

## Effect of electrolyte type on the electrokinetic behavior of sulfonated polystyrene model colloids

D. Bastos and F. J. de las Nieves

Biocolloids and Fluid Physics Group, Department of Applied Physics, Faculty of Sciences, University of Granada, Spain

*Abstract:* Sulfonated polystyrene latex particles were prepared by a two-stage “shot-growth” emulsion polymerization process in the absence of emulsifier. Sodium styrene sulfonate (NaSS) was used as an ionic co-monomer to produce a series of latex particles with the same particle size but with different surface charge densities. The electrophoretic mobility of this functionalized model colloid was studied in the presence of various types of inorganic electrolytes. The  $\mu_e$  curves of these latexes exhibit a pronounced maximum at high electrolyte concentrations:  $5 \cdot 10^{-2}$  M for 1:1 electrolytes and  $10^{-2}$  M for 2:1 and 1:2 electrolytes. When a 3:1 electrolyte ( $\text{LaCl}_3$ ) was used, the electrophoretic mobility changed to positive values at high concentration due to the specific adsorption of lanthanum species. The experimental results for the electrokinetic characterization of these sulfonated polystyrene model colloids suggest that the surface of the particles is covered by a layer of oligomers or polymer chains which shift the shear plane toward the bulk solution, increasing the anomalous surface conductance of the polystyrene microsphere-electrolyte solution interface.

*Key words:* Sulfonated 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 biomolecules, 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 polystyrene latexes prepared in the absence of emulsifier to produce particles with sulfate end groups on the particle surface which result from the use of persulfate initiator in the polymerization [1–6]. However, the surface of these particles may change with the time because of the hydrolysis of the sulfate end groups to carboxyl groups. In order to obtain latexes with stable, strongly acidic surface groups, papers have appeared describing the preparation of sulfonated

polystyrene latexes with independent control of the particle size and surface charge density [7–9]. More recently, the preparation of low size polystyrene latex particles of sulfonate functionality has been reported [10], but in this case the emulsion polymerization included the presence of emulsifier.

The electrokinetic characterization of highly sulfonated polystyrene particles with similar particle size and different surface charge density was started in a previous paper [11]. In that article the effect of an extensive and systematic cleaning process on the electrokinetic behavior was also studied.

The objective of this work is to continue the electrokinetic characterization of sulfonated polystyrene latexes by studying the effect of different electrolytes on the electrophoretic mobility of these latexes. Furthermore, Tamai et al. [7] and de las Nieves et al. [11] have presented several controversies about the relation between the surface charge density and the  $\zeta$ -potential of these types of particles. It has been found that latexes with different

surface charge density ( $\sigma$ ) present electrophoretic mobility curves which pass through a maximum as a function of increasing ionic strength, and the  $\mu_e$  values are similar for several latexes with different  $\sigma$  [11], or even higher for those with a lower surface charge density [7].

Experimental studies concerned with the maximum in the electrophoretic mobility have mainly used simple 1:1 electrolytes [6, 12, 13]. Recently, Elimelech and O'Melia [14] have reported studies with bivalent and trivalent counterions and co-ions, using commercial polystyrene latexes which carry sulfate functional groups. They support the hypothesis about the preferential adsorption of co-ions onto the particles surfaces, as the explanation for the maximum in the electrokinetic potential.

Due to the preparation method of the sulfonated polystyrene latexes and the cleaning process used, these particles seem to be covered by a layer of oligomers or polymer chains chemically bound on the surface [11]. The present paper aims to give new results on the electrokinetic characterization of two sulfonated polystyrene latexes with equal particle size and different surface charge density. In addition, the study of these new model colloids (with a specific sulfonate functionality) in the presence of bivalent and trivalent co-ions and counterions may provide a more direct understanding about the structure of the electric double layer which surrounds these latex particles.

