Cationic and Anionic Poly(N-isopropylacrylamide) Based Submicron Gel Particles: Electrokinetic Properties and Colloidal Stability

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A cationic and an anionic poly(N-isopropylacrylamide) (poly(NIPAM)) microgel latex were synthesized via batch radical polymerization under emulsifier-free conditions. The hydrodynamic properties, colloidal stability, and electrokinetic characteristics of these two samples were studied. The hydrodynamic particle size variation was discussed by considering the effect of salinity and temperature on the shrinkage of the thermally sensitive polymer domains. The colloidal stability also depended on temperature and electrolyte concentration. A stability diagram with two well-defined domains (stable and unstable) was obtained. The flow from one domain to the other was fully reversible due to the peculiar (de)hydration properties of the polymer. The electrokinetic behavior, which depends on electrical and frictional properties of the particles, was analyzed via electrophoretic mobility measurements. Results were discussed by considering both the particle structure dependence on temperature and salinity, and the electric double layer compression. In addition, the electrophoretic mobility data were analyzed using Ohshima’s equations for particles covered by an ion-penetrable surface charged layer, as well as using another simpler equation for charges located on a hydrodynamic equivalent hard sphere. Differences between the properties of both latexes were justified by the presence of a hydrophilic comonomer, aminoethyl methacrylate hydrochloride (AEMH), in the cationic microgel.

Introduction

Microgels are cross-linked polymer particles in the colloidal size range that swell in good solvents and that have a large number of applications in fields as diverse as medicine, biology, industry, or environmental cleanup. One of the most striking properties of microgels is their ability to undergo large volume transitions. This phase change is controlled by competing elastic, solvency, and ionic contributions. Special attention has been paid to temperature-sensitive aqueous microgels since cross-linked poly(N-isopropylacrylamide) (poly(NIPAM)) particles were prepared by Chibante in 1978 and subsequently reported in 1986. Poly(NIPAM) particles exhibit a temperature-induced volume transition. It is generally believed that hydration of the poly(NIPAM) chains originates local ordering in the water molecules around the amide group by means of hydrogen bonding. However, an increase in temperature increases molecular agitation, which in turn causes a disruption of the H-bonding between water and the amide groups. This leads to a breakdown of local water structure around the poly(NIPAM) chains that triggers hydrophobic attraction among isopropyl groups. This feature causes hydration of polymer chains below the lower critical solution temperature (LCST) and, consequently, microgel particles are swollen, while above the LCST the particles collapse. The LCST for poly(NIPAM) in water is around 32 °C.

There are numerous publications which refer to the characterization of anionic poly(NIPAM) particles, many of them reviewed by Saunders and Vincent and recently by Pelton. Characterization can involve gel structure, swelling, surface activity, rheology, electrical properties, colloidal stability, and interactions with other molecules (surfactants, drugs, proteins, etc.). However, characterization of cationic poly(NIPAM) microgels is not so usual in the literature, as these kind of particles have appeared in the past decade. Cationic poly(NIPAM) latexes are usually obtained by adding a positive comonomer together with the NIPAM in the polymerization reaction as well as a cationic initiator, commonly the 2′-azobis-(amidinopropane) di-hydrochloride (V50). Some cationic comonomers that can be found in the literature are (in acronyms) MADAP, DMAEMA, and DMAPAA, but few authors use the aminoethyl methacrylate hydrochloride (AEMH) employed in the present work.

Some properties of cationic and anionic poly(NIPAM) microgels have been analyzed as a function of salinity, temperature, and ionic specificity. Specifically, this paper aims to establish the hydrodynamic properties, the electrokinetic characteristics and colloidal stability of a cationic poly(NIPAM) latex, comparing the results with those of a classic anionic one. This analysis is only performed as a function of salinity (using an inert electrolyte, NaCl) and temperature. A second part will be focused on evidencing ionic specificities in the two poly(NIPAM) samples working with different electrolytes. It should be noted that Daly and Saunders published an excellent paper in which they studied the electrophoretic mobility and hydrodynamic diameter of anionic poly(NIPAM) particles, presenting a novel model for poly(NIPAM) volume phase transitions. Some mobility measurements were analyzed by applying Ohshima’s theory. In fact, Ohshima et al. previously used such a theory.
to analyze the mobility of hard polystyrene particles coated by a polyNIPAM shell and obtained promising results. Thus, part of the present work follows in the footsteps of these authors and, subsequently, some results will be compared with those shown in ref 24.

