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ORIGINAL CONTRIBUTION

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Effect of electrolyte type on the electrokinetic behavior of carboxylated polystyrene model colloids

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Abstract Carboxylated polystyrene latex particles were prepared by emulsifier-free emulsion polymerization of styrene using an azo-initiator (ACPA), which provides carboxyl end groups on the latex surface. Two latexes were characterized using TEM, PCS, conductimetric and potentiometric titrations, and electrophoretic mobility. To determine the hydrophobic or hydrophilic character of these latexes, the maximum adsorption of a non-ionic surfactant (Triton X-100) was also studied and compared with other type of latexes. The electrophoretic mobility of these functionalized model colloids was studied in the presence of various types of inorganic electrolytes. The μ_e–$\log C$ curves of these latexes exhibit a smooth maximum at an electrolyte concentration of around 10^{-3} and $5 \cdot 10^{-3}$ M for 1:1, 2:1 and 1:2 electrolytes. When a 3:1 electrolyte ($LaCl_3$) was used, the electrophoretic mobility changed to positive values at high concentration due to the specific adsorption of lanthanum species. In general, the surface characteristics of these carboxylated latexes are very different in comparison to other latexes with the same functionality because the carboxyl groups are provided by the initiator, while in most of the cases these groups are provided by ionic comonomers (acrylic, methacrylic acids, etc.) used in the copolymerization with styrene.

Key words Carboxyl polystyrene latexes – electrophoretic mobility

Introduction

Monodisperse spherical polystyrene latexes have proven to be model systems which are widely used in many practical applications (calibration standards, supports for bio-molecules, etc.) and are also suitable for studying fundamental colloidal phenomena. The use of such latexes require monodisperse spherical particles having a known amount of covalently bound surface end groups. There are numerous references in the literature concerning the synthesis of carboxylated latexes prepared in the absence of emulsifier to produce particles with carboxyl end groups on the particle surface, which result from the use of several monomers: copolymerization of styrene with acrylic acid, methacrylic acid and others [1–4]. However, there has not been much work on the preparation of carboxylated latexes in which the only monomer is styrene and the end carboxyl groups are provided by the initiator [5–7]. In principle, this type of latex could show different electric double layer structure than that prepared by copolymerization of different monomers.

The synthesis of carboxylated polystyrene particles prepared with the initiator 4,4′-azobis (4-cyanopentanoic acid) (ACPA) and its surface characterization were carried out in a previous paper [5]. The objective of this work is to complete the surface characterization by adsorption of a non-ionic surfactant (Triton X-100) and the electrokinetic characterization of these latexes by studying the effect of different electrolytes on the electrophoretic mobility. Furthermore, several controversies about the relation between the surface charge density and the ζ-potential of polystyrene particles have been presented [1, 8–11]. It has been found that latexes with different surface charge density (σ), present electrophoretic mobility curves which pass through a maximum as a function of increasing ionic strength, and the μ_e values are similar for several latexes with different σ [10], or even higher for those with a lower surface charge density [11].

Experimental studies concerned with the maximum in the electrophoretic mobility have mainly used simple 1:1 electrolytes [11–14]. To explain these results some authors [15, 16] have recently reported a decrease of the hydrodynamic radius as the ionic strength increases due to the compression of the hairy layer. However, Gittings and Saville [17] found similar particle size obtained by TEM (156 nm) or by PCS (160 nm) at no electrolyte concentration. Several authors [9, 18] have reported studies with divalent and trivalent counterions and co-ions, using polystyrene latexes which carry sulfate or sulfonate functional groups. The present paper aims to give new results on the electrokinetic behavior of two carboxylated polystyrene latexes in the presence of divalent and trivalent co-ions and counter-ions. This study may provide a more direct understanding about the structure and nature of the electric double layer which surrounds these carboxylated particles in which the carboxyl end groups are provided by the initiator.

Experimental

Materials

Styrene monomer was obtained from Merck and was distilled under reduced nitrogen pressure at 40 °C. The initiator used in this work was the 4,4′-azobis (4-cyanopentanoic acid) (ACPA) from Aldrich and was used as received. The different electrolytes used throughout this work were analytical grade reagents (all from Merck) and they were used without further purification. Double-distilled and deionized (DDI) water was used throughout.