## Experimental

### Materials

Styrene monomer was obtained from Merck and was distilled under reduced nitrogen pressure at 40 °C. The purified monomer was stored at -5 °C until required. Sodium styrene sulfonate (NaSS) was obtained from Fluka and was used as received. The different initiators (potassium persulfate and sodium bisulfite) and 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 sulfonated polystyrene particles which have the same particle size and differ-

ent surface charge densities, we have followed the recipes developed by Kim et al. [8] using a "shot-growth" emulsion polymerization technique.

Specifically, in order to obtain smaller particles, an initial concentration of 3 mM ionic co-monomer (NaSS) was used in the initial monomer charge. The specific amounts of the different components added to the shot-injection step were previously shown [11]. To obtain latexes with very similar particle size, the copolymerization was carried out in two 250-ml bottles and following the procedure described by de las Nieves et al. [11]. In the present work we have prepared two different latexes by varying the amount of NaSS introduced at this shot-injection stage.

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 200 particles for each sample using a Calcomp Drawing Board Digitizer and taking three different points of the sectional view for each particle. With 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, (PDI, defined as  $D_w/D_n$ ), was less than 1.05.

### 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 previously found by several authors [11, 15]. Following previous results [11], the latexes were centrifuged and redispersed (with the aid of soft sonication) several times until the specific electrical conductivity of the supernatant was found to be lower than 10  $\mu\text{S}/\text{cm}^{-1}$ . Next, the latexes were heated (at 85 °C for 72 h) to hydrolyze the possible residual sulfate end-groups provided by the initiator [8]. Finally, the purified samples were treated with mixed ion-exchange resins followed by serum replacement with DDI water.

Surface charge densities ( $\sigma$ ) of the latexes were determined by conductimetric and potentiometric titrations of the cleaned latexes. The conductimetric and potentiometric titrations were automatically carried out using 40 ml of the diluted latex

(with approximately 0.3% solids) at room temperature. 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 recollected the data, fixed the straight lines and calculated the intersection point. Figure 1 shows the conductimetric and potentiometric titration curves for the sample SN-13. The forward and back titrations were carried out with 19.4 mM NaOH and 22.4 mM HCl solutions, respectively, 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 Zeta-sizer IIc instrument. The electrophoretic mobility values were obtained by taking the average of (at least) six measurements at the stationary level in a cylindrical cell, changing the suspension sample twice. The experimental error was taken as the

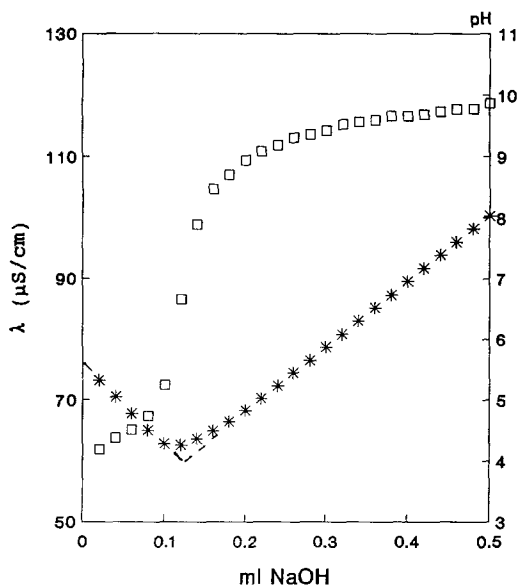


Fig. 1. Conductometric and potentiometric titration curves of latex SN-13, with 19.4 mM NaOH solution

standard deviation in these measurements. For the data shown throughout this paper, the standard deviation was always lower than  $\pm 0.20 \cdot 10^{-8} \text{ m}^2/\text{Vs}$ . Samples were prepared by adding approximately 0.1 ml of the latex to 40 ml of each electrolyte solution.

## Results and discussion

### Surface characterization

Table 1 shows the amount of NaSS added at the shot-injection, the number-average ( $D_n$ ), weight-average ( $D_w$ ) diameters and the polydispersity index (PDI) for two prepared samples. The particle diameters are almost the same for both samples with low standard deviations. The values for the PDI clearly indicate that all latexes were monodisperse.

