ORIGINAL CONTRIBUTION

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Study of the colloidal stability of an amphoteric latex

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Abstract We have studied the colloidal stability of an amphoteric latex (–COOH and NH_2 surface groups) with a low-angle light scattering technique (nephelometry). Measurements were carried out at different pH values and electrolyte concentrations (NaCl or $CaCl_2$). The results show a behaviour in agreement with DLVO theory when the pH of the medium is below the isoelectric point (i.e.p.) of the latex: at low ionic strengths the latex is stable, but it becomes completely unstable and coagulates when electrolyte concentration goes over a particular value (the critical coagulation concentration). However, when pH is raised above the isoelectric point, the latex is completely stable even at high electrolyte concentrations, showing a behaviour clearly opposite to the theory. This could be explained by means of an additional short-range repulsive "hydration force" due to the structure of water molecules that accompany hydrated cations around the hydrophilic latex surface. The morphology and electrical properties of the latex surface have been studied by different methods: dynamic light scattering, electrophoretic mobility, potentiometric and conductometric titrations.

Keywords Amphoteric latex ·
Critical coagulation concentration ·
Stability ratio · Hydration forces ·
Electrophoretic mobility

Introduction

Undoubtedly, the DLVO theory has been and it is still very useful for explaining the stability of colloidal dispersions. This theory was independently developed by Derjaguin and Landau [1] and by Verwey and Overbeek [2] in the forties. According to this theory, the total interaction potential (V_T) between two colloidal particles is the sum of the repulsive electrostatic interaction energy (V_E) and the attractive London–van der Waals (dispersion) energy (V_A). The total interaction energy as a function of the distance between the particles presents a minimum (the primary minimum) close to a maximum at small separations. The maximum represents the energy barrier (V_{max}) opposing coagulation. If particles approach each other with sufficient kinetic energies to overcome V_{max}, coagulation will occur in the primary minimum and the suspension will be destabilized. It is possible that a second minimum appears at larger separations as well. The V_{max} value depends on the surface electric potential of the particles, electrolyte concentration in the medium, valence of the counterions, particle size and Hamaker constant. In particular, an increase in the electrolyte concentration causes a decrease in V_{max} because the ions diminish the repulsive electrostatic interactions between the particles. Thus, there will be an electrolyte concentration (the so-called critical coagulation concentration, c.c.c.) at which the energy barrier vanishes ($V_{max} = 0$). The colloidal dispersion is then completely

unstable at electrolyte concentrations greater than c.c.c.

The classical DLVO theory can successfully explain the stability of many colloidal systems; however, its application has some limitations, as Overbeek himself stated [3]. In particular, this theory is not able to explain the stability of very hydrophilic systems, where repulsive forces arise at very short particle (or surface) separations. These forces are called hydration forces (if the medium is aqueous). There are a lot of examples of hydration forces in the literature [4]. Silica surfaces [5, 6, 7], mica surfaces [8, 9, 10, 11], proteins [12, 13, 14] and lattices [15, 16] are some systems where hydration forces have been detected.

For colloids and interfaces in aqueous media, hydration forces are attributed to the hydration of adsorbed counterions and ionic functional groups in the surface. The intensity of these forces is strongly dependent on the properties of the two approaching surfaces and on the physical and the electrochemical properties of the intervening fluid medium. The origin and nature of the hydration forces have long been controversial, especially in the colloidal and biological literature. A well-known interpretation of this force is that a polar surface induces an ordering of the solvent, which exponentially decays away from the surface. An overlap of the ordered-solvent layers near the two mutually approaching surfaces creates a force. Whatever the reason for hydration of the surface (electrostatic polarization of water or hydrogen bonding), it significantly reduces the free energy of the system. Partial dehydration of the adsorbed ions and/or the surface groups due to the mutual approach of two surfaces, will lead to an increase in the system energy. This results in a repulsive force.

The aim of the present study is to characterize hydrophilic colloidal particles with COO^- and NH_3^+ groups on the surface, which may be used as models to advance the knowledge of colloidal stabilization by hydration forces. In particular, the present paper deals with the quantification of colloidal stability in terms of DLVO theory, the hydrodynamic studies with light scattering to analyse the possible hairy layer, and the influence of different cations on the stability and electrophoretic behaviour.