Preparation of latexes

In order to prepare carboxylated polystyrene particles, we have followed the steps developed by Guthrie [6] of surfactant-free emulsion polymerization of styrene with ACPA as the initiator. This method has the advantage that carboxyl surface groups come from the initiator molecules. Table 1 shows the synthesis conditions used to obtain two samples (called DJL-5 and DJL-6) which were prepared with different amount of initiator. The materials were poured into a 600 cc three-necked glass flask and polymerized in a nitrogen atmosphere. To maintain vigorous stirring, the T-shape stirrer (1 × 5 cm) was fitted 1 cm from the bottom of the flask.

Table 1 Polymerization recipe used in the carboxylated polystyrene latexes

Latex	Styren (g)	ACPA (mM)	NaOH (mM)	Stirrer (rpm)	Temperature (°C)	Reaction time (h)
DJL-5	25	2.76	7.43	350	80.6	10
DJL-6	25	4.14	11.14	350	80.6	7

The particle sizes of the two latex samples were obtained by transmission electron microscopy (TEM) (Servicios Técnicos de la Universidad de Granada). The particle size was determined by direct measurement of at least 500 particles for each sample using a Calcomp Drawing Board Digitizer and taking three different points of the sectional view for each particle. By a computer program the weight-average (D_w), number-average (D_n) diameters and standard deviation for each sample were obtained. The latex was considered to be monodisperse if the polydispersity index (p.d.i., defined as D_w/D_n), was less than 1.05.

The particle size of the two latexes was also determined as a function of NaCl concentration by using a 4700-Malvern Instruments apparatus (PCS). Six measurements were made at each electrolyte concentration with an angle of 90° by optimizing the sample time of the measurement conditions.

Cleaning process and surface characterization

A long and comprehensive cleaning process was followed before measuring the surface charge density of these latexes. The method used proved to be very important in the determination of the surface charge, as it was previosly found by several authors [10, 19]. The latexes were filtered through glass wool, then they underwent repeated cycles of centrifugation–redispersion (with the aid of sonication) and finally they were cleaned using serum replacement with DDI water. After these processes the specific electrical conductivity of the latexes was found to be lower than 10 μS/cm^{-1}.

Surface charge densities (σ_o) of DJL-5 and DJL-6 latexes were determined by conductimetric and potentiometric titrations of the cleaned latexes. The pH-meter (Crison 2002) and conductimeter (Crison 525), together with the dosifier (Metrohm 665 dosimat) were connected to a PC computer (via RS232 interface), which collected the data, fixed the straight lines and calculated the intersection point. Then, the conductimetric and potentiometric titrations were automatically carried out using diluted latex in a stirred vessel under an inert hydrogen atmosphere.

The electrophoretic mobilities of these cleaned latexes were measured at 25 °C under different electrolyte types and concentrations using a Zetasizer IV (Malvern Instruments). The electrophoretic mobility values were obtained by taking the average of (at least) five measurements at the stationary level in a cylindrical cell. The experimental error was taken as the standard deviation in these measurements. For the data shown throughout this paper, the standard deviation was always lower than ± 0.20 10^{-8} m^2/Vs. Samples were prepared by adding approximately 0.01 ml of the latex to 10 ml of each electrolyte solution.

Results and discussion

Surface characterization

Figure 1 shows the particle size distribution of latex DJL-6 obtained by TEM. Similar result was obtained for latex DJL-5. Table 2 shows the diameter (*d*) and the polydispersity index (p.d.i.) for the two prepared latexes. The particle diameters are almost the same for both samples with low standard deviations. The values for the PDI (1.005 or 1.006) clearly indicate that all latexes were monodisperse, although in Fig. 1 a thin scale is used.