Materials and Methods

Reagents. N-Isopropylacrylamide (NIPAM) from Kodak was recrystallized from a toluene/hexane mixture (60:40). N,N-Methylenebisacrylamide (MBA) and aminoethyl methacrylate hydrochloride (AEMH) from Sigma and Polyscience, respectively, were used without further purification. 2-2’-Azobisiso (amidinopropane) di-chloride (V50) from Wako Chemical Group (Germany) was recrystallized from a water/acetone mixture. Potassium persulfate initiator (KPS) and sodium chloride (NaCl) from Sigma (France) were used as received. Water of Milli-Q grade (Millipore, France) was boiled for 2 h under a nitrogen stream before use.

Poly(NIPAM) Microgel Particle Preparation. Two poly(NIPAM) microgel latexes were prepared via batch radical polymerization. Polymerizations were performed under emulsifier-free conditions and were carried out in a 250 mL thermostated reactor, round-bottomed four-necked flask, equipped with a glass anchor-shaped stirrer, condenser, thermocouple, and nitrogen inlet. Well boiled and deoxygenated water was introduced under a constant stream of nitrogen. Monomers (NIPAM/MBA for anionic particles or NIPAM/MBA/AEMH for cationic particles) were first dissolved in water and added in the polymerization reactor. The amounts of each reactant used are given in Table 1. The polymerization temperature was set constant at 70 °C; after temperature equilibrium, the initiator (KPS for anionic particles or V50 for cationic particles) dissolved in water was introduced. The agitation rate was 200 rpm during all the polymerization reaction. The duration of the polymerization reaction in both cases was about 4 h.

Table 1: Masses and Volumes of Each Reactant Used in the Particle Synthesis

<table>
<thead>
<tr>
<th></th>
<th>water (mL)</th>
<th>NIPAM (mg)</th>
<th>MBA (mg)</th>
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Results and Discussions

Since the main objective of this work is to present the colloidal properties and electrokinetic characterization of the elaborated microgel particles, the polymerization kinetics, conversions, and the polymer partition between water phase (water soluble polymer) and particles are not considered in this paper. For more information regarding the polymerization aspects, the readers may consult the references.14,26

Particle Size Analysis. Transmission electron micrographs of dried microspheres (Figure 1) showed spherical particles with a similar size. As other authors have noted,7,10,24 a hexagonal arrangement was observed. The ratio between the particle diameter and the average center-to-center distance for neighboring particles allows an estimation of the decrease upon particle collapse during the drying process. This ratio was approximately 2.5 for both of our samples, which was in line with the PCS data presented below. The mean diameter and polydispersity index values for dried particles are given in Table 2. The high monodispersity of the latex pools is reflected in the PDI values, which are very close to unity in both cases. The mean diameter obtained by TEM cannot be compared with those values given by QELS measurements, as particles are hydrated in this last case. Nevertheless, both techniques showed that the measured as a function of temperature and salinity were detected by QELS. The poly(NIPAM) microspheres were highly diluted in aqueous solutions at a constant ionic strength and temperature, and then the colloidal stability was analyzed by monitoring the hydrodynamic size as a function of time.

Electrokinetic Study. The electrophoretic mobility \( \mu_e \) of microgel particles was measured as a function of salinity and temperature using a Zetasizer 3000HS from Malvern Instruments (Malvern UK). Due to the surface complexity of these microgels, the \( \mu_e \) data have not been translated into zeta potential values, as usual when working with hard colloidal spheres.

\[
D = \frac{kT}{3\pi\eta D_h}
\]

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( \eta \) the viscosity of the medium.

(a) Swelling Processes. To compare the swelling capacity of the two microgels synthesized (cationic and anionic), the swelling ratio \( S_w \) was obtained via

\[
S_w = \frac{V}{V_c}
\]

where \( V \) is the particle volume calculated from the hydrodynamic diameter in a swollen state and \( V_c \) in a collapsed state.