Theory

The DLVO theory considers that the total potential energy V_T between two particles is given by:

$$V_T = V_E + V_A \tag{1}$$

The attractive London−van der Waals energy V_A is expressed as [17]:

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

where a is the particle radius, H is the distance between the surfaces of the particles and A is the Hamaker constant (for latex particles interacting in an aqueous medium, in this case). Eq. 2 does not take the electromagnetic delay into account.

The repulsive electrostatic energy V_E takes the following form [2, 17]:

$$V_E = 2\pi\varepsilon_o\varepsilon_r a\psi_o^2 \exp(-\kappa H) \tag{3}$$

where ε_o is the dielectric constant of vacuum, ε_r is the relative dielectric constant of the medium, ψ_o is the surface potencial of the particles and κ is the inverse of the Debye length, given by the following equation:

$$\kappa = \sqrt{\frac{\sum_i n_i e^2 z_i^2}{\varepsilon_o\varepsilon_r K_B T}} \tag{4}$$

e being the electron charge, K_B the Boltzmann constant, T the absolute temperature, n_i the number concentration in the bulk of ions of type i, and z_i the valence of such ions.

The stability ratio (W) is a criterion for the stability of a colloidal system:

$$W = \frac{K_r}{K} \tag{5}$$

in which K_r is the rate constant that describes rapid aggregation, and K is a rate constant of a particular aggregation. Thus, the inverse of the stability ratio provides a measure of the effectiveness of collisions leading to coagulation.

Theoretically, W can be obtained through the following equation [18, 19]:

$$W = \frac{\int_0^\infty \frac{\beta(H)}{(H+2a)^2}\exp\left(\frac{V_T(H)}{K_B T}\right)dH}{\int_0^\infty \frac{\beta(H)}{(H+2a)^2}\exp\left(\frac{V_A(H)}{K_B T}\right)dH} \tag{6}$$

where $\beta(H)$ is the hydrodynamic correction factor. Its dependence on H can be expressed as [20]:

$$\beta(H) = \frac{6H^2 + 13Ha + 2a^2}{6H^2 + 4Ha} \tag{7}$$

The stability factor can be computed by numerical integration using Eq. 6. In this way, it is necessary to fit the theoretical expression to the experimental points of $log\ W$ versus electrolyte concentration, using A and ψ_o as fitting parameters.

In this work we have obtained the coagulation rate constants of our colloidal particles using the low angle light scattering theory developed by Lips et al. [21, 22]. According to this theory, scattered light intensity for a

dispersion of identical primary particles with a time varying distribution size is:

$$\frac{I(t,\theta)}{I(0,\theta)} = 1 + 2Kn_st \qquad (8)$$

where $I(0,\theta)$ is the initial intensity of light scattered at angle θ ; $I(t,\theta)$ is the intensity of light scattered at angle θ in an instant t; n_s is the initial number of spherical particles and K is the aggregation rate constant (between monomers to give rise to dimers). The scattered light intensity at low angles increases linearly with time in the initial states of aggregation, and then an absolute coagulation rate (K) can be obtained from the slope if the number of primary particles is known.

Experimental methods

All chemicals used were of analytical grade quality. Water was double distilled by reverse osmosis, followed by percolation through charcoal and a mixed bed of ion-exchange resins (Milli-Q System). In aggregation experiments, pH was controlled using different buffers (citrate at pH 3, acetate at pH 4–5, phosphate at pH 6–7, borate at pH 8–10, constant ionic strength 2 mM).

The latex was synthesized upon request by Ikerlat Polymers (Guipúzcoa, Spain). It is a polystyrene latex with carboxyl and amine surface groups. These surface groups come from the monomers used in the synthesis: methacrylic acid (carboxyl groups) and N,N−diethylaminoethyl methacrylate (amine groups), in a relation 2:1. The diameter of the particles is 210 ± 10 nm (measured by transmission electron microscopy, TEM), with a polydispersity index (PDI) of 1.010. This parameter is defined as:

$$PDI = \frac{d_w}{d_n}; \quad d_w = \frac{\sum N_i d_i^4}{\sum N_i d_i^3}; \quad d_n = \frac{\sum N_i d_i}{\sum N_i} \qquad (9)$$

where N_i is the number of particles whose diameter is d_i. A latex having PDI $\leq$ 1.010 can be considered as monodisperse.

