Study on the Colloidal Stability Mechanisms of Acetal-Functionalized Latexes

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In this work the colloid stability mechanisms of polystyrene latexes of acetal functionality are studied. These acetal latexes were prepared by two-step emulsion polymerization. The core was a seed of polystyrene, and the shell was synthesized by terpolymerization of styrene (St), methacrylic acid (MAA), and (methacrylamido)acetaldehyde dimethyl acetal (MAAMA) ternomers. The results were three latexes with different surface characteristics and with charged (carboxyl) and uncharged (acetal) surface groups provided by the MAA and MAAMA monomers, respectively. The anomalous electrokinetic behavior of the acetal latex was a consequence of their electric double layer structure, especially for one of the latexes with a significant highly charged “hairy” surface. The high colloidal stability of the acetal latexes was not explained by the classical Derjaguin–Landau–Verwey–Overbeck theory, and some correction factors, such as the Stern layer thickness (ionic size) and electrostic stabilization mechanisms, were included in this theory. The last mechanism may be due to the existence of a hairy layer formed during the synthesis method. The stability factor was measured in order to obtain quantitative information about some parameters related to the interfacial properties of the colloidal particles, such as the Hamaker constant and diffuse potential. These parameters and the steric stabilization theory were used to calculate the total interaction energy at several electrolyte concentrations. By using the electrostic mechanism to explain the stability results, it was possible to find a set of parameters that provide critical coagulation concentration values that were in accordance with the experimental one.

Introduction

Interaction between particles determines the stability, rheology, and many other properties of polymeric colloidal dispersions. Most applications of polymer colloids require colloidal particles to remain dispersed within a relatively large range of electrolyte concentration. In particular, polymer latex particles are widely used in the biomedical field, mainly in the development of new immunosassays, where the stabilization–destabilization mechanisms are very important because the antigen–antibody reaction takes place at high electrolyte concentrations. The colloidal stability of latex particles can be improved by increasing the surface charge density or by including an additional stabilization, such as steric stabilization. Looking for this type of stabilization, polymer colloids with different surface functional groups and characteristics have been prepared.

On the other hand, to prevent the desorption of the protein molecules and to maintain their native conformation, the chemical binding (or covalent bound) of the protein to the surface microsphere has been proposed. In that way, a new generation of functionalized particles with surface aldehyde groups has been synthesized in order to bond covalently the amino groups of the proteins. However, previously to the application, it is important to study the surface characteristics and colloidal stability of the functionalized latex particles.

In this work, the properties of core–shell polymer latex particles have been investigated. The core is a monodisperse seed of polystyrene, and the shell is a terpolymer with carboxyl and acetal functional characters. Because of the chemical instability of the aldehyde groups, the acetal functionality has been chosen to maintain the reactivity of the particles. By acidification of the acetal groups to aldehyde, direct covalent binding of biomolecules is possible.

Due to the synthesis method of functionalized latexes, surface groups and their supporting polymer chains can

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produce a hairy surface, which can control the colloidal properties of the latex particles by providing an additional stabilization mechanism when the ionic strength is high enough to screen the surface charge. However, the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of the colloidal stability generally fails to predict the stability of hairy latex particles when the dispersium medium is water. In 1986, Vincent et al. proposed a theoretical equation useful for quantifying the extent of the steric stabilization mechanism. It was found that the stability of polymer colloids with poly-electrolytes or ionic surfactant adsorbed on the particle surfaces is also due to electrostatic and steric contributions. The combined effects of these two mechanisms is known as electrosteric stabilization. This explanation could be applied to our acetal latexes, which displayed an anomalously high critical coagulation concentration (CCC). The shells of these acetal latexes were prepared by terpolymerization of styrene, methacrylic acid (MAA), and (methacrylamido)acetaldehyde dimethyl acetal (MAAMA) monomers, which leads to a final dispersion that could be stabilized by electrostatic and steric effects (hydrophilic oligomers on the particle surface). In this work we have studied the colloidal stability mechanisms of the acetal latexes by using the electrosteric stabilization theory and comparing the results with those from the DLVO theory. Three acetal latexes with different amounts of ionic (carboxyl) and nonionic (acetal) surface groups were used. The surface charge density, electrophoretic potential, and stability factor were measured in order to obtain quantitative information about some parameters related to the interfacial properties of the colloidal particles, such as the Hamaker constant and diffusivity. By fitting the experimental results, we have calculated the characteristic parameters of the polymer surface layer which could be responsible of the sterically stabilized mechanism.

