedure is not adequate. Another possible strategy to obtain the same fit was to modify the diffuse potential from 15.74 to 11.58 mV and use a thickness of 1.6 nm. In a later work,<sup>6</sup> we prove that at acid pH, an additional mechanism should be considered to explain the colloidal stability of a carboxyl latex covered with Triton X-100. This mechanism is related with the specific interaction between EO chains and  $\text{COO}^-$  groups through  $\text{H}^+$  ions presented in the medium, which leads to a flat conformation of EO chains. Moreover, electrokinetic studies show a specific adsorption of  $\text{H}^+$  ions onto PS-C/TX100 complexes at acid pHs.<sup>46</sup> This specific adsorption could justify the decrease in diffuse potential that is necessary for fitting the experimental stability curves.

Figure 8 shows the  $W$  values versus electrolyte concentration for the other variable charge system ( $2.0 \mu\text{mol}/$

(44) Mathai, K. G.; Ottewill, R. H. *Trans. Faraday Soc.* **1966**, *62*, 750.

(45) Mathai, K. G.; Ottewill, R. H. *Trans. Faraday Soc.* **1966**, *62*, 759.

(46) Romero-Cano, M. S.; Martín-Rodríguez, A.; de las Nieves, F. J. Manuscript in preparation.

m<sup>2</sup> PS-CAT/TX100) at pH 6. An increase in CCC from (195 ± 30) to (250 ± 50) mM can be observed. Behaviors as above can be observed. In particular, a change in the slope of the W–C curves is obtained. To avoid illogical changes in the Hamaker constant, the diffuse potential was modified to explain the results. A decrease from 24.39 to 19.21 mV was necessary to fit the experimental results ( $\delta = 2.2$  nm). An additional mechanism such as the one mentioned above may also appear in the cationic latex at extreme pHs.<sup>40</sup>

However, in the last theoretical studies the values obtained for  $\delta$  (1.6 and 2.2 nm) were larger than expected for a flat conformation of surfactant as a consequence of EO–surface interaction. Maybe if additional mechanisms are present, the effective volume fraction of surfactant could change because of a flatter conformation of the stabilizer layers. If we considered a layer thickness of 1.0 nm as the most probable for medium coverage complexes, the effective volume fractions that justify the anomalous

behavior for PS-C/TX100 and PS-CAT/TX100 complexes are 0.034 and 0.062, respectively.

### 5. Conclusions

A new equation was employed to reduce the number of fitting parameters of the modified DLVO theory. Two different colloidal stability behaviors were found for covered particles. One of them can be explained directly by the extended DLVO theory, but the other one needs additional considerations. These unexpected results could indicate that electrostatic and steric repulsion energies are not completely independent.<sup>47</sup>

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(47) Einarson, M. B.; Berg, J. *J. Colloid Interface Sci.* **1993**, 155, 165.