Particle size was also measured at different conditions (pH and NaCl concentration) by photon correlation spectroscopy (PCS) with a Malvern 4700 system (Malvern, England). All measurements were performed at 25 °C and a scattering angle of 60°. Samples were sonicated before measurements.

The latex was cleaned by means of serum replacement. Then a sample with 19 m^2 of total surface of latex were added to a NaCl solution (the NaCl final concentration was 40 mM) and they were titrated at 20 °C with 0.94 ± 0.03 M HCl and 1.095 ± 0.020 M NaOH in a stirred vessel flushed with nitrogen. The titration device consists of two Hamilton syringes, pH-meter (Metrohm), pH electrode (Crison), conductimeter (Crison) and conductivity electrode (Crison). The potentiometric and conductometric titrations were carried out independently. All measurements and additions were controlled by computer.

Electrophoretic mobility of the latex was measured as a function of pH at different concentrations of NaCl, NaNO$_3$ and Ca(NO$_3$)$_2$ with a Zeta–PALS instrument (Brookhaven, USA). This instrument is based on the principles of phase analysis light scattering (PALS) [23]. It is very useful to measure very small electrophoretic mobilities, as well as its value at high electrolyte concentrations. A latex particle concentration of 0.01 mg/mL was chosen (a value in the region where the electrophoretic mobility is independent of the particle concentration).

Particle aggregation studies were carried out using a low angle light scattering technique (nephelometry) for the measurement of aggregation rates. Scattered light intensity was followed at 20° for 120 s at different concentrations of NaCl and CaCl$_2$ and several pH values. The light source is a He−Ne laser (633 nm, 10 mW) and the scattering cell shape is rectangular, with 2-mm path length. The cell was thoroughly cleaned with chromic acid and rinsed with distilled water before each set of experiments. Equal quantities (1 mL) of salt and latex solutions were mixed and introduced in the cell by an automatic mixing device. The latex dispersions used for such coagulation experiments had to be sufficiently dilute to minimize multiple scattering effects, whilst still having an experimentally convenient coagulation time. For the latex here used, a concentration of 7×10^9 particles/mL was determined to be satisfactory. Prior to experiments, fresh suspensions of latex were sonicated for a few minutes to break up any initial clusters.

Results and discussion

Conductometric and potentiometric titrations

Conductometric and potentiometric titrations were carried out to determine the surface charge density of the particles and the nature of the charge-imparting groups [24]. A value of 130 ± 50 μC/cm^2 was obtained for the total charge of the latex from conductometric titrations. Due to the intrinsic errors in the graphical calculations, this method is not very accurate.

Potentiometric titrations provide us with detailed information about the pH-dependence of the surface charge density if experimental curves are compared with a blank titration under similar conditions. A computer program is employed to fit the blank titration to a theoretical curve, in such a way that from volume differences of titrator agent it is possible to obtain the charge−pH dependence. A reference point is necessary to draw this curve, for example the zero point of charge (z.p.c.), which was assumed to be the isoelectric point (i.e.p.) [24]. Electrophoretic mobility measurements indicate that the i.e.p. is around 6 (shown later).

The main problem of this method is its inaccuracy at the pH extreme limits (very high and very low pH), because at these limits a great volume of titrator agent is necessary to provoke a small change in the pH. Consequently, more errors may appear when latex and blank titrations are compared at those extreme values. From the data obtained with different titrations, we can estimate that the maximum positive charge (due to amine groups) is 50 ± 10 μC/cm^2 and that the maximum negative charge (due to carboxyl groups) is -110 ± 15 μC/cm^2. These values are in agreement, within the experimental error, with the results obtained in the conductometric titrations.

Therefore, the number of carboxyl groups is roughly twice the number of amine groups in our latex, as expected from the comonomer ratio. Homola and James [24] studied how the i.e.p. of an amphoteric latex depended on this ratio, and they found that when it was 2:1 the i.e.p. of the latex was around 6. This is the value that we have obtained in electrophoretic mobility measurements.

Hydrodynamic diameter

The latex size was measured at different pH values and NaCl concentrations by PCS in an attempt to discern the possible existence of a hairy layer around the particles. It has been pointed out that hydrophilic monomers often form a water-soluble polymer layer surrounding the particles, especially when they have charge [25, 26, 27, 28, 29, 30]. According to the hairy layer model, flexible polymer chains (or hairs) at the surface extend into solution due to the electrostatic repulsion between the ionic groups that terminate the hairs and between these groups and the ionic groups that are anchored at the surface. The thickness of the hairy layer is altered by the presence of electrolyte owing to charge shielding, in such a way that at high ionic strength the hairs collapse back towards the surface.