Materials and Methods

The monomer styrene was distilled under reduced pressure, and all other materials were used as received. Double-distilled and deionized water were used throughout. The functionalized core–shell latex particles with acetal surface groups, LK2, LKN0, and LKM1 were synthesized by two-step emulsion polymerization in a batch reactor. The cores were seeds of polystyrene, and the shells were obtained by terpolymerization of styrene, MAA, and MAAMA, using the seeds obtained previously.

In this work, the acetal-functionalized polymer particles were synthesized by using a noncommercial termonomer, MAAMA, and its synthesis was described in a previous work. Moreover, the polymerization reaction conditions for the cores and for the core–shell polymer particles were the same as those reported previously.

The overall conversions at the end of the polymerizations were determined gravimetrically. The particle size distributions of the seed and the final latexes were obtained by transmission electron microscopy (TEM, Hitachi–7000FA) on representative samples of more than 500 particles. The mean-average diameter and the polydispersity indices were calculated from the particle size distributions.

The amount of surface charged groups was determined by conductometric titration. The latexes were cleaned by means of a serum replacement before the titration. The amount of the CHO surface groups were determined with hydroxylamine following the method described by Yan et al.

The electrophoretic mobility of the latex particles was measured with a Zeta-Sizer IV (Malvern Instruments, U.K.) by calculating the average of six measurements at the stationary level in a cylindrical cell. In these experiments the latex particle concentration was 0.03 mg mL$^{-1}$. Using these mobility values, we obtained the $\zeta$-potential values by the Dukhin and Semenikhin theory.

The buffers used were acetate at pH 4 and 5, phosphate at pH 6 and 7, and borate at pH 8 and 9. The salt concentrations were calculated to get a final ionic strength of 2 mM. Higher ionic strength values were reached with NaCl.

The colloidal stability of the LKM1 and LKN0 latexes was evaluated with a Spectronic 601 spectrophotometer (Milton Roy, U.S.A.) by measurement the optical absorbance as a function of time for different electrolyte concentrations. The stability can be expressed in terms of the stability factor $W$ and the critical coagulation concentration (CCC). The methods and procedure to obtain these parameters were described in a previous paper.

The CCC values were obtained at pH 5 and 7 for the LKM1 latex and at pH 5 for the LKN0 latex. For the LKN0 latex at pH higher than 7 and the LK2 latex at all pHs, it was not possible to obtain the experimental CCC value, which was higher than 1.5 M. In these cases, we tried to estimate the CCC values by using static methods; i.e., the latex particles were mixed at the adequate concentration with NaCl solutions and kept at room temperature for 20 h. The CCC values were determined by measuring the aggregation state with a photon correlation spectroscopy (PCS) technique (4700 Malvern Instruments, U.K.).

### Results and Discussion

The overall conversions of the polystyrene seeds were 100% within the experimental error. The overall conversions at the end of the polymerization reactions (conversion of the shells) were 71.0 ± 2.1 for the LK2 latex and 51 ± 7 and 60 ± 0.8 for the LKN0 and LKM1 latexes, respectively. Table 1 presents the average diameter, the surface charge density, the amount of aldehyde groups, and the CCC of these latexes. The polydispersity indices of the final latexes were 1.007 for the LK2, 1.009 for the LKN0, and 1.02 for the LKM1; thus, the latexes have a