The last row in Table 1 shows the surface charge densities ( $\sigma$ ) of the cleaned latexes. As an example, Fig. 2 shows the forward and backward conductimetric titration curves for the latex SN-8. Similar results were found for the latex SN-13. In both cases the curves exhibited constant slopes which indicated the presence of strong acid groups on the surface of the latexes. The values for  $\sigma$  given in Table 1 represent the average of the forward and back titrations, and the differences between both were always less than 5%. As can be seen in Table 1 the  $\sigma$  values of these latexes increased with increasing the amount of NaSS added in the shot-injection step.

Thus, the results presented in Table 1 confirm the formation of sulfonated polystyrene model colloids with almost identical particle sizes and relatively high and different surface charge densities.

### Electrokinetic characterization

The electrophoretic mobilities of sulfonated polystyrene latexes were measured to characterize

Table 1. Particle size, polydispersity index and surface charge density of sulfonated polystyrene latexes

Latex	NaSS (g) (at shot injection)	$D_n$ (nm)	Standard deviation	$D_w$ (nm)	PDI	$\sigma$ ( $\mu\text{C}/\text{cm}^2$ )
SN-8	1.2	178.5	5.5	179.0	1.003	12.3
SN-13	1.6	177.8	8.3	179.0	1.007	17.0

the electric double layer surrounding the particles. Also, we have conducted experiments to see whether mobility changes on addition of different mono-, di- and trivalent co-ions and counterions.

Mobilities of latexes SN-8 and SN-13 as a function of KBr concentration are shown in Fig. 3. The

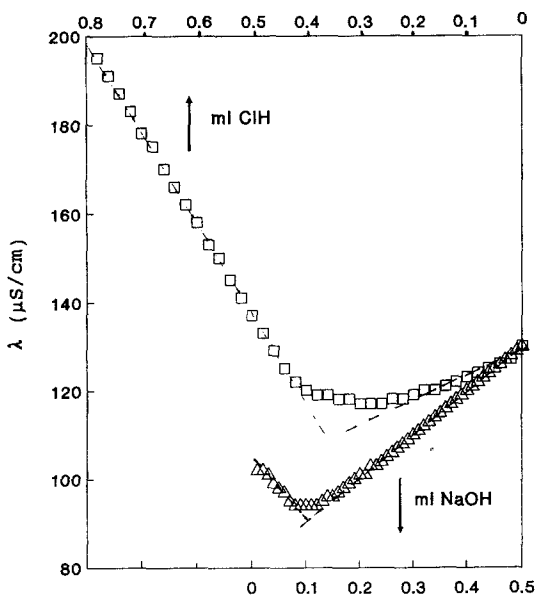


Fig. 2. Forward and back titration curves of latex SN-8, with 19.4 mM NaOH and 22.4 mM HCl solutions, respectively

mobility of the particles increases (in absolute value) with increasing salt concentration, reaching a maximum at a concentration of  $5 \cdot 10^{-2}$  M. This behavior is in a marked contrast with the classical theory of the electric double layer which predicts a continuous decrease in the electrokinetic potential (and, therefore, in the electrophoretic mobility) with increasing salt concentration [16]. Various explanations for this maximum have been proposed [12-14, 17-19], which consider preferential adsorption of co-ions onto the surface or physical changes in particle surface properties (including anomalous surface conductance).

One remarkable result observed in Fig. 3 is the lower  $\mu_e$  values for the latex with a higher  $\sigma$  (SN-13) when the salt concentration is  $\geq 10^{-2}$  M. The same trend was found for other monovalent electrolytes as NaNO<sub>3</sub> and NaCl (see Fig. 4 for NaCl). Thus, the reverse relationship between  $\mu_e$  and  $\sigma$  is a proper result of the sulfonated polystyrene latexes and the same electrokinetic behavior has been found for different monovalent co-ions (Br<sup>-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>). However, de las Nieves et al. [11] previously found similar  $\mu_e$  values for three sulfonated latexes with different  $\sigma$  values. The long cleaning process used in our experiments was similar to that described in ref. [11], the only difference being the sonication of the latexes after centrifugation. We have used a bath sonication of the