The obtained results show that at pH 3 the hydrodynamic size decreases by about 2 nm (from 221 ± 2 nm to 219 ± 2 nm) upon the addition of electrolyte (from 0.005 M to 0.1 M NaCl). On the other hand, at pH 9 the hydrodynamic diameter remains approximately constant with electrolyte concentration, the values being ca. 218 ± 2 nm. The change in diameter with pH at low salt is not significant.

Although it is possible that a hairy layer exists on the particle, the diameter variations obtained by PCS are inconclusive, especially if we have in mind the size error obtained by TEM (210 ± 10 nm).

Electrophoretic mobility

The electric charge and surface potential of clean latex particles are considered to originate from protonation or deprotonation of surface functional groups (COOH and NH_2 groups in our latex). The particle surface potential is correlated with the colloidal stability of particles. Electrophoretic mobility of the latex as a function of the pH at different electrolyte concentrations is plotted in Fig. 1. This figure shows data obtained at 2 mM NaCl, 20 mM NaCl and 500 mM NaNO$_3$. A reaction between Cl^- anions and palladium of the electrode takes place at NaCl concentrations higher than 20 mM [31]. So, we decided to change Cl^- anions for NO_3^- anions. The mobility curves obtained at 2 mM and 20 mM NaNO$_3$ and the corresponding curves with NaCl are identical. Therefore, there is no influence of the anion type on the latex mobility.

As can be seen from Fig. 1, well-defined curves are obtained at 2 mM and 20 mM NaCl. The mobilities depend on pH remarkably, as expected from the amphoteric nature of the latex surface, showing positive values below the i.e.p. (around 6) and negative values above this point. If the salt concentration is increased, the absolute value of the electrophoretic mobility
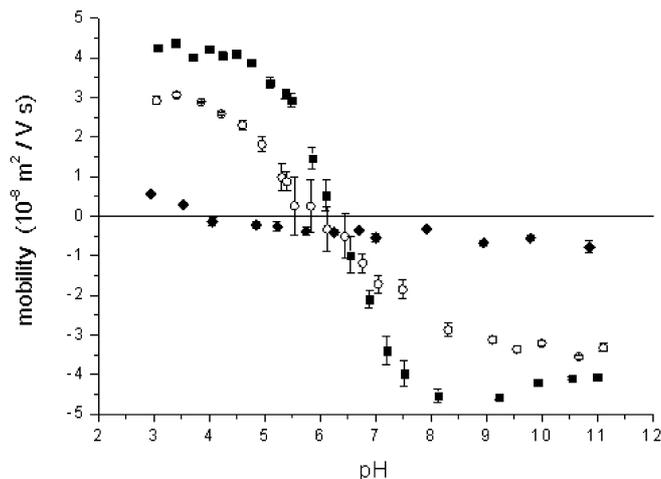

Fig. 1 Electrophoretic mobility as a function of pH at different electrolyte concentrations: ■ 2 mM NaCl, ○ 20 mM NaCl, ◆ 500 mM NaNO$_3$

decreases due to the screening effect of electrolyte ions on the electrical charge on the particle surface region.

In order to better understand the behaviour of the latex, we decided to investigate the electrophoretic mobility in the presence of a polyvalent electrolyte. Divalent counterions may specifically interact with the surface sites, thus affecting markedly the surface properties.

The mobility curves at 2 mM NaCl and at 2 mM Ca(NO$_3$)$_2$ are compared in Fig. 2. It can be observed that in the acid pH range (values lower than the i.e.p.) both curves coincide, whereas for pH values higher than the i.e.p. the mobility is clearly smaller when the counterion present in the medium is Ca^{2+}. On the other
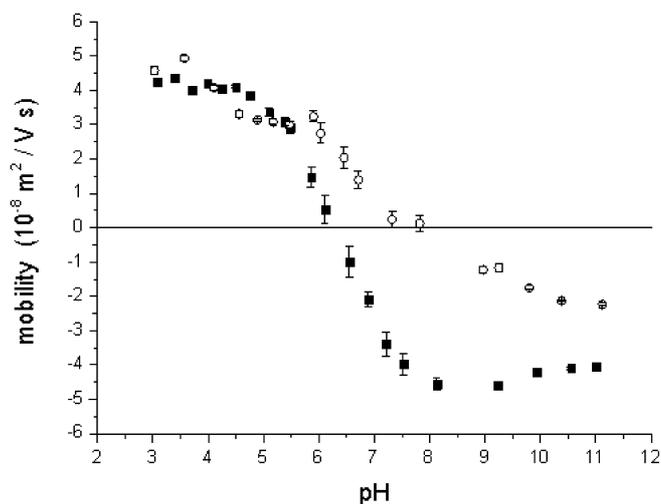