### Table 1. Particle Size, Surface Characteristics, and Critical Coagulation Concentration (CCC) of the Acetal Latexes

<table>
<thead>
<tr>
<th>Latex</th>
<th>Diameter (nm)</th>
<th>$\sigma_0$ ($\mu$C cm$^{-2}$)</th>
<th>Aldehyde groups ($\times 10^3$ mequiv cm$^{-2}$)</th>
<th>CCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>LK2</td>
<td>199 ± 7</td>
<td>$-130 \pm 8$</td>
<td>1.22 ± 0.07</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>LKN0</td>
<td>190 ± 5</td>
<td>$-35.2 \pm 2.4$</td>
<td>0.94 ± 0.05</td>
<td>1450 ± 80</td>
</tr>
<tr>
<td>LKM1</td>
<td>112 ± 3</td>
<td>$-10.1 \pm 0.3$</td>
<td>2.36 ± 0.16</td>
<td>510 ± 30</td>
</tr>
</tbody>
</table>

monodispersity in accordance with the requirements for the application of these kinds of particles in immunoassays.

The latexes used in this work have surface carboxyl groups, responsible for the surface charge of the particles, and acetal groups, without electric charge, which are very important from the point of view of their practical applications. In principle, only the charged groups could affect the electrophoretic mobility ($\mu_e$) of these types of particles. Figure 1 shows the $\mu_e$ values versus the pH for the three latexes. The mobility values diminished below pH 6 as a consequence of the weak acid nature of the surface carboxylic groups, which begin to protonate under these conditions. At neutral and basic pH the mobility should remain constant since the carboxyl groups are completely charged. However, the LK2 latex shows a maximum between pH 6 and 7, with a decrease in the mobility at pH 8 and 9. This behavior could be explained as a consequence of the presence of a layer of charged oligomers anchored on the particle surface. At basic pH the oligomeric chains, with carboxyl groups, would be extended toward the bulk solution, producing a displacement of the shear plane of the electric double layer (edl) and decreasing the electrokinetic charge, which is responsible of the electrophoretic mobility. Tamai et al. found a similar behavior for polystyrene particles synthesized by copolymerization of styrene and a hydrophilic comonomer, such as acrylic acid (PSt/AA) and hydroxyethyl methacrylate (PSt/HEMA), which provide the carboxyl groups. The LK0 latex shows trends similar to the LKN0 latex (with a higher surface charge) is consistent with the presence of water-soluble oligomers on the particle surface.36 The anomalous surface conductance in the polystyrene particle/electrolyte solution interface could play an important role in the anomalous behavior of the latexes, but for our latexes the main factor seems to be their special edl structure.

The $\zeta$-potential of the LK2 and LKM1 latexes versus electrophoretic mobility versus NaCl concentration is shown in Figure 3. These values were calculated using the equations proposed by Dukhin and Semenikhin. From the values found for the surface charge density obtained by conductometric titration (see Table 1) on the assumption of a diffuse structure of the edl, the values of the diffuse potential were calculated for the particles using a formula that includes a correction for the curvature of the surface. The differences between the $\zeta$ and the diffuse potentials are a consequence of the roughness of the latex particle surface.30 The differences increase as the surface charge density increases, as a consequence of the oligomers chemically bound to the acetal latexes surface, which, as we will see next, also produces a very high colloidal stability of these latexes.

Figure 1. Electrophoretic mobility values for the acetal latexes at different pHs and low ionic strength (2 mM): LK2 (○); LKN0 (△); LKM1 (□).

Figure 2. Electrophoretic mobility versus NaCl concentration for the acetal latexes: LK2 (○); LKN0 (△); LKM1 (□).
latexes. Using the Dukhin-Semenikhin theory, which takes into account the anomalous surface conductance, the relationship between the ζ potential and the surface charge density is the reverse: as the electrophoretic radius increases, the LK2 latex (with a higher surface charge) displays a higher ζ potential than that for the LKM1 latex (with a lower surface charge). At low κa the ζ potential values show a plateau when a continuous decrease would be expected. This is a consequence of the difficulties of the application of the Dukhin-Semenikhin theory for an electrophoretic radius of lower than 20. The anomalous surface conductance, however, cannot be neglected to explain the electrophoretic behavior of the acrylic latexes and can contribute to the anomalous electrophoretic behavior together with the layer of oligomer anchored on the particle surface.