Figure 2 shows the conductimetric and potentiometric back titration curves for the sample DJL-6. Similar curves were obtained for latex DJL-5. It is not possible to know the total surface charge densities (σ_o) from direct titration in latexes with weak acid groups on their surface, as it is necessary to have protonated all these groups (COOH); this occurs at pHs around 3, and in this conditions the colloidal systems would be completely aggregated. This is why we have employed back titrations to obtain the σ_o values [5]. In Fig. 2, we can see that the changes in the slopes in the conductivity curve coincide with the inflexion points of the potentiometric one. The last row in Table 2 shows the surface charge densities (σ_o) of the cleaned latexes, which were calculated as the average of several titrations, and the differences were always less than 5%.

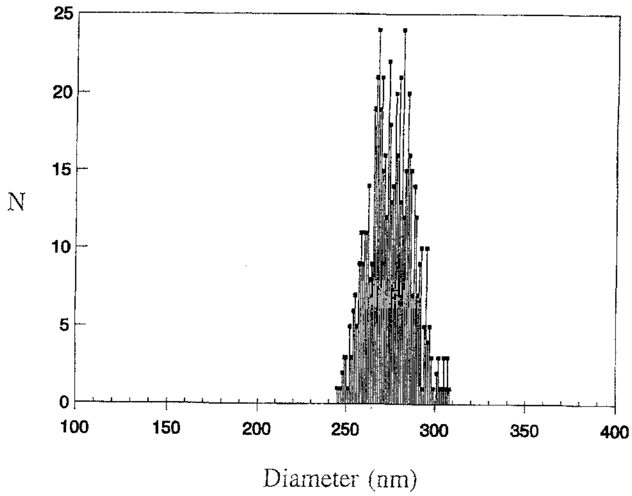


Fig. 1 Size distribution for DJL-6 latex

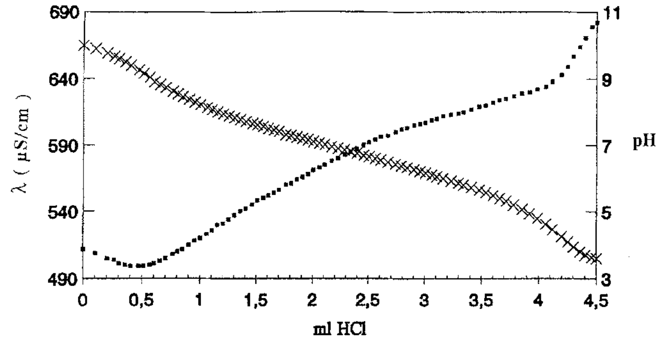


Fig. 2 Conductimetric (λ) and potentiometric titration for DJL-6 latex: ■, λ; ×, pH

Table 2 Characteristics of carboxylated polystyrene latexes: particle size TEM, polydispersity index (p.d.i.) and surface charge density (σ_0)

Latex	*d* (nm)	p.d.i.	σ_0 ($\mu C/cm^2$)
DJL-5	276 ± 12	1.0052	16.3 ± 0.7
DJL-6	281 ± 13	1.0060	19.2 ± 0.8

The results presented in Table 2 confirm the formation of carboxylated polystyrene model colloids with almost identical particle sizes and a slight difference in the surface charge density: the latex DJL-6 has 18% more of charge than DJL-5. Thus, the increase of 50% in the amount of initiator only produces a slight increase in the surface charge and the same particle size. The latter effect is due to the fact that for increasing the surface charge we have to increase the initiator concentration which also tends to produce a diminuition in the particle size; but also the

NaOH concentration has to be increased to dilute the initiator, which would yield a higher ionic strength and, therefore, an increase in the particle size [20].

Electrokinetic characterization

The electrophoretic mobilities of carboxylated polystyrene latexes were measured to characterize the electric double layer surrounding the particles. Besides, we have conducted experiments to see whether mobility changes on the addition of different mono-, di- and trivalent co-ions and counter-ions.

