

Effect of Electrolyte Type on the Electrophoretic Mobility of Polystyrene Latex Colloids

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(Received 6 April 1989; accepted 5 July 1989)

ABSTRACT

Electrophoretic mobility studies of surfactant-free polystyrene latex particles in various types of inorganic electrolytes are reported. The particles carry sulfate functional groups and cover a wide range of surface charge. The electrophoretic mobility curves of all latices exhibit a pronounced maximum as a function of 1:1 electrolyte (KCl) concentrations. With 2:1 and 3:1 electrolytes (CaCl₂ and LaCl₃ respectively), the electrophoretic mobility curves pass through a minimum followed by a maximum. The results are discussed in terms of models that have been previously proposed to explain these maxima in the mobility curves. Our results suggest that the increase of mobility with salt concentration may be attributed to the approach of co-ions close to the hydrophobic surface of the particles. It is also suggested that three competing processes at the interface determine the shape of the mobility curves.

INTRODUCTION

Latex particles have been used extensively in the past two decades as model colloids in studies of a variety of colloidal phenomena [1-4]. The particles are spherical and monodisperse and are considered to have well defined functional groups. The preparation and characterization of such particles is well established [5-10].

Conventionally, the electrical charge and potential of clean latex particles is considered to originate from dissociation of surface functional groups. However, growing evidence of anomalous behavior of electrokinetic potential as a function of the concentration of simple electrolyte has accumulated recently in the literature [11-15]. It has been found that electrokinetic potential curves pass through a maximum as a function of increasing ionic strength. This behavior contradicts the current double layer models which predict a continuous decrease in potential.

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Various qualitative explanations for this maximum have been proposed [12,16–18]. Two of these models are the preferential adsorption of co-ions onto the surface and the so-called *hairy layer* model. Preferential adsorption of co-ions onto the hydrophobic portion of the surface of latex particles was invoked by Kamel et al. [12] and Zukoski and Saville [16,17] to explain the maximum in the electrokinetic potential of negatively charged latices as a function of electrolyte concentration. This model of co-ion adsorption is supported by considerable experimental evidence in which negative electrokinetic potentials are observed for non-ionogenic surfaces in water [19–21]. Another qualitative explanation which has become popular recently is the hairy layer model [13,18]. According to this model, the surface of polymer latices is comprised of polyelectrolyte chains carrying the surface charge. This layer expands upon decreasing the ionic strength due to repulsion of the functional groups, and contracts with increasing ionic strength. The expansion and contraction of the hairy layer affects the location of the plane of shear and consequently the electrokinetic potential.

Experimental studies concerned with the maximum in the electrokinetic potential were limited to simple 1:1 electrolytes [14,15,23]. Other studies supporting the hairy layer model have been conducted with organic macromolecules [18,24]. Such studies may be difficult to interpret accurately since macromolecules alter the particle interface in a rather complicated way [25,26]. Studies with bivalent and trivalent counterions and co-ions, on the other hand, may provide a more direct understanding of the observed maximum in the electrokinetic potential.

In the present work, electrophoretic mobilities of well-characterized latex particles covering a wide range of surface charge under various types of counterions and co-ions were investigated. The results are compared with qualitative explanations which have been proposed for the maximum in the mobility curves. A qualitative model for the observed shape of the mobility curves of the latex particles is proposed.

EXPERIMENTAL

Materials

All inorganic chemicals were analytical reagent grade. Inorganic salt solutions were filtered through 0.2 μm membrane filters. Solutions and suspensions were prepared using distilled deionized water (Milli-Q system, Millipore Corp., Bedford, MA).

Four different sizes (0.378, 0.400, 0.753, 0.793 μm in diameter) of surfactant-free polystyrene latex particles were used (Interfacial Dynamics Corp., Portland, OR). The particles were extensively dialyzed by the manufacturer to remove impurities. The latices were prepared with potassium persulfate as an

initiator and, as a result, they carry sulfate functional groups. The reported density of the particles is 1.055 g cm^{-3} and the refractive index is 1.591 at 590 nm.