(b) Volume Phase Transition Temperature. The volume phase transition temperature \( T_{VPT} \) was obtained by measuring the hydrodynamic particle size variation induced by changing the medium temperature. As usual, the volume phase transition occurs in a relatively wide range of temperatures, and thus there is a need for a criterion to select the \( T_{VPT} \) as objectively as possible. The maximum of the \( \partial D_h / \partial T \) curve versus temperature was chosen as the best criterion.

(c) Colloidal Stability. Colloidal aggregation as a function of temperature and salinity were detected by QELS. The poly(NIPAM) microspheres were highly diluted in aqueous solutions at a constant ionic strength and temperature, and then the colloidal stability was analyzed by monitoring the hydrodynamic size as a function of time.

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anionic particles were much bigger than the cationic ones. The lower size of the positive particles can be justified by the presence of the AEMH co-monomer. During the polymerization reaction, the effect of this charged co-monomer on the nucleation step enhances the colloidal stability of the particles that were formed initially and, consequently, reduces the final particle size (compared to the free co-monomer recipe).

(a) Volume Phase Transitions. The hydrodynamic diameter of the microgel particles was first examined as a function of temperature in a 10$^{-3}$ M NaCl nonbuffered solution. The data are shown in Figure 2. The hydrodynamic particle size for both microspheres decreases with increasing temperature (from 20 to 45 °C). Drastic changes in the diameters were observed in the vicinity of the LCST of the pure poly(NIPAM) polymer (32 °C). Therefore, the volume reduction is attributed to the hydrogen bonding disruption between water and the polymer. The temperature that separates the regime wherein water behaves as a good solvent from the other one where it behaves as a poor solvent ($T_{VPT}$) was calculated from the maximum of the $\delta D_h/\delta T$ curve versus $T$, using a polynomial fitting. The $T_{VPT}$ values obtained in this way were 31.7 °C and 32.4 °C for the anionic and cationic samples, respectively. This small difference is plausible, and it may be originated by the presence of the water-soluble co-monomer (AEMH) in the cationic particles, which enhanced the hydrophilic character of these particles. This increment in hydrophilicity would make the $T_{VPT}$ shift toward higher values.

The particle swelling ratios ($S_w$) were calculated from the hydrodynamic volumes at 20 °C (swollen state) and 50 °C (collapsed state), and the data are also shown in Table 2. As can be seen, the swelling capacity of the cationic latex is higher than that of the anionic one. Once again, this difference in the swelling behavior may be caused by the effect of the AEMH co-monomer, which, in addition to its tendency to be hydrated, probably alters the internal structure (cross-linking density) during the synthesis of the positive particles.

(b) Salt Effect. The effect of salt concentration on the hydrodynamic diameters was studied in two different ways: (i) on one hand, by studying how the ionic strength shifts the volume phase transition temperature, and (ii) on the other hand, by observing the effect of salinity on the swelling processes at a fixed temperature.

In the first study, the particles were dissolved in solutions with different NaCl concentrations (from 10$^{-3}$ M to 10$^{-1}$ M). For each salt concentration the diameter evolution versus temperature was registered. Data corresponding to the cationic system are shown in Figure 3. Due to the low colloidal stability of the collapsed particles when increasing both salinity and temperature, it was not possible to determine the particle diameter in some cases. Thus, the curves shown in Figure 3 finished when the aggregation process began. Nevertheless, a clear relationship can be seen between the ionic strength and the volume phase transition temperature: $T_{VPT}$ values decrease when salt concentration is increased. This behavior (which was also observed for the anionic particles) is attributed to the effect of salt on the solubility of poly(NIPAM) chains. The hydration behavior of poly(NIPAM) microgels in NaCl solutions is shown in Figure 4.
of the ions generates an important competition for the water molecules that hydrate polymer chains. Addition of NaCl to the dispersion produces dehydration of the poly(NIPAM) chains, leading to particle deswelling, which becomes more pronounced with increased electrolyte concentration. In addition, most recently data suggest that the salting-out of the isopropyl group in NIPAM chains is also due to the increase of the surface tension of the aqueous solution with the addition of salt.29,30