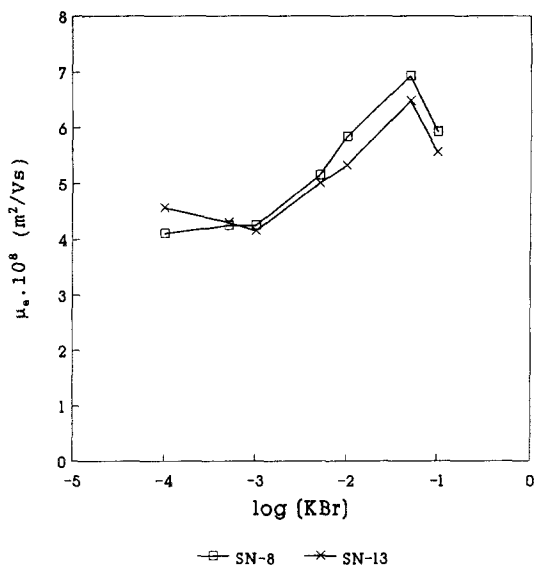


Fig. 3. Electrophoretic mobility of both sulfonated polystyrene latexes ( $\square$ , SN-8;  $\times$ , SN-13) versus KBr concentration

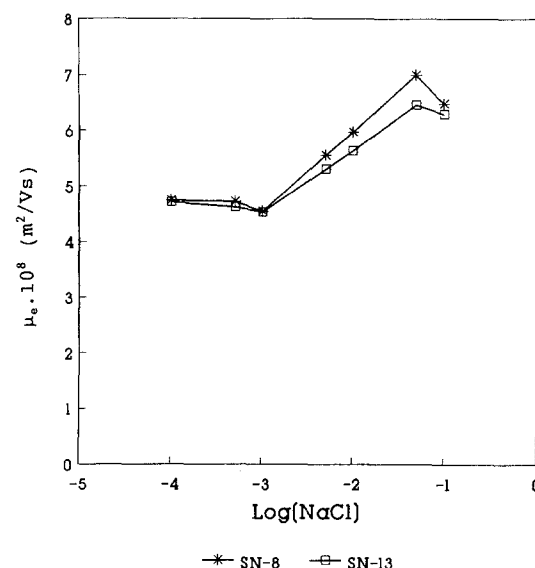


Fig. 4. Electrophoretic mobility of sulfonated polystyrene latexes ( $\square$ , SN-13,  $*$ , SN-8) versus NaCl concentration

latexes (soft sonication), while previously we used strong sonication (with a probe) in each centrifugation-redispersion cycle.

Due to the method of preparation of our St/NaSS latexes, we believe that a layer of water soluble polymers or oligomers exists on the surface of these particles. That layer shifts the shear plane toward the bulk solution and thereby diminishes the electrokinetic potential and the  $\mu_e$  values. The thickness of this layer increases with the amount of NaSS added at the shot-injection which provokes lower  $\mu_e$  values for the latex with higher surface charge density. With the use of strong sonication during the redispersion process the majority of the macromolecules which were physically adsorbed should have been removed thus the different latex samples should have given similar  $\mu_e$  results [11]. However, with the use of soft sonication some of the water soluble polymers or oligomers physically adsorbed cannot be removed and these produce a larger shift of the shear plane for the latex with a larger amount of NaSS added at the second stage. This explanation could be confirmed by the results of Tamai et al. [7]. They reported a reverse relationship between  $\zeta$ -potential and  $\sigma$  values, although they cleaned their latexes by centrifugation/redispersion cycles, but did not report the use of sonication in each cycle.

The apparent polyelectrolyte desorption after vigorous stirring of "cleaned latexes" was reported by German et al. [15, 20]. They used a seeded and shot-growth emulsion polymerization method to prepare their latexes, and even after six centrifugations the serum of the resulting latexes still contained detectable concentrations of polyelectrolytes. Thus, "vigorous stirring" during the strong sonication procedure seems to be a necessary condition for the complete removal of physically adsorbed polyelectrolytes or oligomers.