The electrophoretic mobility values (μ_e) for latexes DJL-5 and DJL-6 were measured as a function of pH at a constant ionic strength of 0.002 M KBr. The pHs were controlled using different buffers (acetate at pH 4 and 5, phosphate at pH 6 and 7, and borate at pH 8 and 9). The results given in Fig. 3 show that the μ_e values were almost constant when the pH increased from 6 to 10 with a pronounced decrease at a lower (acid) pH. From the results for both latexes, it is possible to recognize the weak acid character of the surface end-groups which were provided by the initiator. One remarkable result observed in Fig. 3 is the similar values of μ_e for both different samples, even when the surface charge density varied from 16.3 to 19.2 μC/cm^2 (i.e., an increase of 18%). However, it can be expected that the mobility of the most charged latex (DJL-6) would be higher. This result is contrary to the predictions of the classical electric double layer models. Some authors [21, 22] have explained this anomalous electrokinetic behavior on the basis of the surface conductance between the shear plane and the particle surface. Since the surface conductance is directly proportional to the surface charge density it could account for the disagreement between the σ_o and the μ_e values. In a previous paper [5], with this type of latex it was also found that the μ_e values remained constant between pH 6 and 9 although the surface charge decreased by almost 50%. The insensitivity of the mobility data against the surface charge variations has been a usual behavior of polystyrene model colloids with sulfonate [10] or amidine [23] end-groups on the surface.

Mobilities of latexes DJL-5 and DJL-6 as a function of KBr concentration are shown in Fig. 4. The results confirm that there is no significant differences in the μ_e values in all the salt concentration range for both latexes. The same trend was found for other monovalent electrolyte as NaCl (see Figs. 6 and 7 for NaCl). Thus, the insensitivity between μ_e and σ_o is a proper result of the carboxylated polystyrene latexes prepared with the use of ACPA as initiator, and the same electrokinetic behavior has been found for two monovalent co-ions (Br^- and Cl^-) and when the mobility was measured versus the pH.

Figure 4 also shows that the mobility of the particles increases (in absolute value) with increasing salt concentration, reaching a maximum at a concentration of 5 10^{-3} M. Similar electrokinetic behavior was also found with sulfonated latexes [9] with surface charges between 12.3 and 17.0 μC/cm^2, i.e., the same quantity as the carboxylated latexes now studied. However, the increase in the mobility was of around 2.5 units, while in Fig. 4 it is 1 unit or less. Furthermore, the maximum appears at a lower concentration: $5 \cdot 10^{-2}$ M for the sulfonated latexes and $5 \cdot 10^{-3}$ M for the carboxylated ones. This difference seems to be a consequence of the different character of the surface end groups. The mobilities in Fig. 4 were measured without control of the pH, i.e., pH around 5.5 or 6, where all the carboxyl groups are not dissociated and the

Fig. 3 Electrophoretic mobility (μ_e) against pH for both latexes

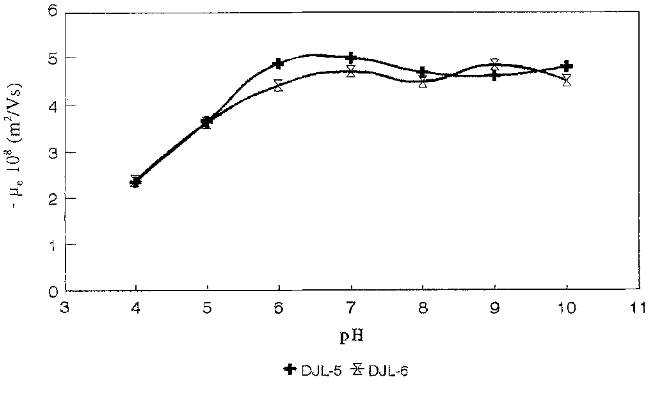
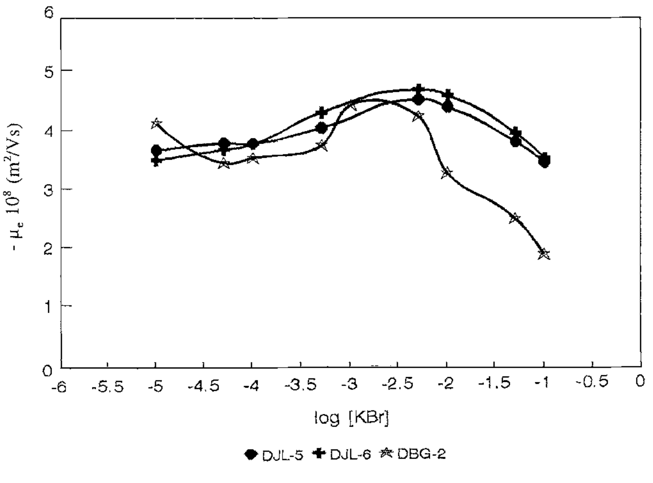


