

# Hofmeister Effects in the Stability and Electrophoretic Mobility of Polystyrene Latex Particles

Teresa López-León, Ana B. Jódar-Reyes, Delfi Bastos-González, and Juan L. Ortega-Vinuesa\*

*Biocolloid and Fluid Physics Group, Department of Applied Physics, University of Granada, Av. Fuentenueva S/N, 18071 Granada, Spain*

*Received: July 23, 2002; In Final Form: March 11, 2003*

Specific ionic effects on numerous solid–aqueous solution interfaces have usually been ranked in the so-called Hofmeister series. Ion specificity has experimentally been manifested in many ways. In this work, the colloidal stability and electrophoretic mobility of three different polystyrene latex samples are analyzed in the presence of different electrolytes. The effects on their colloidal stability and electrokinetic behavior provoked by four anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SCN}^-$ ) and three cations ( $\text{NH}_4^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$ ) located in different positions in the Hofmeister series are shown. Some of these ions specifically modified the pair potential interaction of the colloidal particles yielding results not explained by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory. A modification in the repulsive electrostatic term of this theory is then proposed to consider the ionic specificity. In addition, general but qualitative explanations about the subjacent mechanisms involved in the Hofmeister effects are also summarized.

## Introduction

Interactions between particles dissolved in aqueous solutions are sometimes significantly affected by the presence of different electrolytes. The nature of the different salts, even those having identical charge characteristics, specifically affects the interaction pair potential between surfaces. This is a phenomenon experimentally known a long time ago, although a satisfactory theoretical interpretation is still missing.

The introduction of this paper can be divided in two clearly different parts. The first one aims to present the state of the art of the specificity of the ions, summarizing the main features of this topic, highlighting the complexity of the problem, and discussing two simple microscopic models that can help to understand the ionic specificity. The second part deals with the specific research developed in this work, in which different ions have been used to destabilize polystyrene latex particles.

**Hofmeister Series.** The ionic effects on the aggregation or stabilization phenomena of particles immersed in aqueous solutions have been extensively studied since 1888. Lewith<sup>1</sup> and Hofmeister<sup>2</sup> published accounts of great differences between the minimum concentration of various salts required to precipitate a given protein from solution, even among those with identical charge characteristics. Many ions have been ranked in sequences called Hofmeister series (henceforth HS), depending on their specific effects on different experimental systems. These effects are manifested by a plethora of experimental measurements (i.e., polymer cloud points, protein solubility, chromatographic selectivity, critical micelle concentration, etc.) as listed in a comprehensive review published by Collins and Washabaugh.<sup>3</sup> Therefore, there should be so many HS as different physical or chemical magnitudes and systems are analyzed. Nevertheless, although the relative position of ions in the numerous existing Hofmeister series does not exactly coincide, only slight alterations appear in the characteristic rank

ordering. Consequently, a representative Hofmeister series can be given for anions and cations, albeit, as mentioned, their relative positions should be thought of as indicative only.

$\text{citrate}^{3-} > \text{SO}_4^{2-} > \text{PO}_4\text{H}^{2-} > \text{F}^- > \text{CH}_3\text{COO}^- >$   
(kosmotropic anions)

$\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{SCN}^-$   
(chaotropic anions)

$\text{N}(\text{CH}_3)_4^+ > \text{NH}_4^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ >$   
(chaotropic cations)

$\text{H}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$   
(kosmotropic cations)

Despite the broad spectrum of experimental results existing at the present date, the molecular origins of the HS remains unravelled. There are some hypotheses about the underlying mechanisms, although a general rule capable of explaining all of them still seems to be elusive. Whatever the molecular mechanism is, the HS emerges from a combination of effects in which the water structure is the cornerstone of the problem. If a Hofmeister series is obtained from systems in which interaction between surfaces takes place (i.e., adsorption of macromolecules on interfaces, protein crystallization, colloid aggregation, and so on), not only the water structure around the solvated ions but also that surrounding the immersed surfaces plays a significant role. This is why establishing a general explanation to all of the existing HS becomes almost impossible, because it results from ion–water, water–water, surface–water, surface–ion, and surface–surface interactions. What can be done to simplify the study is to analyze separately all of these contributions.