Using cationic polystyrene latexes, Moleón-Baca et al. [21] also found a reverse relationship between  $\mu_e$  and  $\sigma$  values, although they used a conventional emulsion polymerization process and cleaned their latexes by ion-exchange over a mixed bed. In this case the results were explained as being due to the influence of surface conductance on electrophoresis because the anomalous conduction mechanism would increase with the surface charge density [17]. Our results in Figs. 3 and 4 show that the differences between latexes SN-8 and SN-13 appear at a concentration of around  $10^{-2}$  M or higher,

and so, the anomalous conductance is not the main effect. We believe that the remaining physically adsorbed oligomers are the reason for the differences in the  $\mu_e$  of both sulfonated latexes with different  $\sigma$  values, because they were cleaned without strong sonication.

Also, we have checked the effect of divalent co-ions on the  $\mu_e$  values of both sulfonated samples. Figure 5 shows the  $\mu_e$  values for both latexes versus the concentration of  $\text{Na}_2\text{SO}_4$ . The maximum appears at an electrolyte concentration of  $10^{-2}$  M for both latexes, but this displacement seems to be due to the higher ionic strength in comparison with the same concentration for 1:1 electrolytes. Again the  $\mu_e$  values are lower for the latex with a higher surface charge density (SN-13), which confirms the previous results. For comparison, in the same figure we have plotted the electrophoretic mobility of latex SN-13 with an univalent co-ion salt ( $\text{NaNO}_3$ ). The  $\mu_e$  values of latex SN-13 for the univalent and bivalent salts are very similar at electrolyte concentration lower than  $10^{-2}$  M. At a concentration of  $10^{-2}$  M the  $\mu_e$  values showed a maximum for the bivalent electrolyte, while the maximum appeared at  $5 \cdot 10^{-2}$  M for the univalent electrolyte. The different ionic strengths for both electrolytes at the same concentration seems, again, to be the reason for that

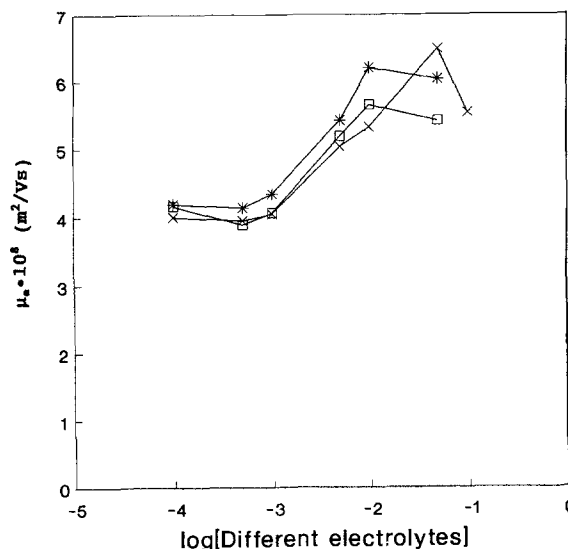


Fig. 5. Electrophoretic mobility of sulfonated polystyrene latexes ( $\square$ , SN-13;  $*$ , SN-8) versus  $\text{Na}_2\text{SO}_4$  concentration and  $\text{NaNO}_3$  concentration (for SN-13,  $\times$ )

difference. However, at low concentration, where the effect of the anomalous conductance or co-ion adsorption should be significant, there are no differences. However, Elimelech and O'Melia [14] have found significant differences for the  $\mu_e$  values of an anionic latex in the presence of  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ , because the bivalent anions are expected to increase the negative electrokinetic potential more than univalent  $\text{NO}_3^-$  anions. We have repeated the same measurements with this latex (SN-13) and with the other sulfonated latex (SN-8) (see Fig. 6), and the differences were much lower than the experimental error. In Fig. 6 the mobilities are equal at low concentrations, just when the influence of the different adsorbed co-ions should be more significant. Thus, for sulfonated latexes two co-ions as different as  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  give the same  $\mu_e$  results, which again suggests that the anomalous behavior of polystyrene latex particles is not related to co-ion adsorption.