Figure 4 shows the second set of experiments, where salinity is increased at constant temperature (25 °C). As can be seen, particle size decreases with an increase in ionic strength, and the shrinkage is more important at high salt concentrations. At low salt concentrations, the hydrodynamic diameter of both microgel particles remains almost unaltered by the medium salinity. However, there is a critical salt concentration from which particle size rapidly diminishes. This concentration is about 330 mM and 480 mM for the anionic and cationic sample, respectively. Once again, this difference is a result of the presence or absence of the hydrophilic AEMH co-monomer in the particles. Competition between ions and polymer chains for hydration becomes more intense if soluble AEMH molecules are interspersed in the poly(NIPAM) skeleton. This is why the salt concentration needed to dehydrate the microgel particles is higher for the positive sample.

Despite the differences, both latex pools present similar behavior that can be justified as follows. (1) The first and most important factor in the decrease in particle size induced by addition of salt is the solubility reduction of poly(NIPAM) domains. In fact, the LCST of homopoly(NIPAM) is dramatically affected by salinity. As has been discussed above, this is due to the perturbation of the water cage surrounding the isopropyl group caused by the competitive hydration of the added ions. Consequently, poly(NIPAM) chains collapse at lower temperatures in the presence of ions than in free salt solutions.11,28,32 (2) In addition, the osmotic pressure of the solution increases for increasing ionic strength. Therefore, water is released from the inside of the microgel by means of an osmotic mechanism, reducing the mean particle diameter.18,33 (3) Finally, a hairy particle model also would explain the particle size reduction by salt. If particle surfaces are formed by polyelectrolyte chains, the addition of salt would screen electrostatic repulsion between them, promoting the collapse of the chains.34

Although these three mechanisms occur simultaneously, the size variation is mainly given by the first one. At the very least, a simple theoretical treatment can be used to confirm that osmotic pressure increment is not the major driving mechanism. The influence of salt on the osmotic pressure theoretically produces a size decrease with asymptotic behavior:33,35 $D_h \sim c_s^{-1/5}$, where $c_s$ is the salt concentration, irrespective of the particle network charge. This linear behavior has been also plotted in Figure 4. As shown, the experimental size reduction is much sharper than was theoretically predicted, which demonstrates that a mechanism other than that related to the osmotic pressure must be responsible for the particle deswelling.

**Colloidal Stability as a Function of Salinity and Temperature.** The Hamaker constant of swollen poly(NIPAM) microgels is similar to that of water. Thus, van der Waals attraction forces between these particles embedded in water is almost nonexistent. In addition, polymer tails are extended from the gel structure enhancing steric repulsion which also contributes to the stability of the system. Therefore, colloidal aggregation is possible only for deswollen particles, where the van der Waals attraction becomes significant28 and the steric barrier disappears. Due to the high sensitivity shown by the volume transition of the poly(NIPAM) particles on both ionic strength and temperature, the colloidal stability was also studied considering these two parameters. To elaborate a stability diagram, aggregation was analyzed as described below. Stability was studied at different temperatures keeping the salinity constant. Aggregation was detected by monitoring the temporal evolution of the particles’ diameter, as shown in Figure 5. If the system was stable, the particles would continue to be single entities and the hydrodynamic diameter would remain constant. On the contrary, if aggregation took place the average hydrodynamic diameter would increase. So, temperature was carefully changed degree by degree at constant salinity to determine the critical temperature that separated the stable from the unstable domain. As an example, the positive particles did not aggregate at 25 °C in a 750 mM NaCl solution, but they did so at 26 °C. This laborious procedure gives the critical flocculation temperature (CFT) and the critical flocculation ionic strength (CFI), which are used to plot the stability diagram shown in Figure 6. It exhibits two domains (stable and unstable). The limit between both domains was found to be similar for the two microgels, indicating that interactions involved in colloidal stability of the two samples are similar. Therefore, aggregation must be governed by the hydration/dehydration characteristic of the poly-
et al.28 Although the technique used by these authors to evaluate moderate and high salinity, particles aggregate almost at room make particles overcome the potential barrier. However, at particles are stable (a potential barrier exists), and aggregation (NIPAM) chains. At very low salinity concentration, shrunken Figure 6. Stability diagram for the negative (●) and positive (■) microgels as a function of salt concentration and temperature. (NIPAM) microgels. At very low salinity concentration, shrunken Figure 7. Electrophoretic mobility of the negative (●) and positive (■) microgels as a function of temperature in a 10−3 M NaCl solution. particles are stable (a potential barrier exists), and aggregation effects.36 All these results illustrate the complexity of the stability is different and insufficient data were collected in that case, their results agree with those shown in Figure 6. It is worth highlighting the reversibility of the aggregation process. Aggregates can be completely broken yielding to individual stable particles just by reducing temperature and/or ionic strength. The reversible aggregation of soft particles has also been theoretically justified by means of osmotic and elastic effects.38 All these results illustrate the complexity of the colloidal stability of poly(NIPAM) particles, where interaction potentials are a combination of van der Waals, electrostatic, steric, and hydration contributions.