The stability factor W has been extensively used in the literature to characterize the stability of hydrophobic colloids. W is given as the ratio of the rate constants for rapid and slow coagulation kinetics, respectively. A typical experimental method developed to obtain W values for a colloidal system is based on the study of the time evolution of the turbidity of a sample during an agglutination process. The electrolyte concentration at which W becomes equal to 1 is the critical coagulation concentration (CCC). The values of this parameter were obtained at pH 5 and 7, after the addition of NaCl, and are shown in Table 1. The high surface charge density could be responsible for this high colloid stability, which depends on the pH because of the weak acid character of the surface groups. At pH 5 begins the protonation of the carboxyl groups, and therefore, the surface charge decreases. However, the stability of the acrylic particles at this pH, although it is lower than that at neutral pH, remains very high. For example, the CCC of the LKM1 latex (κ0 = −10.1 μC/cm²) is higher than that corresponding to a conventional sulfate latex with 10.4 μC/cm² (CCC = 450 mM at pH 5) or a carboxylic latex with 19.2 μC/cm² (CCC = 450 mM at pH 7 and CCC = 250 mM at pH 5). These types of results have also been confirmed by Asmalazova and Bogdanova, who obtained particles much more stable when the polymerization occurred in the presence of hydrophilic monomers such as acrylic and methacrylic acids. Therefore, the presence of hydrophilic monomers on the particle surface increases the colloidal stability because of the formation of a hairy layer structure on the latex surface. This is especially important for the LK2 latex (at both pHs) and the LKN0 latex (at pH 7), which were stable at a concentration higher than 1.5 M NaCl.

The stability factor was not measured at these experimental conditions, and it was not possible to apply the theoretical treatment used. Therefore, only for LKM1 and LKN0 (at pH 5) latexes will the study about the stabilization mechanisms developed in the theoretical section be applicable.

The experimental W values can be used to calculate the characteristic parameters which control the colloidal stability, that is, the Hamaker constant (A), which characterizes the attraction between two particles, and the diffuse potential (ΨD), which is related to the diffuse double-layer repulsion. This calculation can be carried out following different methods, which are described next.

Considering the DLVO theory, Reerink and Overbeek related the slope of the stability curve (−d log W/d log C) to the particle radius, the diffuse potential, and the electrolyte valence. In this way, it is possible to obtain a relation among CCC, the Hamaker constant, and the diffuse potential associated with the charged polymer surface.

If the Stern layer thickness is considered, this relation must be modified, since, in the original DLVO theory, the reference planes for attractive and repulsive energy coincide. However, Vincent et al. refined this idea by shifting the reference plane for the repulsive energy outward over a distance corresponding to the thickness (Δ) of the Stern layer. When this correction is taken into account, the relation between the CCC and the Hamaker constant is

\[
CCC = cte \frac{\gamma^4}{A^2z^4} \left[ 1 - \frac{3}{2\kappa a} + \frac{4}{3\kappa a} \ln \kappa a \left( 1 + \frac{2\Delta}{a} \right) e^{4\Delta/kT} \right]
\]

where \(a\) is the particle radius, \(z\) is the electrolyte valence, \(\kappa\) is the Debye parameter (referred to as the reciprocal double-layer thickness), and \(\gamma\) is

\[
\gamma = \tanh \left( \frac{2e\psi_D}{4kT} \right)
\]

where \(k\) is the Boltzmann constant and \(T\) is the absolute temperature.

Using the Reerink and Overbeek approximation and the thickness of the Stern layer, we calculate A and ΨD. It is necessary to know the ionic size (Δ) of the adsorbed ions, taking into account, or not, the degree of hydration for the counterion. A situation of total or partial ionic hydration has been found by several authors. Bijsterbosch, however, found the most likely situation was to calculate the Hamaker constant with the counterions completely dehydrated. Therefore, both options, hydration and dehydration, were used in our calculations and the results compared. For Na⁺ the distance between the solid surface and the center of the ion is 0.096 nm in the dehydrated situation and 0.372 nm with hydration.