The appearance of the maximum in the  $\mu_e$  data for different monovalent ( $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$ ) and divalent ( $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Ca}^{2+}$ ) co-ions was also found with cationic polystyrene latexes [22]. Thus, due to the large differences in the physical properties of the co-ions used in our work ( $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ), and those used in ref. [22], it can be concluded that the maxima in mobility have to be due to physical changes in particle surface prop-

erties rather than co-ion adsorption, as suggested by Zukoski and Saville [12] and, more recently, by Elimelech and O'Melia [14]. Together with this model of the electric double layer structure, some authors [17–19, 23] support the idea of an anomalous electrical conduction into the e.d.l. This surface conductance probably increases at lower electrolyte concentration due to the increase of the thickness of this layer (between the surface and the shear planes), making its influence especially important at low ionic strength and reducing the  $\mu_e$  values by a much greater percentage.

Counterion valences could play an important role in the electrokinetic behavior of latex particles. In addition, a marked effect of the charge of the counterions on location of the maximum in the mobility/log electrolyte concentration could be expected if this maximum were due to ion adsorption on the latex surface. For that reason we have conducted some electrophoretic mobility measurements of both sulfonated polystyrene latex samples with electrolytes of different valences:  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{LaCl}_3$ . Figures 7 and 8 show the  $\mu_e$  values versus these electrolyte concentrations for the latexes SN-8 and SN-13, respectively. For comparison, the  $\mu_e$  values obtained with  $\text{Na}_2\text{SO}_4$  electrolyte are also shown. The first significant result of these figures is the low  $\mu_e$  values over all the concentration range when the counterion valences

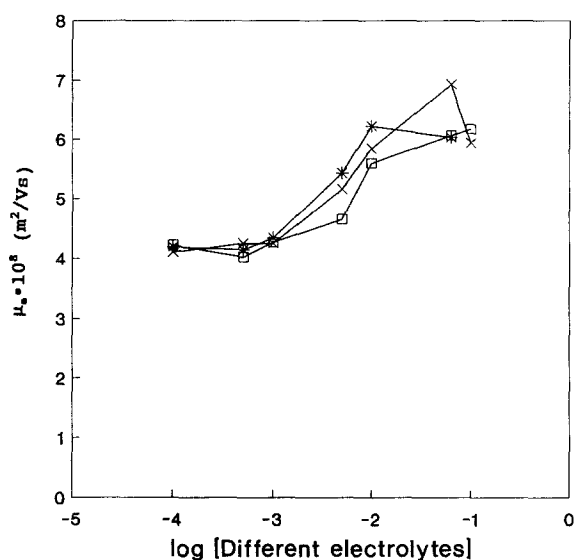


Fig. 6. Electrophoretic mobility of latex SN-8 versus electrolyte concentrations: \*,  $\text{Na}_2\text{SO}_4$ ; □,  $\text{NaNO}_3$ ; ×,  $\text{KBr}$

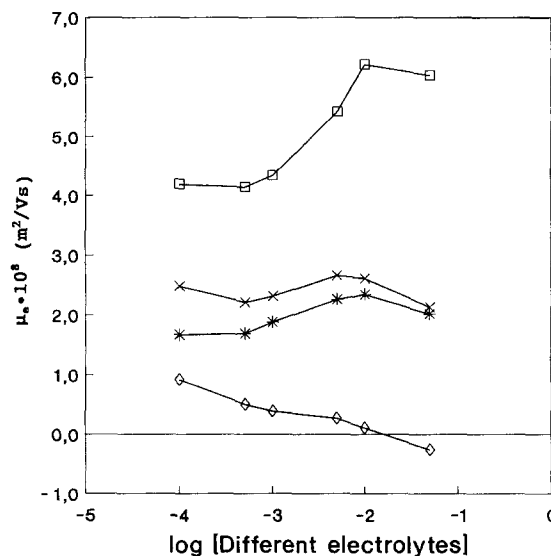


Fig. 7. Electrophoretic mobility of latex SN-8 versus electrolyte concentrations: □,  $\text{Na}_2\text{SO}_4$ ; ×,  $\text{CaCl}_2$ ; \*,  $\text{MgSO}_4$ ; ◇,  $\text{LaCl}_3$