Electrokinetic Properties as a Function of Temperature. The electrophoretic mobility of poly(NIPAM) microparticles was studied as a function of temperature at a constant salinity (10−3 M NaCl) in a nonbuffered solution. The data are shown in Figure 7. The positive mobility found for the cationic latex would confirm that the AEMH copolymer was incorporated into the polyNIPAM mesh. Results can be explained taking into account the fact that the motion of microparticles under an external electric field is the result of a competition between electric and frictional forces.37 Below 32 °C, the electrophoretic mobility of both microgels is found to be around zero, reflecting both the low surface charge density and the high friction coefficient of the swollen particles. However, a dramatic change in the electrophoretic mobility versus temperature was observed above the T_VPT. As expected, the absolute values of the electrophoretic mobility increase with an increase in temperature, reflecting the thermal sensitivity of the elaborated particles. This \( \mu_e \) increment is attributed to three factors: (i) the increase in the surface charge density due to the reduction in the particle size, (ii) the enhancement of the local charge concentration on the particle’s surface owing to the reorganization of the charged groups, which would tend to be relocated in hydrophilic environments when particles shrink, and (iii) the frictional coefficient reduction of the particles when they collapse.

A deeper analysis shows that both latexes differ when comparing the hydrodynamic (Figure 2) and the electrophoretic data (Figure 7). The T_VPT was defined as the temperature where the \( \delta D_e / \delta T \) curve versus T reached a maximum. Daly and Saunders24 defined an analogous term for the temperature associated with transitions in the electrophoretic mobility, namely, “electrokinetic transition temperature” (T_ET). The T_ET values obtained from Figure 7 were 33.2 °C and 33.0 °C for the anionic and cationic sample, respectively. A difference between the T_VPT and T_ET values \( (\Delta T) \) would suggest that the collapse of polyNIPAM microgel particles occurs in different stages.24 This difference was 1.5 °C and 0.6 °C for the anionic and cationic nanogels, respectively. Although the \( \Delta T \) value for the anionic particles is lower than those reported in refs 24 and 38, it triples the value for the cationic sample. Accordingly to Daly and Saunders,24 the internal structure of the anionic particles could be heterogeneous, with a core made of high density cross-linked polyNIPAM chains and a lightly cross-linked periphery. This structure would support a volume transition in different stages, which would lead to differences between the T_VPT and T_ET values. As the \( \Delta T \) value for the cationic latex is very low, no different transition stages should be expected. Therefore, the cationic nanogel would present a more homogeneous internal structure promoted by the addition of the AEMH copolymer during the particle synthesis. To confirm this statement about hetero- or homodistribution of polymer chains, another simple theoretical treatment can be applied by using both Helmholtz’s and Smoluchowski’s formulae, as reported by Pelton et al.38 If particles are considered as hard spheres with all the charged groups located at the surface (which is a rather bad approximation for polyNIPAM particles), the electrophoretic mobility can be related to the surface charge density and the hydrodynamic particle radius \( r_h \) using the following equation: \( \mu_e = -Ne/4\pi\eta kr_h^2 \), where \( k \) is the reciprocal Debye length, \( \eta \) the viscosity of the medium, \( e \) the elementary charge, and \( N \) the number of superficial charged groups per particle. The thermal shrinkage of the hydrogel particle leads to an increase in the surface charge density and, subsequently, in the electrophoretic mobility (in absolute value) as experimentally observed. In this way, the electrophoretic mobility was plotted versus \( r_h^{-2} \) and its value was controlled by the incubation temperature, as shown in Figures 8a and 8b. Again, a difference between the anionic and the cationic sample is observed. A single linear dependence is observed for the latter, while a two-step linearity is found for the former. Regions with different linearity represent different stages of collapse. Daly and Saunders24 found three stages for their anionic polyNIPAM
particles. We observe a two-stage transition for the anionic sample and only one stage for the cationic one, which must be caused by differences in the internal structure among both samples. The anionic latex must have a heterogeneous distribution, while a homogeneous chain distribution would be expected in the cationic sample, as depicted in Figure 9. Finally, the good linearity observed in Figures 8a and 8b allows us to obtain some quantitative information.