Fig. 2 Electrophoretic mobility as a function of pH at 2 mM of different electrolytes: ■ NaCl, ○ CaCl$_2$

hand, the i.e.p. moves towards a higher value for the divalent cation. These results point out a high affinity of Ca^{2+} for the hydrophilic surface. Probably, calcium counterions neutralize the negative charge of the particles in a specific manner different to the electrostatic interaction (specific adsorption).

Colloidal stability

Initial data of scattered light intensity obtained by nephelometry during the aggregation processes were fitted to a straight line according to Eq. 8. From the slope of that linear relationship we can estimate the aggregation rate constant K, and from the maximum slope value we obtain K_r (rapid aggregation rate). The stability factor, calculated for each coagulation experiment, was obtained using Eq. 5. It is usual to show $log\ W$ as a function of the electrolyte concentration in order to study the stability domains of a colloidal system.

The results obtained with NaCl as electrolyte, at three different pH values smaller than the i.e.p., are shown in Fig. 3a. These results are in agreement with the DLVO theory: $log\ W$ decreases as the salt concentration (c_e) increases until a certain value is reached (the c.c.c.), from which the curve remains parallel to the concentration axis. Besides the experimental data, theoretical curves have been drawn. These curves were obtained from Eqs. 2, 3, 6 and 7 using A and ψ_o as fitting parameters. Reerink and Overbeek [32] have shown that, with several approximations, a linear relationship exists between $log\ W$ and $log\ c_e$ near c.c.c. From this linear relationship the c.c.c. can be estimated as the electrolyte concentration at which $log\ W=0$. Table 1 shows the values obtained for A and ψ_o, in addition to c.c.c values. We can observe that c.c.c. increases as pH decreases. This is expected since the charge of the latex grows up as pH separates from the i.e.p. The high c.c.c. values reflect high surface charge on the latex.

The values obtained for A and ψ_o fit the experimental data satisfactorily in all cases (with the exception perhaps of the curve at pH 5 with NaCl). For example, ψ_o decreases with surface charge (increasing pH) as expected. Strictly, Eq. 3 is only valid for $\psi_o < (K_BT/ze)$, that is, $\psi_o < 25$ mV for the case of NaCl electrolyte, and practically all ψ_o values in Table 1 are higher than this value. However, some authors [17] have found that it is possible to use the previous V_E expression without introducing significant errors when $\psi_o < (2K_BT/ze)$.

The theoretical Hamaker constant for polystyrene particles in water is 1.379×10^{-20} J [33, 34]. Our results are smaller than the theoretical value. Besides, they are dependent on pH and electrolyte type. The Hamaker constant increases as pH decreases (or surface charge grows). Similar behaviours have been observed by other authors [19]. The general explanation for this discrep-
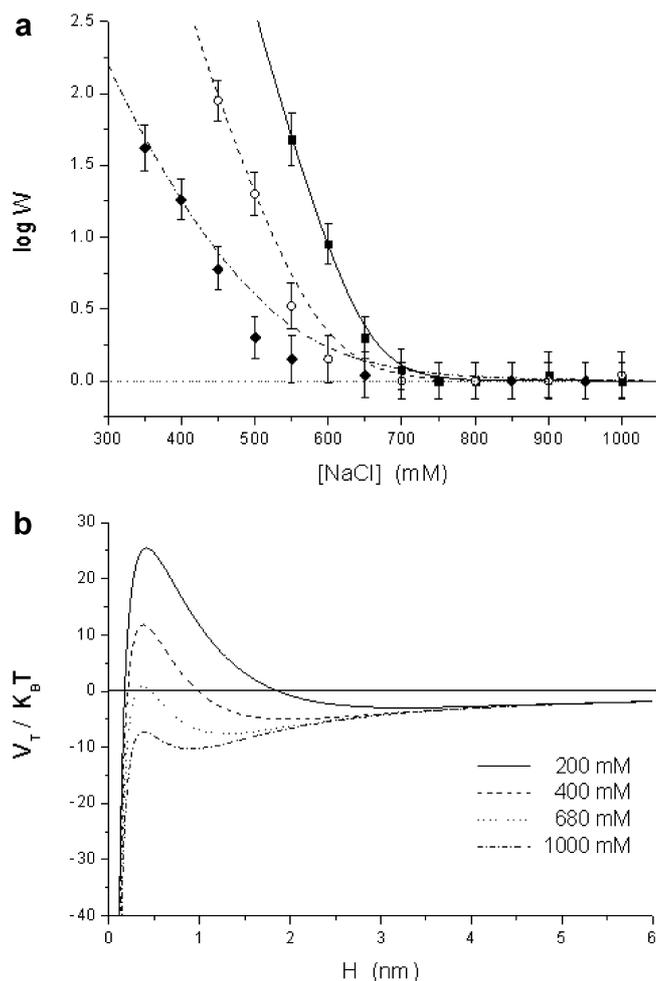