Potentiometric and conductometric titrations

Latex particles were ion-exchanged into the H^+ form before titrations following the procedure described by van den Hul and Vanderhoff [27]. Analytical grade ion exchange resins (Bio Rad, Richmond, CA) were used. Titrations were carried out at a temperature of $25.0 \pm 0.1^\circ\text{C}$ in CO_2 -free suspensions by bubbling purified N_2 into the titration vessel. A YSI model 31A (YSI Co. Inc., Yellow Springs, OH) conductance bridge with platinum-iridium electrodes was used for conductivity measurements. Research grade combination pH electrodes (Orion model 91-03) with an internal Ag/AgCl reference system were used for potentiometric titrations.

Electrophoretic mobility

Electrophoretic mobility studies were carried out at 25.0°C using a Mark II microelectrophoresis apparatus (Rank Brothers, Cambridge, U.K.). A thin-walled cylindrical cell with a four electrode arrangement was employed. A 3 mW laser was used for the illumination of the smaller particles. Latex concentrations for mobility studies were in the range of 0.0001–0.0003% w/w (by weight). For each sample the reported mobility represents an average of ~ 20 measurements of individual particles. The coefficient of variance was found to be in the range of 3 to 11%. When the mobility of the latices was studied as a function of salt concentration, the pH of the solution was adjusted to 6.8 by adding $5 \cdot 10^{-5} \text{ M NaHCO}_3$. Experiments with LaCl_3 were conducted at pH 6.0 to prevent hydrolysis of the lanthanum.

RESULTS AND DISCUSSION

Surface charge density and pH dependence

Conductometric and potentiometric titrations were carried out in order to determine the surface charge density of the particles and the nature of the charge-imparting groups as to whether they are strong or weak acids. A typical curve of these titrations is presented in Fig. 1. As observed, the end points of the conductometric and potentiometric titrations are similar.

The charge and site densities of the latex particles, as determined in this work, are given in Table 1. The average distance between the functional groups on the surface of the particles, assuming a quadric arrangement, is also given in Table 1. The large distance between the functional groups may be an im-

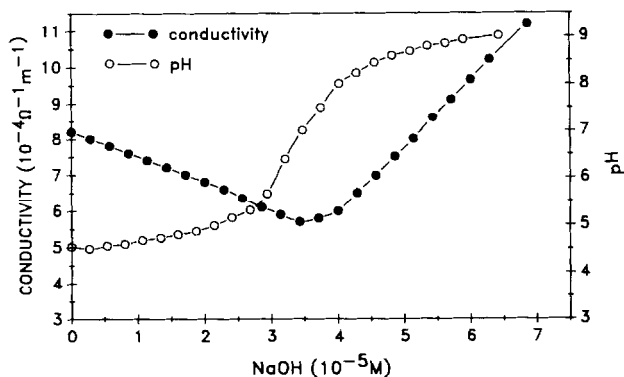


Fig. 1. Conductometric and potentiometric titration curves for latex C (solids content 0.84% w/w). The conductivity and pH readings are plotted as a function of the concentration of base in the titration vessel after the addition of NaOH.

TABLE 1

Surface charge and site densities of latex particles used in this research

Latex	Diameter (μm)	Charge (mC m^{-2})	Area per site ^a (nm^2)	Average distance between sites ^b (nm)
A	0.378	42.5	3.77	1.94
B	0.400	6.8	23.56	4.85
C	0.753	56.4	2.84	1.69
D	0.793	76.0	2.11	1.45

^aCalculated from titrated surface charge.

^bAssuming a quadric arrangement of sites on the surface.

portant factor in determining the electrokinetic properties of these particles. The surface properties of the particles can be dominated by hydrophobic effects because of the low surface site density.