**Ion–Water Interactions.** It is known that the origin of the HS features lies in the different ways in which ions influence the structure of the water in which they are embedded. Interactions do not arise only from electric ion–dipole forces

\* To whom correspondence should be addressed.

but also, and sometimes more importantly, from the ability of ions (and even noncharged cosolutes, such as urea) to give or accept a couple of electrons to or from the water molecules. Then the local natural hydrogen-bonding network of water changes. That is, the Lewis base or Lewis acid character of the ions, together with their charge and size, must be taken into account.<sup>4</sup> Chromatographic studies<sup>3</sup> and vibrational spectroscopic evidence<sup>5</sup> support a correlation between the HS and water structure. Ions that interact with water more strongly than water itself are known as structure makers or *kosmotropes*, whereas ions having the opposite effect are known as structure breakers or *chaotropes*. The Hofmeister series shown above have been ordered according to their degree of hydration. Strongly hydrated anions (kosmotropes) are on the left and weakly hydrated anions (chaotropes) are on the right. Cations are just ordered on the contrary; chaotropes, weakly hydrated cations, are on the left and the kosmotropes on the right. It should be noticed that the effects of kosmotrope anions are opposite to kosmotrope cations as, although both of them structure water molecules strongly, the orientation of the oxygen and hydrogen atoms toward the ions surface is also opposite. That is, the water structure induced by a kosmotropic anion must produce a result similar to that of a chaotropic cation, and vice versa. Finally, the effects shown by the Hofmeister series usually present an inversion at about  $\text{Cl}^-$  (for anions) and  $\text{Na}^+$  (for cations). So, the position of these two ions is usually considered as a null point in the specific ions effects.

**Water–Water Interactions.** It should be noted that models that only consider the state of single water molecules immediately adjacent to the ion surface break down for explaining satisfactorily the HS. Therefore, the interaction between the ion and the solvent must be transmitted beyond this first water layer. This is done by a cooperative mechanism by means of water–water hydrogen bonding that is propagated through several molecular layers.<sup>6</sup> The cooperativity of water–water hydrogen bonding is crucial for understanding many conceptual difficulties of different items, not only the nature of the HS but also the hydrophobic hydration of surfaces, the magnitude of hydrophobic force, or the protein folding, as stated by Wiggins.<sup>7</sup>

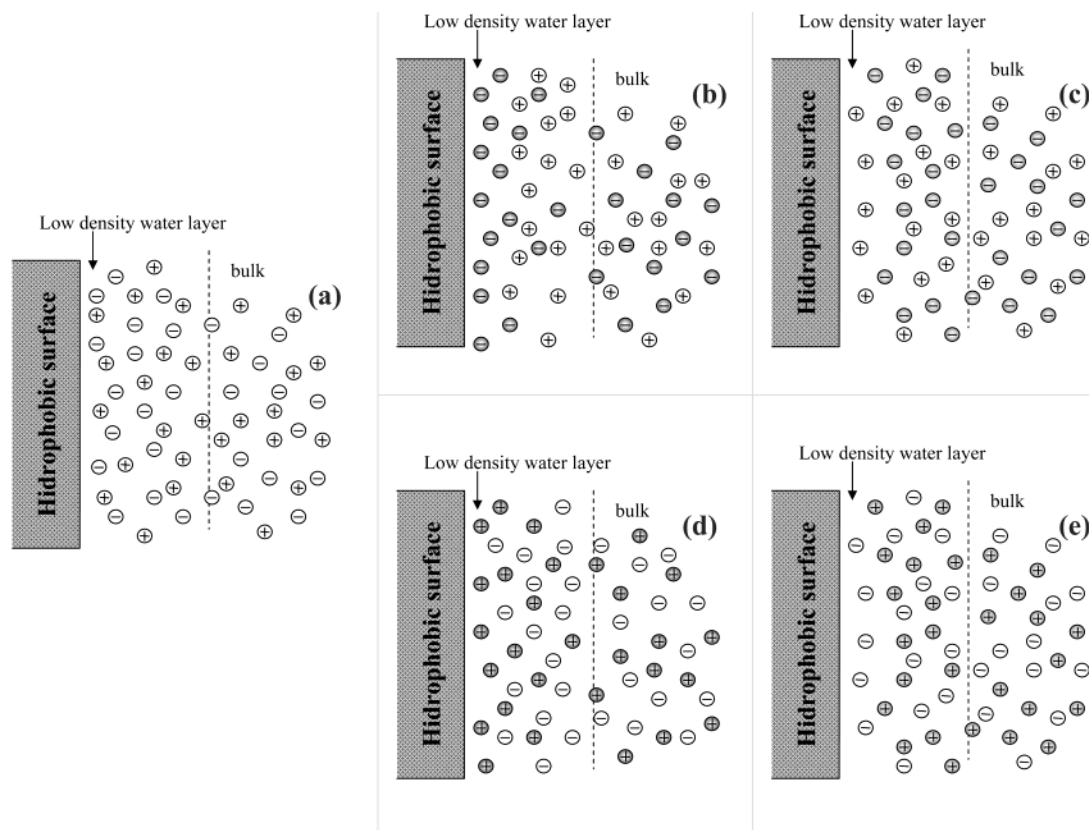
**Surface–Water Interactions.** Water also becomes cooperatively structured when it is put into contact at any kind of surface. If the surface is hydrophobic, a particular rearrangement of water molecules is proposed<sup>7–10</sup> leading to aqueous layers adjacent to the surface with a lower density than that found in normal water. The effect of any hydrophilic surface is the opposite, generating a high density layer of water around it. Independently of the surface nature, interfacial water molecules exhibit spatial orientations different from that of bulk water.