Table 2 shows the A and ΨD values obtained from DLVO theory considering two possibilities for the thickness of the Stern layer. The ΨD values at pH 5 are similar for both latexes; although their surface charge densities are different, which is a consequence of the reduction in the...
number of effective carboxyl groups at this pH. However, the value for the LKM1 latex at pH 7 is substantially increased as a consequence of the increase in the charge of the surface groups.

The theoretical nonretarded Hamaker constant value obtained by Prieve and Russel\textsuperscript{47} 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,\textsuperscript{48} a comparison of the theoretical Hamaker constant with those derived from experimental results shows that, in a large number of cases, the value from colloidal studies deviates substantially from the theoretical one. The difference between both values is a consequence of the use of incomplete theories.

The $A$ values of Table 2 have been obtained by including the size of the ions of the Stern layer, and they are different depending on the $\Delta$ value used. The $A$ values were more similar to the theoretical one when the ions were considered in a hydration situation. For the LKM1 latex at pH 7, the $A$ value was slightly higher than the theoretical one.

The interaction potential energy is determined by two particle interaction energies, repulsive ($V_R$) and attractive ($V_A$). $V_R$, according to the Gouy–Stern double-layer model and the Derjaguin approximation, is due to the overlap between the diffuse double layers of the particles and decays approximately exponentially with the distance of separation. $V_A$ is due to the London–van der Waals energy and decays following a power law. $V_R$ is sensitive to the electrolyte concentration, while $V_A$ is not. The net interaction potential energy is given by

$$V = V_R + V_A = 2\pi\varepsilon_0 [A + \Delta] \left( \frac{4kT}{2e^2} \right)^2 e^{-\kappa H - 2\Delta}$$

In eq 3, $\varepsilon_0$ is the permittivity of the vacuum, $e$ is the dielectric constant of the electrolyte solution, $e$ is the elementary charge, $\kappa$ is the Debye parameter, and $H$ is the distance between the boundaries of two spheres. We have used the repulsive potential by taking into account the thickness of the Stern layer (ionic size) and the assumption of low diffuse potential. On the other hand, eq 3 contains the nonsimplified expression for the attractive potential.

The interaction potential energy between particles as a function of the separation distance is calculated using eq 3, and the $A$ and $V_R$ values are shown in Table 2. The curves obtained at different electrolyte concentrations for the LKM1 latex, at pH 5 and 7, are shown in Figures 4 and 5 (with the $A$, $V_R$, and $\Delta$ values as indicated in the figure legends). At pH 5 (Figure 4) the energy barrier decreases approximately exponentially with the distance of separation.

Figure 4. Interaction potential versus distance for the LKM1 latex (pH 5) at different NaCl concentrations. Fitting parameters: $\Delta = 0.372$ nm; $A = 0.23 \times 10^{-20}$ J; $V_R = 8.7$ mV.

Figure 5. Interaction potential versus distance for the LKM1 latex (pH 7) at different NaCl concentrations. Fitting parameters: $\Delta = 0.372$ nm; $A = 1.43 \times 10^{-20}$ J; $V_R = 20.9$ mV.

Figure 6. Interaction potential versus distance for the LKN0 latex (pH 5) at different NaCl concentrations. Fitting parameters: $\Delta = 0.372$ nm; $A = 0.57 \times 10^{-20}$ J; $V_R = 12.3$ mV.

that prevents the aggregation does not disappear at an electrolyte concentration similar to the CCC value, which is the condition that characterizes the CCC from an energetic point of view.\textsuperscript{15–17} However, for this latex at pH 7 (Figure 5) and for the LKN0 latex at pH 5 (Figure 6), the energy barrier disappears at an electrolyte concentration lower than the CCC values. Thus, the colloidal stability of LKM1 and LKN0 latexes cannot be explained using this theoretical treatment.