The shape of the conductometric titration curve indicates that the surface functional groups are strong acids. These are sulfate groups ($\equiv\text{OSO}_3^-$) with a $\text{p}K_a$ in the range of 1 to 2 [28]. No evidence for weak acid surface sites was found in the conductometric titrations. The absence of weak acid groups is also demonstrated in Fig. 2 in which potentiometric titrations of latex C in different ionic strengths are presented. The curves at different ionic strengths are identical within experimental error and have the same shape as that of the blank titration curve. This behavior indicates that the surface sites are strong acids which are fully dissociated over the pH range employed in the titrations [28,29]. Electrophoretic mobility measurements conducted in this research demonstrated that the mobility values at a given ionic strength ($10^{-2} M \text{ KCl}$) are

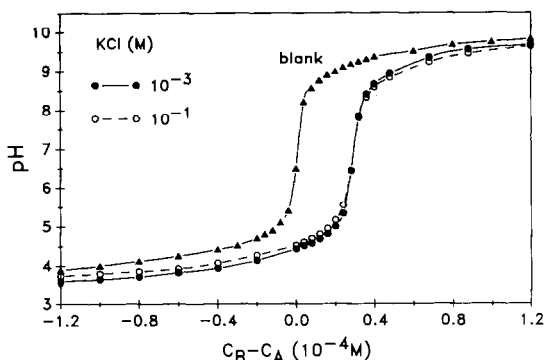


Fig. 2. Potentiometric titration of latex C at different ionic strengths. ($C_B - C_A$ is the excess of base (NaOH) or acid (HCl) added, solid content 0.60% w/w.) The blank titration solution contains no particles.

constant at pH values of 3.5 to 10. This implies that the electrokinetic potential and charge are constant at that pH range in agreement with the charge density studies presented earlier.

Mobility as a function of 1:1 electrolyte concentration

Mobilities of latices A–D as a function of KCl concentration are shown in Figs 3 and 4. The mobility of the latex particles increases with increasing salt concentration, reaching a maximum in the range of 10^{-3} to 10^{-2} M KCl and then decreases continuously (the terms increase, decrease and maximum with respect to electrophoretic mobilities relate to the absolute values of the mobilities).

Electrophoretic mobilities of colloidal particles are not directly related to the electrokinetic potential; for a given spherical particle this relationship depends also on the electrolyte concentration and valency. Calculations of electrokinetic potentials from the measured electrophoretic mobilities, using extant theories which account for the retardation and relaxation effects [22] as calculated in this research and by others [13–15,23] showed that similar anomalous maxima in the electrokinetic potential curves are obtained. This behavior is in a marked contrast with the classical theory of the double layer which predicts a continuous decrease in the electrokinetic potential with increasing salt concentration [22].

The following mechanism is proposed to explain the shape of the mobility curves of these latices. As the KCl concentration increases, co-ions (Cl^-) enter into the interfacial region adjacent to the hydrophobic surface and increase (more negative) the electrokinetic potential of the particles. Concurrently the increase in ionic strength and counterion concentration tends to reduce the

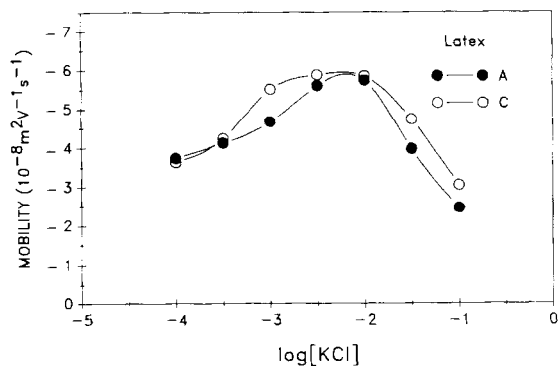


Fig. 3. Electrophoretic mobility of latices A and C as a function of log molar concentration of KCl (pH 6.8).