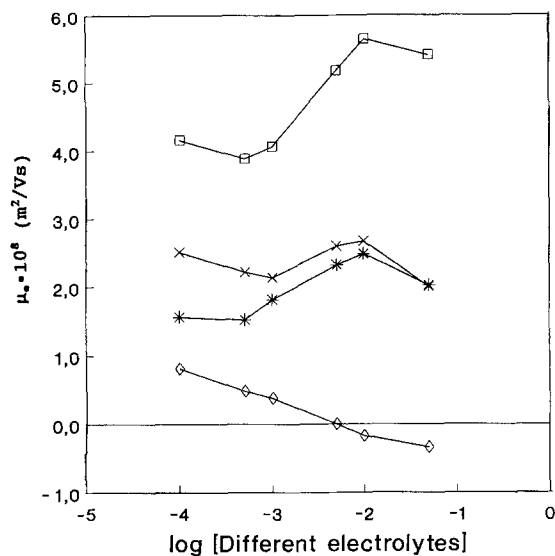


Fig. 8. Electrophoretic mobility of latex SN-13 versus electrolyte concentrations: □, Na<sub>2</sub>SO<sub>4</sub>; ×, CaCl<sub>2</sub>; \*, MgSO<sub>4</sub>; ◇, LaCl<sub>3</sub>

were + 2. For CaCl<sub>2</sub> and MgSO<sub>4</sub> the results were similar and the mobility maximum appeared again at a concentration of 10<sup>-2</sup> M. The same concentration was found for the mobility maximum when the electrolyte was Na<sub>2</sub>SO<sub>4</sub>. Thus, these results confirm our previous finding: the displacement of the maximum toward low concentrations as compared with 1:1 electrolytes; this seems to be due to the increase in the ionic strength. The explanation for its appearance could be the same as for 1:1 electrolyte.

The lower  $\mu_e$  values for CaCl<sub>2</sub> and MgSO<sub>4</sub> could be due to a more effective neutralization of the electric double layer charge which causes a compression of the diffuse double layer and, therefore, a decrease in the mobility. Both electrolytes can be considered as indifferent, because they provoke only a decrease in electrical double layer thickness and, therefore, a decrease in the  $\mu_e$  values, but the sign of  $\mu_e$  is the same. For both latexes, the  $\mu_e$  values were lower in the presence of Mg<sup>2+</sup> than Ca<sup>2+</sup> ions. Therefore, counterions of the same valence exert different effects on the mobility. The low ionic radius of Mg<sup>2+</sup> seems to be the reason. These counterions come nearer the latex surface than Ca<sup>2+</sup> ions and compress the e.d.l. in a more effective way reducing the  $\mu_e$  values of the latex particles.

The effect of a trivalent counterion as La<sup>3+</sup> is somewhat different, as observed in Figs. 7 and 8, for both sulfonated latexes. The  $\mu_e$  values are smaller than those found with calcium and magnesium ions and they become positive when the LaCl<sub>3</sub> concentration is 10<sup>-2</sup> 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 [24] found the occurrence of the hydrolysis depending of 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<sup>-4</sup> to 5 · 10<sup>-2</sup> M) the pH varied from 5.1 to 5.4 (without any tendency), the counterions in solution are essentially La<sup>3+</sup> [24], 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<sup>3+</sup> ions, modifies the e.d.l. structure in a very significant way, with the maximum disappearing or shifting it toward very low concentrations. The effect of trivalent counterions on the  $\mu_e$  of cationic polystyrene latexes [22] also showed the reversal in the electrokinetic charge due to the specific adsorption of this type of ions. For cationic latexes the maximum appeared again at higher concentration because the neutralization of the electrokinetic charge took place at very low concentration (approximately 10<sup>-5</sup> M). In our experiments the neutralization occurs at a concentration of 10<sup>-2</sup> M and it is not possible to measure at very high concentrations. Using the same salt, Elimelech and O'Melia [14] found the charge reversal at the same concentration, due to the specific adsorption of La<sup>3+</sup> species.