The special structure of the surface of these latexes leads us to think about an additional contribution due to the presence of oligomers anchored on the particle surface. Thus, it is possible to consider the influence of steric effects in the interaction potential energy between particles as a function of the separation distance. Vincent et al.\textsuperscript{20} made

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
latex & pH & $\Psi_D$ (mV) & $\Delta$ \\
\hline
LKM1 & 5 & 8.7 ± 0.1 & 0.096 nm \\
LKM1 & 7 & 20.9 ± 0.4 & 0.44 ± 0.06 \\
LKN0 & 5 & 12.3 ± 0.2 & 0.13 ± 0.01 \\
\hline
\end{tabular}
\end{table}
a quantitative study of the steric stabilization effect including two contributions: osmotic and coil compression. If there are polymeric chains covering the external surface of a particle, with 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 that pushes the particles apart.\(^{49}\) In that case the osmotic potential of repulsion \( (V_{osm}) \) can be considered as

\[
V_{osm} = \frac{4 \pi \kappa T}{v} \frac{\Phi^2}{2} \left( \frac{1}{2} - \chi \right) \left( \delta - \frac{H}{2} \right)
\]

where \( v \) is the molecular volume of the solvent, \( \Phi \) is the effective volume fraction of segments in the adlayer, and \( \chi \) is the Flory–Huggins solvency parameter.

If, however, the two particles are closer than a distance equal to \( \delta \), the elastic effect appears and 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 \( (V_r) \) related to the restriction of the movement of the hydrophilic coils extended toward the solvent. This elastic–steric repulsion is given as

\[
V_r = \left( \frac{2 \pi \kappa T}{P_m} \Phi^2 \rho \right) \frac{H}{2} \ln \left( \frac{3 - H / \delta}{2} \right) - 6 \ln \left( \frac{3 - H / \delta}{2} + 3(1 - H / \delta) \right)
\]

where \( P_m \) and \( \rho \) are the molecular weight and density of the adsorbed polymer, respectively. This modifies the osmotic potential, which is now given by

\[
V_{osm} = \frac{4 \pi \kappa T}{v} \Phi^2 \left( \frac{1}{2} - \chi \right) \delta \left( \frac{H}{2} \right) - \frac{1}{4} \ln \left( H / \delta \right)
\]

In all of the interaction energies for the polymeric layer, the Derjaguin approximation is valid for \( \delta \gg \delta \). For the electrostatic 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:

\[
V_t = V_A + V_R + V_{osm} + V_{vr}
\]

Nevertheless, this assumption of additivity (made in this work) has recently been questioned by Einaron and Berg,\(^{50}\) who claim that the electrostatic repulsion \( (V_{el}) \) and the steric repulsions \( (V_{osm} \text{ and } V_{vr}) \) are not totally independent.

Including these electrostatic effects, Ortega–Vinuesa et al.\(^{38}\) have explained the colloidal stability of a hydrophilic (PS–HEMA) latex. For this type of stabilization, the total interaction energy is obtained by the combination of an attractive and three repulsive terms—electrostatic, osmotic, and elastic—as was indicated in eq 7. We have used this electrostatic mechanism to explain the colloidal stability behavior of the acetal latexes. First, a numerical computation of the stability factor has been done by using the equation derived by Fuchs\(^{51}\) considering slow coagulation as a diffusion process that relates the resultant potential energy with \( W \):

\[
W = 2a \int_0^\infty \frac{e^{V_{el}}}{(2a + H)^2} \, dH
\]

The theoretical curve was fitted to the experimental points of \( \log W \) versus log \([NaCl]\), with the diffuse potential related with the slope while the Hamaker constant depends on the CCC value. Thus, both can be used as independent fitting parameters.\(^{52}\) In the electrosteric mechanism of stabilization, eqs 4–6 must be included to calculate the total interaction potential (eq 7) and it is necessary to know the value for the solubility parameter, \( \chi \), the thickness of the oligomeric layer, \( \delta \), and the volume fraction occupied for the segments, \( \phi \).