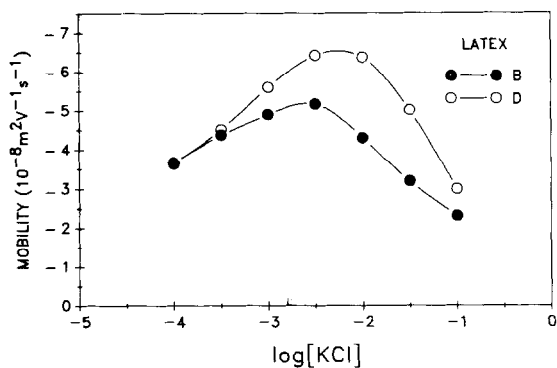


Fig. 4. Electrophoretic mobility of latices B and D as a function of log molar concentration of KCl (pH 6.8).

electrokinetic potential due to compression of the diffuse double layer and charge neutralization. In the ascending leg of the mobility curves the increase of the electrokinetic potential caused by the action of co-ions at the interface is the dominant mechanism. At the maximum of the mobility curve these processes are comparable and subsequent increase of the ionic strength results in a continuous decrease of the electrokinetic potential. In this region of the curve compression of the diffuse double layer and charge screening are the dominant mechanisms.

Recent studies by Brouwer and Zsom [23] suggested that particles with low surface charge (less than about 20 mC m^{-2}) show the normal continuous decrease rather than an increase to a maximum with increasing salt concentration. This behavior was explained by the proposition that at very low surface charge, the particles do not have a significant hairy layer. Our results show that the maximum in the mobility occurs with even smaller surface charge

densities (6.8 mC m^{-2} for latex B). The conclusion of Brouwer and Zsom with regard to latices with low surface charge may be inaccurate since their latex suspension with the low surface charge was prepared with surfactant, in contrast to the other particles which were surfactant free.

Mobility in the presence of polyvalent salts

In order to better understand the behavior of these latex particles, it was decided to investigate the electrophoretic mobility of the particles in the presence of polyvalent electrolytes. Bivalent and trivalent counterions may specifically interact with the surface sites, thus affecting markedly the surface potential of the particles.

Representative results for the mobility curves with CaCl_2 are given in Fig. 5. The mobilities were investigated as a function of CaCl_2 concentration while the concentration of KCl as a background electrolyte remained constant during the specific run. The results show that without KCl as a background electrolyte the mobility first decreases with CaCl_2 concentration (region I) and then increases to a maximum between 10^{-3} and 10^{-2} M of calcium chloride (region II), followed by a continuous decrease (region III). In the presence of KCl as a background electrolyte this behavior is less pronounced and disappears with 10^{-2} M KCl. At this KCl concentration the mobility decreases linearly with log molar concentration of CaCl_2 over the entire range investigated.

The mobility curves as shown in Fig. 5 can be explained by the following mechanism. In the absence of KCl, as the calcium chloride concentration increases some of the Ca^{2+} counterions specifically interact with the sulfate groups and reduce the negative charge, while other calcium counterions neutralize the negative charge of the particles in a non-specific manner. Simultaneously, co-ions enter the interfacial region adjacent to the particle surface

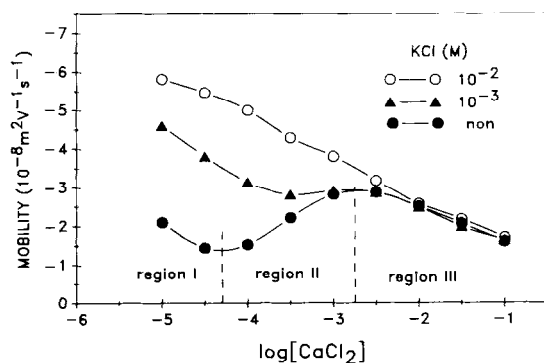


Fig. 5. Electrophoretic mobility of latex C as a function of log molar concentration of CaCl_2 with KCl as a background electrolyte (pH 6.8).

and increase the negative charge of the particles. In region I, the decrease of the electrokinetic potential due to the action of counterions is the dominant mechanism. When these processes are comparable, the mobility approaches a minimum which is followed by an increase to a maximum upon increasing calcium chloride concentration. In the ascending leg of the curve (region II) the negative potential acquired by the approach of co-ions close to the surface of the particles is much larger than the reduction of the electrokinetic potential caused by the action of counterions and the increase of ionic strength. At the mobility maximum, the contribution of these processes is comparable and subsequent increase of CaCl_2 concentration causes a decrease in the mobility due to compression of the diffuse double layer and neutralization of negative charge on the surface.