**Surface–Ion and Surface–Surface Interactions.** Interactions between surfaces immersed in electrolyte solutions are usually originated by electrical and dispersion forces, and generally they have been studied by continuum theories.<sup>11</sup> The most important feature for the ions is the charge, and those for the surfaces are the Hamaker constant (considering the medium in which they are embedded) and the surface potential. Ion concentrations near a surface differ from those of the bulk, and they are obtained by using a Boltzmann distribution in which only electrical energies are taken into account. However, when two particles approach each other, the modified solvent “shells” begin to overlap and the local water structure becomes highly directional.<sup>12</sup> The role of water is probably crucial. Despite that, the structure of water molecules is usually neglected when studying surface interactions, and then, the continuum interfacial theories always fail to explain the Hofmeister effects. To our knowledge,

only Ninham and Yaminsky<sup>13</sup> have tried to theoretically justify the Hofmeister effects that are reflected in changes of the surface potential of an interface. They propose a molecular explanation based on the specific ion adsorption and exclusion by taking into account dispersion interactions between ion and surface by using a continuum analysis. They argued that the dispersion interactions can be dominant in ion adsorption processes. The dispersion potential essentially depends on the excess polarizability of ions related to water. So, these authors try to present a way to systematize the HS based on the excess of polarizability of the ions. They only, however, attain to properly justify the order of four anions, namely, acetate,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , but nothing is said about  $\text{SCN}^-$  or  $\text{NO}_3^-$ , which present very striking effects. Because both surface and ions change the solvent properties around them, the theoretical approaches to the Hofmeister series must be done using discontinuum models and taking molecular considerations. Until now, nobody has solved the problem.

Although there is not any theory that satisfactorily explains how Hofmeister ions specifically affect surface–surface interactions, there are qualitative explanations about how the presence of chaotropic or kosmotropic ions could modify the surface potential ( $\Psi_0$ ). Concretely, there exist two different molecular mechanisms, which are discussed below. Some diagrams have also been included, and although they are rather simple, the schemes can help to understand the HS better.

(1) On one hand, there is a microscopic interpretation of the Hofmeister effects that explains changes in  $\Psi_0$  by means of a specific exclusion or accumulation mechanism of ions at the surface. It should be noted that this mechanism is fundamentally based on entropy changes and thus it differs from that proposed by Ninham and Yaminsky<sup>13</sup> previously commented. To simplify as much as possible this idealization, an uncharged surface is considered, avoiding any Boltzmann distribution of ions. In addition, no ion–ion correlation is considered either. Therefore, the accumulation or exclusion of ions will be only led by the structure of the water molecules adjacent to both the surface and the solvated ions. As explained above, if a hydrophobic surface is taken into account, the water molecules located at the surface present a modified structure (compared to that of the bulk water) caused by a cooperative mechanism that yields a low-density water structure.<sup>7</sup> It is broadly assumed that chaotropic ions disrupt the water structure around them provoking somehow a local “chaos”. So, they tend to accumulate in these low-density water layers because they prefer to be embedded in this “previously” restructured water than to be immersed in “normal” water, which structure they have to reorganize. It should be noted that the surface does not attract chaotropic ions by itself. The accumulation mechanism is mediated by the molecular structures of the water molecules that surround both the surface and the ions. The effect of the hydrophobic surface on a kosmotropic ion is opposite. Kosmotropic ions strongly interact with water, and they do not tend to be immersed in regions where water has a low density. The just-discussed mechanism is depicted in the Scheme 1. It becomes easy to understand why the effect induced by a chaotropic anion can be similar to that of a kosmotropic cation. If a nonspecific electrolyte is dissolved, that is,  $\text{NaCl}$  (picture a in Scheme 1), there must not be any specific exclusion or accumulation of ions at the interface, at least as a primary hypothesis. However, if a salt containing a chaotropic anion and a nonspecific cation is now added, that is,  $\text{NaSCN}$  (Scheme 1, picture b), an accumulation of anions would result near the surface. This would reduce the surface potential, being the  $\Psi_0$