Fig. 4 Electrophoretic mobility (μ_e) against electrolyte concentration (KBr) for both carboxylated latexes and sulfonate latex (DBG-2)



effective surface charge is lower. This could be the reason why the mobility curve is softer and the maximum appears at lower concentration for the latexes DJL-5 and DJL-6. In fact the stability of this type of latex is lower at pH 5, as was shown in a previous paper [5].

In order to compare the intensity of the maximum for latexes with very different surface charge, in Fig. 4, we also show the mobility values of a sulfonated latex (called DBG-2) with a surface charge of $(1.3 \pm 0.1)\ \mu C/cm^2$ and a particle size of (287 ± 12) nm. This latex was prepared from the recipe described in ref. [9], but without second injection. A more significant maximum was obtained even though the surface charge is lower than that of the carboxylated latexes. However, the maximum appears at lower concentration (10^{-3} M) for the latex with a lower surface charge. Thus, the position of the maximum in the concentration range seems to be related with the surface charge of the particles, but the variation in σ_o cannot explain the form of the curve and the intensity of the maximum.

The existence of a maximum in the μ_e–log C curves is in marked contrast to the classical theory of the electric double layer which predicts a continuous decrease in the electrokinetic potential (and, therefore, in μ_e) with increasing salt concentration [24]. Various qualitative explanations for this maximum have been proposed [12–18, 21, 25, 26]. A preferential adsorption of co-ions onto the surface was invoked by several authors [12, 18]. The existence of polyelectrolyte chains on the surface of polymer colloids is considered in the hairy layer model [13]. Physical changes in particle surface properties were also invoked by other authors [26]. In the last case, the authors consider that the shift of the shear plane toward the bulk solution is due to the surface roughness or to the existence of polyelectrolyte chains on the surface of latex particles. This displacement of the shear plane results in a decrease of the mobility in the usual way and lowers it to a much larger extent by introducing ionic conduction (or surface conductance) between the solid surface and the shear plane. The surface conductance is especially important at low ionic strength and reduces the mobility values by a much greater percentage.

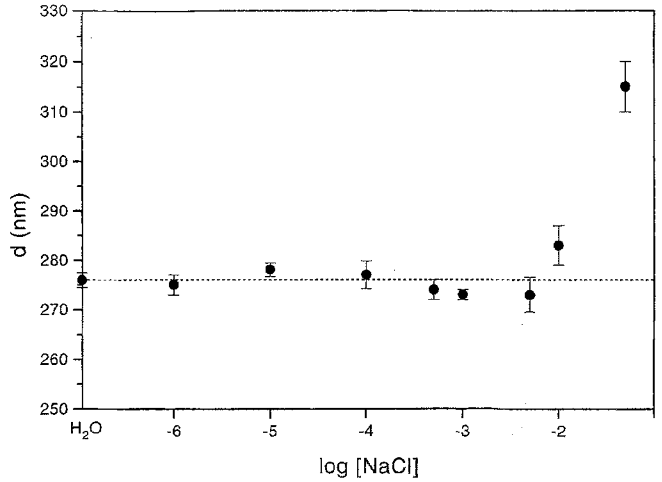


Fig. 5 Hydrodynamic radius (d) against electrolyte concentration (NaCl) for DJL-5 latex