The Flory–Huggins solubility parameter is tabulated for a lot of polymers in different solvents.\(^{53}\) This parameter has a value of around 0.45, depending on the substrate of the surface oligomers (latex synthesis).\(^{27}\) The thickness of the oligomeric layer can be estimated from the relationship between the \( \zeta \) and \( \Psi_D \) potentials given by the equation of Everse and Boardman:\(^{54}\)

\[
\ln \tan \left( \frac{\pi \zeta^2}{4kT} \right) = \ln \tan \left( \frac{\pi \Psi_D^2}{4kT} \right) - \kappa \delta
\]

By using the \( \zeta \) and \( \Psi_D \) data from Figure 3 for an electrophoretic radius higher than 20, the \( \delta \) values were calculated for both latexes, LKM1 and LKN0, and the same value, \( \delta = 0.9 \text{ nm} \), was obtained. This value seems to be too low to produce an electrosteric stabilization; however, Corner and Gerrard\(^{55}\) found that, even with low molecular weight (and low thickness) stabilizing chains, the CCC of a latex in NaCl was 1.6 M. With higher molecular weight, the latex was stable in saturated solutions of NaCl and CaCl₂. The thickness values obtained were in agreement with the experiments of PCS carried out to measure the hydrodynamic radius of the latex particles. The polyelectrolyte chains with weak acid groups would have a maximum extension at neutral and basic pH, while at acid pH the protonation of the carboxyl groups would produce a shrinkage of these oligomeric chains. This difference in the extension of the hairy layer would be undetectable if the extension of the oligomeric chains is too small in comparison with the particle size. The same situation appears when the electrolyte concentration is increased and the particles remain stable.\(^{14}\) In our systems no changes have been found in the particle size (using PCS) when the pH or the ionic strength is modified. We will use, therefore, the value of \( \delta \) previously estimated, and the volume fraction \( \phi \) will be used as a fitting parameter.

Figure 7 shows the theoretical lines and experimental points for \( \log W / \log [NaCl] \) plots. Good agreement between both plots was found when the \( \phi \), \( \Psi_D \), \( \delta \), and \( \phi \) values used for fitting the experimental values were those shown in Table 3. For the LKM1 latex at pH 5, the best fit was obtained with \( \phi = 0.10 \). This value is similar to those obtained by other authors\(^{27,38,50}\) that use the same theoretical treatment to explain the colloidal stability of particles with surface oligomers. Furthermore, the Hamaker constant value was \( 0.89 \times 10^{-20} \text{ J} \), which is near


\((51)\) Fuchs, N. Z. Phys. 1934, 89, 736.
the theoretical one. Figure 8 shows the total interaction potential energy for the LKM1 latex as calculated with the previous parameters, at pH 5 and different electrolyte concentrations. The energy barrier disappears at 500 mM NaCl, which is equal to the experimental CCC of this latex at pH 5.

At pH 7, the LKM1 latex has a CCC value of 930 mM. In these conditions, the electrostatic interaction must be higher than that at pH 5 because the ionic groups begin to acquire charge. Figure 9 shows the total interaction potential energy for the LKM1 latex as calculated with the previous parameters (Table 3), at pH 7 and different electrolyte concentrations. As can be seen in Table 3, the diffuse potential substantially increased, which is related with the increase in the electrostatic interaction; the volume fraction is the same as that at pH 5, since there are the same amounts of surface oligomers; and the Hamaker constant is similar to that previously found at pH 5 and to the theoretical value. In this situation, the energy barrier disappears at a concentration of 900 mM, which is similar to the experimental CCC of this latex. Using, therefore, a theoretical model that takes into account an electrosteric mechanism of stabilization, it is possible to explain the high colloidal stability of this acetal latex from an energetic point of view. Furthermore, it is important to note that the Hamaker constant values are similar to the theoretical one.