Fig. 3 a *LogW* versus NaCl concentration (mM) at different pH values: ■ pH 3, ○ pH 4, ◆ pH 5. *Lines* are fitting curves obtained from Eqs. 2, 3, 6 and 7. **b** Interaction potential energy curves at different NaCl concentrations (pH 3)

Table 1 NaCl critical coagulation concentration, surface potential (ψ_o) and Hamaker constant (A) for latex, calculated using DLVO theory at different pH values

	c.c.c. (mM)	ψ_o (mV)	A (10^{-20} J)
pH 5	530 ± 50	20.0	0.27
pH 4	630 ± 50	27.6	0.54
pH 3	680 ± 50	32.5	0.74

ancy is the dependence on ionic concentration of the zero-frequency contribution of the van der Waals force. This zero-frequency part is reduced by a factor roughly proportional to $exp(-2\kappa H)$. On the other hand, the Hamaker constant depends on the separation distance if the electromagnetic delay is taken into account [35].

Using the surface potential and Hamaker constant values obtained (Table 1) and Eqs. 1, 2 and 3 we can compute interaction energy curves for different pH

values. As an example, Fig. 3b shows these interaction energy curves at pH 3 and at different NaCl concentrations. It can be observed that the increase in electrolyte concentration provokes a decrease in the height of the potential maximum. The latter (that prevents aggregation) finally disappears, or is lower than $3 \times K_B T$, when the electrolyte concentration is similar to the experimental c.c.c., in agreement with the theoretical prediction, at least in a qualitative way.

The latex was very unstable at pH 6 (i.e.p.). The turbidity of the sample increased quickly as soon as the latex was added to a low ionic strength buffer (without adding salt). This result is expected because the net charge of the particles at pH 6 is close to zero and the contribution of the repulsive interaction to the total potential is negligible. When the colloidal stability of the latex was studied at pH above the i.e.p. (pH 7, 8, 9 and 10) an anomalous behaviour was observed: the latex was completely stable at any NaCl concentration. This phenomenon is, of course, quite contrary to DLVO theory, since addition of electrolyte is generally expected to cause coagulation.

If we observe Fig. 1 we can note that at 500 mM $NaNO_3$ the mobility is practically null at any pH. At this concentration the latex aggregates at pH 4 and 5, but it is stable at pH 7, 8 and 9. However, the mobility is practically the same at these pH values. This indicates that the stability at pH 7, 8 and 9 is not due to electrostatic repulsion. The existence of soluble polymer chains protruding into solution could provide latex particles with steric stabilization (especially at low ionic strength). However, since this possible extension of polymer chains should be more or less symmetric respect to the i.e.p. of the particle, it can not be invoked to explain an anomalous stability of the latex at pH values above the i.e.p., but a normal (DLVO) behaviour below this point. There should be another mechanism of stabilization in the basic pH range, where the net charge of the latex is negative and an excess of cations is present. Since cations exist in aqueous media highly hydrated, while anions practically are not hydrated [4], a relation of the stabilization mechanism with the presence of adsorbed hydrated cations on the hydrophilic particle surface seems plausible. This stability may be due to the energy required to dehydrate or desorb the adsorbed counterions and to allow a close approach of the surfaces (a hydration barrier at the hydrophilic surface prevents the aggregation). The idea of liquid structuring near solid surfaces (and the consequent structural force between solid bodies immersed in liquids) has long been a subject of discussion and speculation in colloid and surface science. There is now little doubt that there is a measurable disturbance of the structure of a liquid in the vicinity of a surface, and that this structure gives rise to an interaction when two surfaces approach. These structural forces are called hydration forces when they

are repulsive. These forces reflect the work required to remove the bound water layer around the solid surface.