The carboxylated latexes prepared in this work by emulsion polymerization using ACPA as initiator, are different from those synthesized by copolymerization of styrene and other ionic comonomer (acrylic or methacrylic acids, for instance). In the last case a hydrous polyacrylic acid layer exists on the surface which can prevent the approach of antibodies or antigens to the polymer surface. In some cases, the thickness of this layer can even be of 10 Å [27]. In our case, using the same procedure as Shirahama and Suzawa [27], the position of the shear plane is 2.5 Å from the polymer surface. This result seems to confirm that the carboxylated latexes prepared by ACPA as initiator have a thinner solid–liquid interface layer than those prepared by copolymerization with an ionic comonomer. Several authors [14–16] have reported a decrease in the particle size of 9 nm [15] or 4–7 nm [16] as the ionic strength increases, which could explain the mobility maximum as a consequence of the electrophoretic relaxation coupled with a variable shear plane. In Fig. 5, we show the hydrodynamic radius of the DJL-5 latex particles versus the NaCl concentration measured by PCS. The dotted line shows the initial particle size (in water) which was the same as that obtained by TEM, because the difference of 2 nm between both types of measurement is completely within the experimental error. The increase in particle size at a concentration of 10^{-2} M or higher is a consequence of the begining in the aggregation of the carboxylated latex at neutral pH. For lower NaCl concentrations it is difficult to establish a particle size variation versus the ionic strength as a consequence of the presence of a hairy layer.

These results are in agreement with those obtained by Gittings and Saville [17] on the coincidence of the measurements obtained by PCS and TEM in absence of ionic strength, where the thickness of the assumed hairy layer should be larger. Shubin et al. [7], using the same type of carboxyl particles as in this work, claim that the lower polarity of the carboxyl group and its higher propensity for counterion binding would lead to a thinner hairy layer. Therefore, the more attenuated mobility maximum presented for these carboxylated latexes, in comparison with sulfated or sulfonated ones, could be explained by their different surface character which produces a thinner hydrodynamic layer.

Table 3 Occupied area per surfactant molecule for each latex

Latex	Å^2/molecule
DJL-5	110 ± 4
DJL-6	111 ± 5
Sulfate	120 ± 4
Sulfonate	131 ± 6

In order to detect any difference in the hydrophobic or hydrophilic character of the surface of these carboxylated latexes, we have measured the maximum adsorption of a non-ionic surfactant as Triton X-100. The adsorption experiments were carried out at pH 7, ionic strength of 2 mM and an excess of surfactant in solution to be sure for total coverage. Table 3 shows the area occupied per molecule of surfactant for these latexes. To compare the results we have also introduced the data obtained for sulfonate and sulfate latexes. The DJL-5 and DJL-6 latexes show the lower surface area per molecule (larger adsorption) which means a more hydrophobic character in comparison with the sulfate latex; while the sulfonate is the more hydrophilic as corresponds to the use of a hydrophilic comonomer (sodium styrene sulfonate) in the copolymerization reaction. Using latexes prepared by copolymerization of styrene and acrylic acid or 2-hydroxi-ethyl-methacrylate (HEMA) as comonomers [8] the carboxylated latexes were significantly more hydrophilic in comparison with a conventional sulfate latex. Therefore, the surface characteristics of the carboxylated latex prepared by polymerization of styrene and ACPA as initiator are significantly different to those prepared by copolymerization of styrene and other ionic comonomers. This result confirms the previous one about the thinner solid–liquid interface layer in the ACPA latexes. The more hydrophobic character of these latexes could produce an interface that probably has not (or at least has less) oligomers or other polyelectrolytes on the surface, in comparison with the latexes prepared with hydrophilic comonomers. The hydrophobic character of the carboxylated latexes in comparison with the sulfonated ones (see Table 3) could partially explain the electrokinetic results, but the differences in Table 3 seem to be not large enough as to justify the electrokinetic responses of both types of latex. Another aspect to take into account is the character of the charged surface groups (weak acid for ACPA latexes and strong acid for sulfonate latexes), because with a lower charge the sulfonate latexes give a more pronounced maximum. These characteristics, the more hydrophobic character and the different type of charge, could produce a lower surface conductance in the ACPA latexes and therefore a less pronounced maximum in the μ_e–log C curves.