Finally, the same treatment is used for the LKN0 latex at pH 5. Figure 7 also shows the experimental values and theoretical fitting of the stability factor for this latex at pH 5. The parameters used to fit the experimental values are shown in Table 3. The diffuse potential is slightly lower than that of the LKM1 latex at the same pH, which is representative of the important decrease of the charge at acid pH. This latex has a higher amount of surface groups than the LKM1 latex. However, the thickness of the polymeric layer obtained previously was the same for both latexes. Therefore, the increase of surface groups must be related to an increase of the volume fraction occupied ($\phi = 0.15$). The increase in this parameter with respect to the LKM1 latex seems to be proportional to the increase in the total amount of surface groups; ionic and nonionic, since the amount of carboxyl groups is 3 times higher for the LKN0 latex but the amount of acetal groups is approximately 2 times as high for the LKM1 latex (see Table 1). Furthermore, the Hamaker constant value is $1.00 \times 10^{-20}$ J, similar to the theoretical one. Figure 10 shows the total interaction potential energy for the LKN0 latex at pH 5 and 1000 mM NaCl. Only when the electrosteric interaction is considered and the volume fraction is 0.15 is the energy barrier sufficiently high to prevent the aggregation of the latex particles at so high electrolyte concentration.

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**Table 3. Characteristic Parameters of the Colloid Stability for the Acetal Latexes As Obtained by Theoretical Adjustment of the Experimental Stability Factor (Ionic Size $\lambda = 0.096$ nm)**

<table>
<thead>
<tr>
<th>latex</th>
<th>pH</th>
<th>$\Psi$ (mV)</th>
<th>$10^{20}A$ (J)</th>
<th>$\delta$ (nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LKM1</td>
<td>5</td>
<td>23.5</td>
<td>0.89</td>
<td>0.9</td>
<td>0.10</td>
</tr>
<tr>
<td>LKM1</td>
<td>7</td>
<td>33.5</td>
<td>1.10</td>
<td>0.9</td>
<td>0.10</td>
</tr>
<tr>
<td>LKN0</td>
<td>5</td>
<td>19.6</td>
<td>1.00</td>
<td>0.9</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Figure 7.** Numerical computation of the stability factor for the acetal latexes with an electrosteric mechanism of stabilization. Experimental data: LKM1, pH 5 (○); LKM1, pH 7 (×); LKN0, pH 5 (○). Theoretical data (solid line) by eq 5 including the contributions from eq 11. The fitting parameter values are shown in Table 3.

**Figure 8.** Interaction potential versus distance for the LKM1 latex (pH 5) at different NaCl concentrations. Fitting parameters: $\Delta = 0.096$ nm; $A = 0.89 \times 10^{-20}$ J; $\Psi = 23.5$ mV; $\delta = 0.9$ nm; $\phi = 0.1$.

**Figure 9.** Interaction potential versus distance for the LKM1 latex (pH 7) at different NaCl concentrations. Fitting parameters: $\Delta = 0.096$ nm; $A = 1.10 \times 10^{-20}$ J; $\Psi = 33.5$ mV; $\delta = 0.9$ nm; $\phi = 0.1$.

**Figure 10.** Interaction potential versus distance for the LKN0 latex (pH 5) and [NaCl] = 1 M, at two $\phi$ values. Fitting parameters: $\Delta = 0.096$ nm; $A = 1.0 \times 10^{-20}$ J; $\Psi = 19.6$ mV; $\delta = 0.9$ nm; $\phi = 0.15$. 

Although a stabilizing mechanism in latex suspensions related to a reduction of the van der Waals attraction caused by hairy layers has recently been commented on by Wu and van de Ven, the same authors indicate that, for high salt concentrations, the hairy layers are expected to overlap and the additional stabilizing mechanism becomes steric repulsion.

In summary, we have tried to explain the high colloidal stability of acetal latexes as a consequence of the special structure of the edl formed during the synthesis. The electrokinetic characterization allows one to assume an oligomeric layer is present on the particle surface. When a steric contribution is included in the DLVO theory, the correlation between theory and experiment seems to be very good and we can obtain Hamaker constant values which are similar to the theoretical one. Therefore, if we try to explain the stability results by an electrosteric mechanism, it is possible to find a set of parameters which provide CCC values which are in accordance with the experimental one.

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