Support for this qualitative mechanism is given by the curves of the mobility in the presence of KCl as a background electrolyte. In this case the absolute values of the mobility at low calcium chloride concentration are larger than those without KCl. This is caused by the increased number of co-ions (Cl^-) at the interfacial region adjacent to the hydrophobic surface of the particles. At 10^{-2} M KCl the negative potential and charge acquired by the action of co-ions at the interface is maximal, as found in the studies with 1:1 electrolyte, and addition of calcium chloride salt causes a continuous decrease in the mobility, a result of charge neutralization and compression of the diffuse double layer.

The effect of a trivalent salt (LaCl_3) is somewhat similar, as observed in Fig. 6. The absolute values of the mobility are smaller than those with calcium chloride, and the maximum of the mobility without KCl is less pronounced. These results are in qualitative agreement with the mechanism proposed earlier. Trivalent cations are more effective in reducing the electrokinetic potential of colloidal particles than bivalent cations and, as a result, the process of

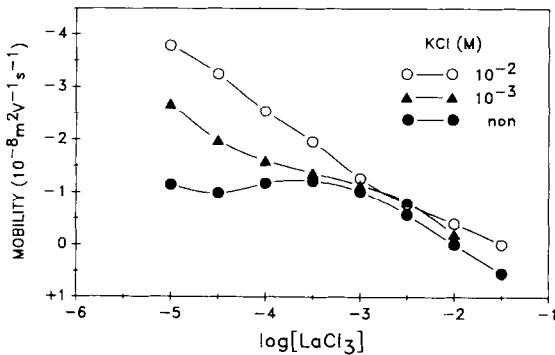


Fig. 6. Electrophoretic mobility of latex C as a function of log molar concentration of LaCl_3 with KCl as a background electrolyte (pH 6.0).

reducing the negative electrokinetic potential by counterions competes more successfully with the process of increasing the negative potential by the co-ions. The positive mobility observed in high LaCl_3 concentration indicates charge reversal of the latices due to specific adsorption of lanthanum species.

The difference between the mobility curves with 1:1 electrolyte (Figs 3 and 4) as compared to 2:1 and 3:1 electrolytes (Figs 5 and 6) is attributed to the fact that the counterions of 1:1 electrolyte are less effective in reducing the negative electrokinetic potential of the particles as compared to polyvalent counterions. As a result, the increase of the negative potential acquired by the action of co-ions, when 1:1 electrolyte is used, dominates over all salt concentrations below the value corresponds to the maximum in the mobility curve. This also explains (i) the higher value of the mobility at the maximum, (ii) the steeper slope of the ascending leg of the mobility curve, and (iii) the absence of a minimum in the mobility curve when 1:1 electrolyte is used, as compared to 2:1 and 3:1 electrolytes.

Mobility with bivalent co-ions as compared to univalent co-ions

Further experiments to support the qualitative model described earlier were conducted. The model can be tested experimentally by measuring the mobility with salts of similar counterions but of co-ions of different valency. Electrophoretic mobility studies with a univalent co-ion salt (NaNO_3) were compared to those with a bivalent co-ion salt (Na_2SO_4). The results for latices B and D are presented in Figs 7 and 8 respectively. The mobility with Na_2SO_4 was more negative than that with NaNO_3 until the maximum (in the absolute value) was reached; then this mobility became less negative. This behavior is in accord with our proposed model. The SO_4^{2-} bivalent anions are expected to increase the negative electrokinetic potential more than the univalent NO_3^- an-

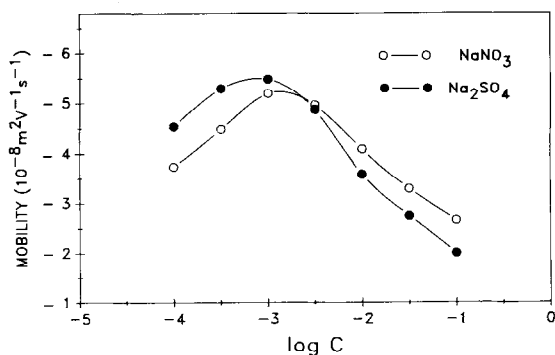


Fig. 7. Electrophoretic mobility of latex B as a function of log molar concentration of Na_2SO_4 and NaNO_3 (pH 6.8).