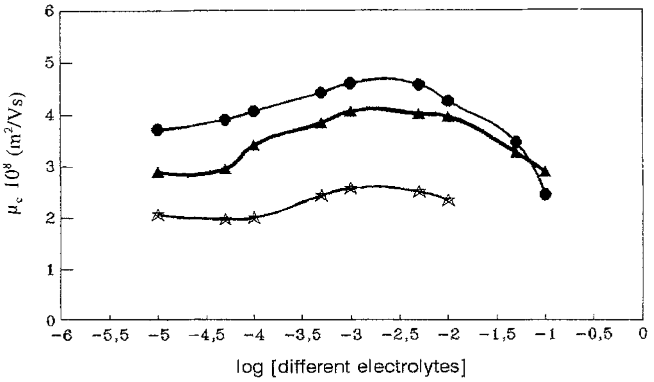


Fig. 6 Electrophoretic mobility (μ_e) against different electrolyte concentrations for the DJL-5 latex: ●, Na_2SO_4; ▲, NaCl; ☆, $MgSO_4$

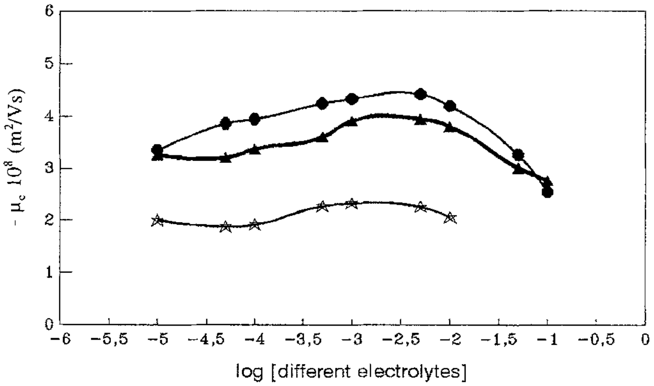


Fig. 7 Electrophoretic mobility (μ_e) against different electrolyte concentrations for the DJL-6 latex: ●, Na_2SO_4; ▲, NaCl; ☆, $MgSO_4$

Also, we have checked the effect of divalent co-ions on the μ_e values of both carboxylated samples. Figures 6 and 7 show the μ_e values of DJL-5 and DJL-6 latexes, respectively, versus the concentration of NaCl, Na_2SO_4 and $MgSO_4$. The maximum appears at an electrolyte concentration of around $5 \cdot 10^{-3}$ M for both latexes and the three electrolytes. For both latexes the μ_e values for the bivalent salt Na_2SO_4 are higher than those obtained with NaCl, except at high electrolyte concentration (0.1 M). However, with sulfonate latexes and the same salts [9] this type of difference in the mobility values was not found. Therefore, the mobility seems to be less sensitive to the valence of the co-ion when there is a hairy layer on the particle surface than when the latex has a more hydrophobic character and there are no oligomers on the surface. In Figs. 6 and 7 the effect of the $MgSO_4$ on the μ_e values is mainly controlled for the counter-ion (Mg^{2+}), which produces the decrease in the mobility for all the concentration range.

Counterion valencies could play an important role in the electrokinetic behavior of latex particles. In addition, a marked effect of the counterion charge on location of the maximum in the μ_e–log C could be expected if this

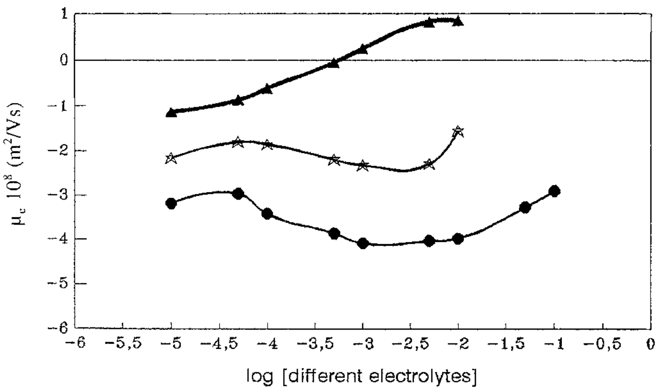


Fig. 8 Electrophoretic mobility (μ_e) against different electrolyte concentrations for the DJL-5 latex: ●, NaCl; ☆, $CaCl_2$; ▲, $LaCl_3$