The results obtained with $CaCl_2$ as electrolyte are very similar to the previous ones with NaCl as electrolyte. Figure 4a shows the dependence of $logW$ on the electrolyte concentration of $CaCl_2$ at pH 4 and 5 together with the theoretical curves. The c.c.c. values obtained (see Table 2) are smaller than the corresponding
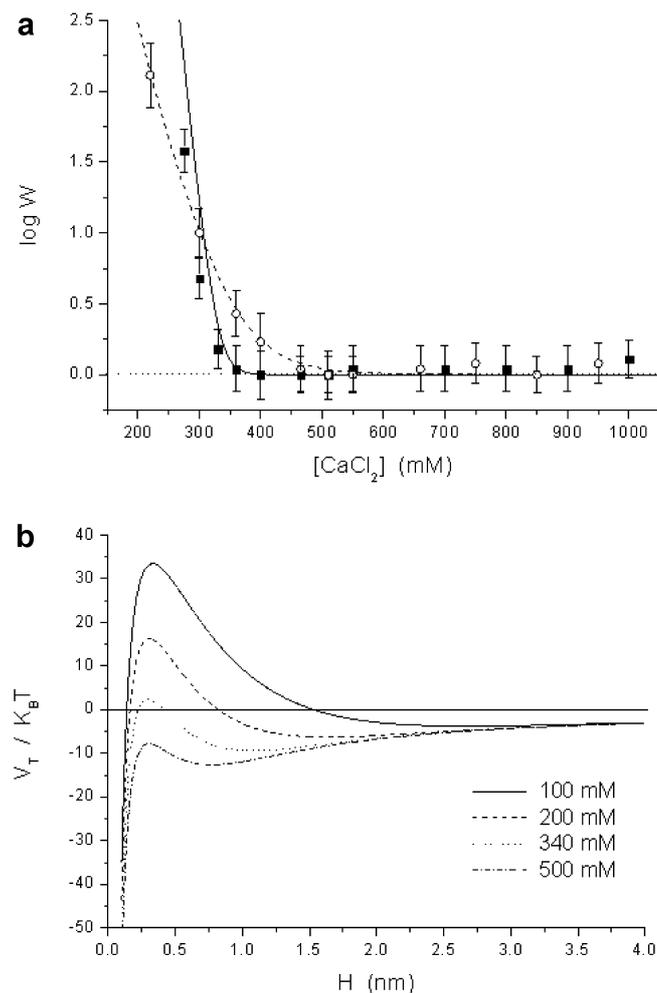

Fig. 4 a $LogW$ versus $CaCl_2$ concentration (mM) at different pH values: ■ pH 4, ○ pH 5. *Lines* are fitting curves obtained from Eqs. 2, 3, 6 and 7. **b** Interaction potential energy curves at different $CaCl_2$ concentrations (pH 4)

Table 2 $CaCl_2$ critical coagulation concentration, surface potential (ψ_o) and Hamaker constant (A) for latex, calculated using DLVO theory at different pH values

	c.c.c. (mM)	ψ_o (mV)	A (10^{-20} J)
pH 5	370 ± 70	21.1	0.21
pH 4	340 ± 30	35.6	0.74

NaCl values. As expected, a 2:1 salt causes a more effective neutralization of the electric layer charge and therefore an important decrease in the colloidal stability. The c.c.c. at pH 5 is slightly higher than the c.c.c. at pH 4, but its uncertainty is higher too. The A and ψ_o values obtained from DLVO theory are shown in Table 2. Introducing these parameters in Eqs. 1, 2 and 3 we can estimate the interaction energy curves, which could explain the observed colloidal stability. In Fig. 4b we present the interaction energy curves obtained at pH 4 and at several $CaCl_2$ concentrations.