\[ N = \text{slope of the linear regression} \]

The \( N \) value for the cationic latex is \( 4.6 \times 10^3 \), whereas that of the anionic particles is equal to \( 1.0 \times 10^5 \). A higher \( N \) value would be expected for the cationic sample, as it contains charges supplied by the EAMH co-monomer; however, the results are opposite to those expected. Moreover, these large differences in the number of superficial charged groups cannot be justified taking into account the similar values of electrophoretic mobility obtained for both microgels (see Figure 7). Therefore, this theoretical treatment only fits the experimental results qualitatively but not quantitatively.

**Electrokinetic Properties as a Function of Ionic Strength.**

The effect of ionic strength on the electrophoretic mobility of the cationic microgel was studied at different temperatures. Data of this positive latex are shown in Figure 10. The mobility exhibited a continuous decrease, irrespective of the temperature value, although different patterns could be observed above and below the \( T_{VPT} \). Below \( 32^\circ C \) the \( \mu_e \) shows an exponential behavior. The exponential decay disappears as soon as particles begin to collapse. Above the \( T_{VPT} \), there is a linear behavior that changes to a convex curve as temperature increases. The convexity, along with the mobility reduction at high ionic strengths, is a common feature found in hard colloidal particles, which usually show a maximum. This widespread behavior has been often explained by referencing hairy layer models, preferential ion adsorptions or anomalous surface conductances.\(^39\) It should be noted that the convexity becomes more marked at high temperatures where the particle size is reduced to its minimum value, increasing the hardness of the microgel as much as possible.

Nevertheless, a deeper analysis can be made for these soft particles using Ohshima’s theory,\(^40\) which is applicable to systems with an ion-penetrable layer located at the water/particle interface. Ohshima et al.\(^25,26\) successfully applied such a theory for polystyrene particles coated by an adhered polyNIPAM layer. Daly and Saunders\(^24\) also checked the validity of the theory for pure polyNIPAM nanogels. To apply this theory to our \( \mu_e \) data, the logarithmic scale shown in Figure 10 has been converted into a linear scale (see Figure 11). In addition, it must be assumed that the nanoparticles consist of a relatively high cross-linked core and a lightly cross-linked shell that contains most of the charged groups incorporated from the initiator and the water-soluble poly(AEMH). The latter is assumed to be equivalent to Ohshima’s surface charged layer and has a thickness \( \delta \). Provided that \( \delta \) is larger than the double layer
thickness \( (1/\kappa) \) the following equations can be applied:

\[
\mu_e = \epsilon_0 \epsilon_r \frac{\Psi_r/k_m + \Psi_{\text{DON}}/\lambda}{1/k_m + 1/\lambda} + \frac{z e N}{\eta \lambda^2}
\]

with

\[
\Psi_{\text{DON}} = \frac{kT_v e}{v e} \ln \left[ \frac{z N}{2 v m} + \left( \frac{z N}{2 v m} + 1 \right)^{1/2} \right] + \frac{2 v m}{z N} \ln \left[ 1 - \left( \frac{z N}{2 v m} + 1 \right)^{1/2} \right]
\]

\[
\Psi_0 = \frac{kT_v e}{v e} \left[ \ln \left( \frac{z N}{2 v m} + \left( \frac{z N}{2 v m} + 1 \right)^{1/2} \right) + \frac{2 v m}{z N} \ln \left[ 1 - \left( \frac{z N}{2 v m} + 1 \right)^{1/2} \right] \right]
\]

\[
\lambda = \left( \frac{\gamma}{\eta} \right)^{1/2}
\]

\[
\kappa_m = \kappa \left[ 1 + \left( \frac{z N}{2 v m} \right)^{3/4} \right]
\]

\[
\kappa = \left( \frac{2 k T_v e}{\epsilon_0 \epsilon_r kT} \right)^{1/2}
\]