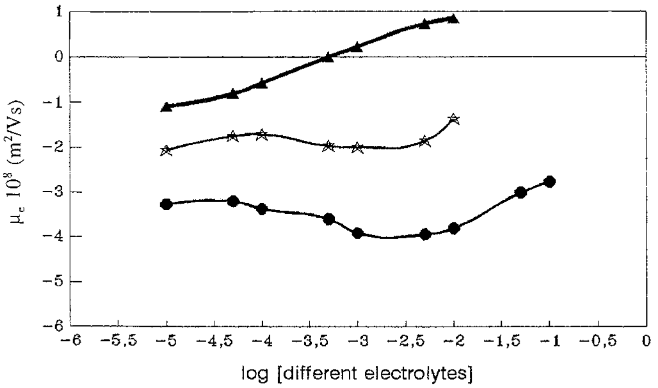


Fig. 9 Electrophoretic mobility (μ_e) against different electrolyte concentrations for the DJL-6 latex: ●, NaCl; ☆, $CaCl_2$; ▲

maximum was due to ion adsorption on the latex surface. For that reason, we have conducted some electrophoretic mobility measurements of both carboxylated polystyrene latexes with electrolytes of different valences: NaCl, $CaCl_2$ and $LaCl_3$. Figures 8 and 9 show the μ_e values versus these electrolyte concentrations for the latexes DJL-5 and DJL-6, respectively. The first significant result of these figures is the low μ_e values over all the concentration range when the counterion valence was +2. For $CaCl_2$ the mobility maximum is less pronounced and appears at a concentration around 10^{-3} and $5 \cdot 10^{-3}$ M, similar to that previously found for the mobility maximum when the electrolyte was NaCl or Na_2SO_4 (see Figs. 6 and 7). Therefore, the location of the maximum is little affected by the valence of the counterion (Na^{1+} or Ca^{2+}). Furthermore, the presence of Ca^{2+} ions is most important than the sulfate coions because the counterions can neutralize in a more effective way the electric double layer charge, which causes a compression of the diffuse double layer and, therefore, a decrease in the mobility and a smoother form of the μ_e–log C curves.

The effect of a trivalent counterion such as La^{3+} is somewhat different, as observed in Figs. 8 and 9, for both carboxylated latexes. The μ_e values are smaller than those found with calcium ion and they become positive when the $LaCl_3$ concentration is 10^{-3} M. The charge reversal observed for both latexes seems to be due to specific adsorption of lanthanum species. Working with lanthanum nitrate, Ottewill and Shaw [28] found the occurrence of the hydrolysis depending on the pH of the solution. Therefore, in some cases there are different ionic species and the behavior of the samples should be due to adsorption of hydrolyzed species. Since for the electrolyte concentrations used in our work (10^{-4} to $5 \cdot 10^{-2}$ M) the pH varied from 5.1 to 5.4 (without any tendency), the counterions in solution are essentially La^{3+} [28], and the adsorption of this ion could explain our results.

Furthermore, the maximum of the mobility disappears within the concentration range used. In this case, the compression of the e.d.l., together with the specific adsorption of La^{3+} ions, modifies the e.d.l. structure in a very significant way, with the maximum disappearing or shifting it toward very low concentrations. Similar results were found with sulfonate polystyrene latexes [9] although the charge reversal took place at a concentration of 10^{-2} M, probably due to the higher surface charge of the sulfonated latexes. In our case, the lower surface charge of the carboxyl latex at neutral pH provokes a charge reversal at low concentration.

In conclusion, monodisperse polymer colloids of carboxyl functionality were prepared by emulsifier-free emulsion polymerization of styrene using ACPA as initiator. By increasing the initiator concentration the surface charge density slightly increased and the particle size was practically the same. The more hydrophobic surface of these carboxylated latexes in comparison with other prepared by copolymerization of styrene with ionic comonomers (acrylic, methacrylic acids, etc.) could explain some of the results obtained in this work. The electrokinetic behavior of both carboxyl latexes was the same which indicated the insensitivity of the electrophoretic mobility to small changes in the surface charge density of these latexes. The μ_e–log C curves showed a smoother form in comparison with other latexes with similar surface charge and the location of the maximum mobility was not sensitive to the coion or counterion type, except for La^{3+} ions which were specifically adsorbed.

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