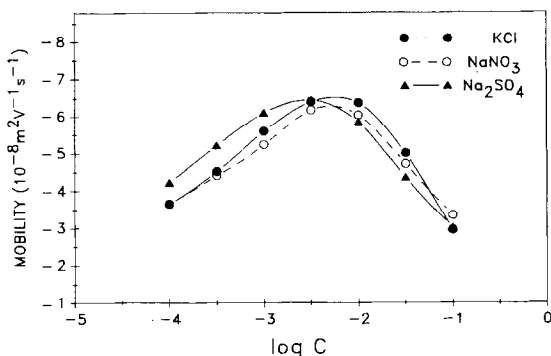


Fig. 8. Electrophoretic mobility of latex D as a function of log molar concentration of Na_2SO_4 , KCl and NaNO_3 (pH 6.8).

ions since each sulfate anion carries two charges. This is evidenced in the ascending leg of the curves where the dominant mechanism of imparting charge is the approach of co-ions close to the surface of the particles. In the descending leg of the curves, where compression of the double layer and charge neutralization dominates, the mobility is less negative with Na_2SO_4 since each mole of this salt contributes two moles of sodium counterions. For comparison the curve of KCl is also presented in Fig. 8. The curves for KCl and NaNO_3 are comparable which may imply that NO_3^- and Cl^- have a similar contribution to the negative electrokinetic potential of the particles. The slight difference between the curves with NaNO_3 and KCl may be due to experimental error and/or the different action of the K^+ and Na^+ counterions at the interface.

Preferential adsorption of co-ions onto surfaces

Preferential adsorption of co-ions has been suggested as a source of surface charge more than half a century ago. Abramson [19] has reported that paraffin oil droplets in aqueous suspensions of simple electrolytes have negative electrokinetic potential. This potential was attributed to the preferential adsorption of anions at the oil water interface. Other studies with various types of non-ionogenic surfaces revealed similar behavior which was explained in terms of anion adsorption [20,21]. The preferential adsorption of anions was explained by the fact that anions, which are less hydrated than cations, are closer to the apolar surface. Recent studies with positive charged latices reported a similar formation of a maximum in the mobility curve [24,30]. These results exclude the possibility that anions are preferentially adsorbed at the interface of polystyrene latices.

The approach of co-ions close to the hydrophobic surface of latex particles is not believed to be a specific process in which they are chemisorbed onto specific sites. The similarity in the mobility curves obtained with various types

of univalent co-ions, in this study (Fig. 8) and others [14,32], indicates that the process is not specific. It is rather the valency of the co-ions which affects the magnitude of the electrokinetic potential, as found in this study. The sulfate functional groups may not prevent the co-ions from approaching close to the surface because they are spaced far away from each other. The driving force behind this mechanism and the role of the surface properties and functional groups of the particles remain subjects for further investigation.

The hairy layer model

In the hairy layer model a special structure is ascribed to the surface layer on the latex particles [13,18]. This layer is considered to be comprised of flexible chains terminating in the sulfate groups. The repulsion between the charged end groups increases with decreasing ionic strength causing the hairy layer to expand into the solution phase. Consequently, the plane of shear moves outwardly causing the electrokinetic potential to decrease. The presence of a hairy layer on latex particles has not been demonstrated conclusively but some hydrodynamic studies may support its presence [31].

Van den Hoven and Bijsterbosch [18] suggested that the hairy layer must be sensitive to the nature of the electrolyte ions, especially if they show strong specific interaction. The hypothesis was further tested by adsorbing $3 \cdot 10^{-4} M$ tetrabutylammonium (TBuA^+) ions to negatively charged latex particles and measuring the electrophoretic mobility as a function of KCl concentration. Their results showed that the electrokinetic potential curve as a function of KCl concentration has a less pronounced maximum. It was suggested that the contraction of the hairy layer, by the adsorption of TBuA^+ ions to the negatively charged sites, caused the mobility to behave in the normal manner, i.e., a continuous decrease in the electrokinetic potential with increasing ionic strength. However, close inspection of their results shows that the zeta potential was almost constant over the range of 10^{-4} to $10^{-2} M$ KCl with a small maximum. This behavior thus resembles the anomalous behavior of our latex particles.