In conclusion, for indifferent electrolytes the location of the maximum mobility is not sensitive to the coion or counterion type, and for different valences the changes are due to the variation of the ionic strengths. These results again suggest that this anomalous electrokinetic behavior of sulfonated polystyrene latexes is mainly related to particle surface properties. Due to the preparation method the surface of the particles is covered by a layer of oligomers which is not affected by the valence and type of co-ions. The use of smooth cleaning methods does not remove the physically

adsorbed oligomers, which leads to a reverse relationship between the  $\sigma$  and  $\mu_e$  of the latex particles.

#### Acknowledgements

This work is supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT), proyect no MAT 90-0695-C02-01 MAT93-0530-C02-01 and by Centro para el Desarrollo Tecnológico Industrial (CDTI), proyect no 89-IE-0044-C02-00.

#### References

1. Ottewill RH, Shaw JN (1967) *Kolloid z z Polym* 218:34
2. Kotera A, Furusawa K, Takeda Y (1970) *Kolloid z z Polym* 239:677
3. Furusawa K, Norde W, Lyklema J (1972) *Kolloid z z Polym* 250:908
4. Bijsterbosch BH (1978) *Colloid Polym Sci* 256:343
5. Goodwin JW, Hearn J, Ho CC, Ottewill RH (1973) *Br Polym J* 5:347
6. Brouwer WM, Zsom RLJ (1987) *Colloids Surfaces* 24:195
7. Tamai H, Niino K, Suzawa T (1989) *J Colloid Interface Sci* 131:1
8. Kim JH, Chainey M, El-Aasser MS, Vanderhoff JW (1989) *J Polym Sci, Polym Chem Ed* 27:3187
9. Tsaur SL, Fitch RM (1987) *J Colloid Interface Sci* 115:450
10. Graillat C, Pichot C, Guyot A (1991) *Colloids Surfaces* 56:189
11. de las Nieves FJ, Daniels ES, El-Aasser MS (1991) *Colloids Surfaces* 60:107
12. Zukoski CF, Saville DA (1985) *J Colloid Interface Sci* 107:322
13. Van der Put AG, Bijsterbosch BH (1983) *J Colloid Interface Sci* 92:499
14. Elimelech M, O'Melia CR (1990) *Colloids Surfaces* 44:165
15. Van Streun KH, Belt WJ, Piet P, German AL (1991) *Eur Polym J* 27:931
16. Hunter RJ (1981) In: Ottewill RH, Rowel RL (eds) *Zeta-Potential in Colloid Science*. Academic Press, New York
17. Midmore BR, Hunter RJ (1988) *J Colloid Interface Sci* 122:521
18. Baran AA, Dukhina LM, Soboleva NM, Chechik OS (1981) *Kolloid z* 43:211
19. Chow RS, Takamura K (1988) *J Colloid Interface Sci* 125:226
20. Twigt F, Piet P, German AL (1991) *Eur Polym J* 27:939
21. Moleón-Baca JA, Rubio-Hernández FJ, de las Nieves FJ, Hidalgo-Alvarez R (1991) *J Non-Equil Thermodyn* 16:187
22. Galisteo F, de las Nieves FJ, Cabrerizo M, Hidalgo-Alvarez R (1990) *Progr Colloid Polym Sci* 82:313
23. Hidalgo-Alvarez R, Moleón-Baca JA, de las Nieves FJ, Bijsterbosch BH (1992) *J Colloid Interface Sci* 149:23
24. Ottewill RH, Shaw JN (1968) *J Colloid Interface Sci* 26:110

Received May 28, 1992;  
accepted September 25, 1992

Authors' address:

Dr. F. J. de las Nieves  
Biocolloids and Fluid Physics Group  
Department of Applied Physics  
University of Granada  
18071 Granada, Spain