Here, \( \eta \) is the viscosity of the medium, \( \gamma \) is the frictional coefficient of the hydrogel layer, \( \epsilon_0 \) is the permittivity of a vacuum, \( \epsilon_r \) is the electronic charge, \( \Psi_r \) is the Donnan potential of the hydrogel layer, and \( \Psi_0 \) is the potential at the boundary between the surface layer and the surrounding solution. \( \kappa_m \) is the reciprocal of the double layer thickness within the surface charge layer. \( N \) is the density of charged groups of valency \( z \) in the surface layer, and \( n \) is the density of electrolyte ions of valency \( v \) in the bulk. Thus, \( z e N \) represents the density of fixed charges in the hydrogel layer. \( \lambda \) represents the degree of friction experienced by the liquid flowing through the surface layer. \( 1/\lambda \) is a softness parameter that approaches zero as a particle becomes rigid. Finally, \( k \) is the Boltzmann constant and \( T \) the absolute temperature.

The fitting procedure explained by Daly and Saunders was then used by means of a Mathematica software. Despite having few experimental data in the \( 10^{-3} - 10^{-1} \) M range, where Ohshima’s theory works well, the data were properly fitted by the theoretical predictions, as shown in Figure 11. The \( 1/\lambda \) and \( N \) values obtained by the fitting process are plotted as a function of temperature in Figure 12. The softness parameter \( (1/\lambda) \), which serves as a measure of the flow penetration, decreases with increasing temperature, as expected. Moreover, the density of charge groups \( (N) \) increases with particle collapse, which was also expected. The trends are similar to those obtained by Ohshima et al. and Daly and Saunders. However, our \( 1/\lambda \) values are lower than those obtained by the last authors working with anionic polyNIPAM microparticles. Therefore, the presence of EAMH co-monomers must originate a special cross-linked structure that gives more rigid nanogels (low \( 1/\lambda \) values), lower particle size (see Figure 2), and different volume phase transition mechanisms (see Figures 8 and 9) than conventional anionic polyNIPAM formulations.

Finally, mobility versus electrolyte concentration at different temperatures (Figure 10) can be also plotted as \( \mu_e \) versus temperature varying the ionic strength, as shown in Figure 13. Although both figures (10 and 13) clearly show the mobility diminution for increasing salt concentration, only the latter allow us to observe how the increase in ionic strength makes the \( T_{\text{VPT}} \) shift slightly toward lower values. This feature was already observed with the \( T_{\text{VPT}} \) (see Figure 3). The drastic relationship between the \( \mu_e \) and the structure of the particles makes
electrophoretic mobility be a powerful tool to evaluate volume transitions of thermal sensitive microgels.

Conclusions

Two highly monodispersed poly(NIPAM) microgel latexes were synthesized via surfactant free polymerization. Swelling/deswelling properties, electrokinetic behavior and colloidal stability have been studied as a function of temperature and NaCl concentration. Cationic particles showed higher $T_{VP}^p$ than that of the anionic latex. The presence of a hydrophilic co-monomer (AEMH) in the formulation of the positive microgel produces an increase in the solubility of the thermally sensitive polymer domains. For the same reason, the amount of salt needed to dehydrate the polymer chains, and subsequently shrink the particles, was higher in the cationic sample. The colloidal stability was very sensitive to temperature and ionic strength. A stability diagram with two clearly defined domains (stable and unstable) was obtained. Aggregation was fully reversible, and passing from one domain to another was possible simply by controlling the temperature and/or the electrolyte concentration. Finally, electrophoretic mobility measurements have become a useful tool to obtain some information about the structure of anionic and cationic polyNIPAM particles. The former seem to present a heterogeneous distribution of polyNIPAM chains with a compact core and a soft external layer, while the cationic sample seems to be made of a more rigid and homogeneous mesh.

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References and Notes

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