In another recent study [24] negatively charged latices were covered with positively charged poly-L-lysine, and positively charged latices were covered with negatively charged poly-L-glutamic acid. The mobility of the covered particles was measured as a function of KCl concentration. Fully covered particles exhibited a similar maximum in the mobility as that of bare particles but of opposite sign. The results were explained by the fact that the maxima in the mobility curve of covered and uncovered latices are related to the presence of a hairy layer of polyelectrolyte chains at the particle interface.

The interpretation of the results in the above mentioned studies is not straightforward. The interaction of TBuA^+ ions and polypeptides with latex

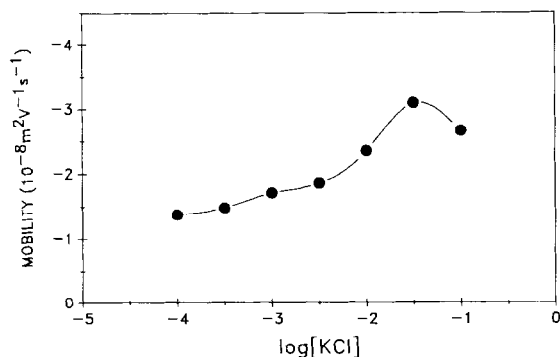


Fig. 9. Electrophoretic mobility of latex C as a function of log molar concentration of KCl in the presence of $10^{-4} M$ LaCl_3 as a background electrolyte (pH 6.0).

particles involves not only electrostatic, but also hydrophobic interaction. The conformation of these macromolecules at the interface alters its nature and affects the adsorption of simple ions.

In order to test the apparent existence of a shrinkable hairy layer it is useful to use electrolyte ions which are strongly adsorbed to the negatively charged sites but do not alter the nature of the polystyrene surface. For this purpose trivalent salts such as LaCl_3 may be used. La^{3+} cations are very effective in neutralizing negatively charged particles, causing a marked decrease in surface potential. Figure 9 describes the mobility of latex D as a function of KCl concentration in the presence of $10^{-4} M$ LaCl_3 . If the mechanism proposed by the hairy layer model operates, the layer would shrink owing to the presence of LaCl_3 so that the mobility would decrease continuously with increasing KCl concentration. However, as shown conclusively in Fig. 9, the mobility increases with KCl concentration, in agreement with our proposed qualitative model.

While the hairy layer model is able to explain qualitatively the mobility behavior with 1:1 electrolytes it fails to explain the results with polyvalent counterions and co-ions (Figs 5-9). It is also unable to explain the normal decrease in the mobility with salt concentration for hydrophilic latices with high surface charge [12,33]; these particles have a significant hairy layer. It should be emphasized that the results presented here do not exclude the possibility that a hairy layer exists on the latex particles. However, it is demonstrated that the shape of the electrophoretic mobility curves is not determined by contraction and expansion of such a layer.

CONCLUSIONS

The electrokinetic potential of negatively charged polystyrene latex particles with strong acid groups and low surface charge is determined by the com-

bined action of co-ions and counterions at the interface. Three competing processes are involved in determining the shape of the mobility curve in the presence of inorganic salts:

(1) Neutralization of negative charge on the surface by adsorption of counterions causing a decrease in the electrokinetic potential (less negative).

(2) Approach of co-ions close to the hydrophobic surface of the particles, causing an increase of the electrokinetic potential (more negative).

(3) Compression of the diffuse double layer due to high bulk concentration of electrolyte, causing a decrease in electrokinetic potential (less negative).

The extent of each process along the mobility curve determines the shape of the electrokinetic potential as a function of electrolyte concentration.

ACKNOWLEDGEMENT

The authors acknowledge the support of the U.S. Environmental Protection Agency under Research Grant R812760.

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