At pH 9 the latex was stable at any $CaCl_2$ concentration. However, at pH 7 (Fig. 5) the latex was unstable at very low $CaCl_2$ concentrations and it became stable at concentrations above 20 mM. This indicates the possible existence of hydration forces in our system, which could explain the latex stability at high electrolyte concentrations when the pH was above the i.e.p. Electrophoretic mobility measurements point out that this stability at basic pH values is not only due to electrostatic repulsion: at 500 mM $Ca(NO_3)_2$, for example, the mobility is practically null at any pH (results not shown). Electrostatic repulsions cannot account for the observed high stability, especially in the case of pH 7 with $CaCl_2$, close to the i.e.p. It can be interpreted as follows: a low concentration of Ca^{2+} ions (which probably have a high affinity for hydrophilic surfaces) is sufficient to screen the electrostatic repulsion, but insufficient to form a water structured layer around the particles. This way, latex is unstable at low $CaCl_2$ concentrations. If salt concentration increases (about 20 mM) the water structured layer around the particles is developed and the system is stabilized by hydration forces.
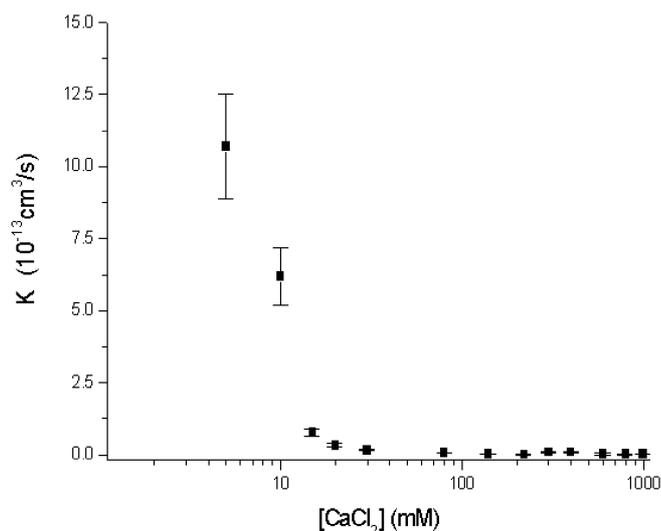
We do not observe aggregation at low NaCl concentrations at pH 7 because Na^+ ions screen less than Ca^{2+} ions. A higher NaCl concentration is necessary to screen the electrostatic repulsion, but the water structured layer is probably present around the particles at that concentration. Therefore, the latex is stabilized by electrostatic repulsions at low NaCl concentration and stabilized by hydration forces at higher concentrations. It may explain why no aggregation is observed at any NaCl concentration.

Conclusions

This paper presents a study of the colloidal stability of an amphoteric latex with a maximum positive charge (due to amine groups) of 50 ± 10 $\mu C/cm^2$ and a maximum negative charge (due to carboxyl groups) of -110 ± 15 $\mu C/cm^2$. These values were obtained by means of potentiometric titrations.

The stability study was carried out using a low angle light scattering technique for the measurement of aggregation rates. NaCl and $CaCl_2$ were used as electrolytes. The results show a behaviour according to DLVO theory at pH values below the i.e.p. (≈ 6) of the latex: it aggregates at sufficiently high electrolyte concentrations. However, the latex is stable at any electrolyte concentration when the pH is larger than the i.e.p. At pH 7 the latex aggregates at low $CaCl_2$ concentrations, but it is stable at concentrations above 20 mM.

The experimental data at pH values below i.e.p. have been fitted using the DLVO theory. The obtained interaction energy curves can qualitatively explain the latex stability.

Electrophoretic mobility measurements using NaCl, $NaNO_3$ and $Ca(NO_3)_2$ as electrolytes point out that:

1. There is no influence of the anion type (Cl^- or NO_3^-) on the mobility
2. The stability of the latex at high electrolyte concentrations and basic pH values can not be explained by electrostatic or steric repulsions
3. A high affinity of Ca^{2+} for latex surface seems to occur, but no charge inversion is observed

Taking into account that the surface of our latex is hydrophilic and that Na^+ and Ca^{2+} are hydrated cations, we propose the existence of hydration forces to explain the stability of our latex at high electrolyte concentrations and pH values above the i.e.p.

Fig. 5 Aggregation rate constant as a function of $CaCl_2$ concentration at pH 7

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