**SCHEME 1. Modifications in the Surface Potential Induced by Means of an Ion Accumulation or Exclusion Mechanism<sup>a</sup>**

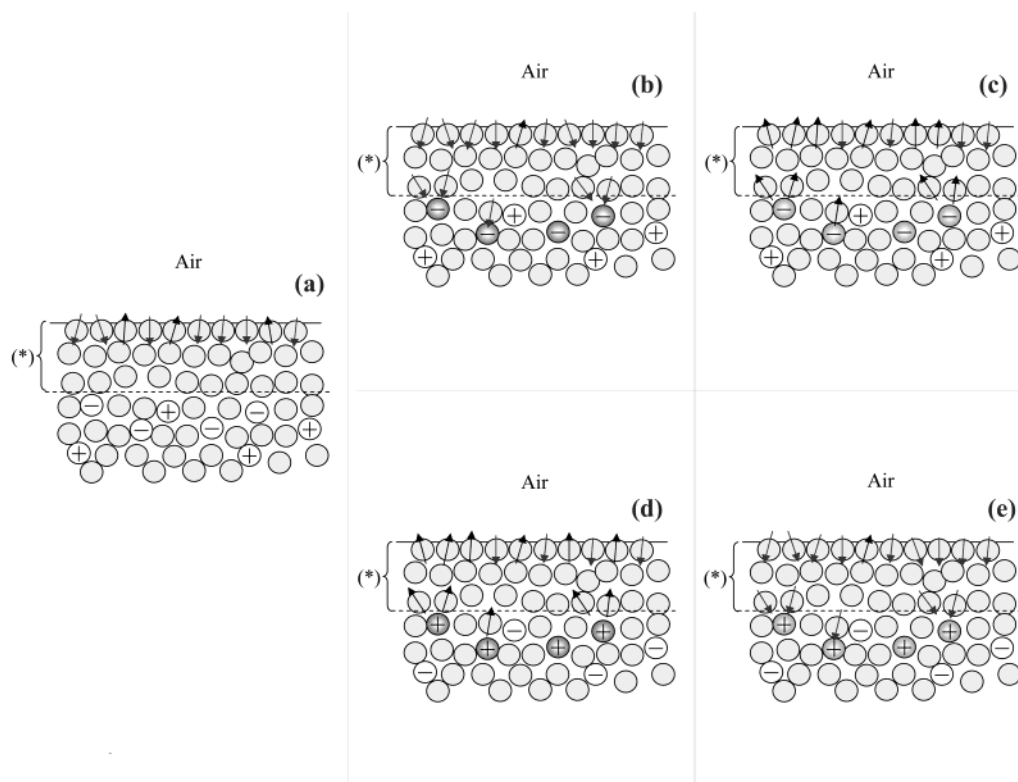
<sup>a</sup> Dark gray circles represent chaotropic ions, which tend to accumulate near hydrophobic surfaces; light gray circles represent kosmotropic ions, and clear circles represent nonspecific ions. Picture (a) depicts nonspecific anions and cations. Picture (b) depicts chaotropic anion and nonspecific cation. Picture (c) depicts kosmotropic anion and nonspecific cation. Picture (d) depicts chaotropic cation and nonspecific anion. Picture (e) depicts kosmotropic cation and nonspecific anion. More details are provided in the main text.

reduction shaper for increasing chaotropic degree. Nevertheless, if the solvated salt was formed by a kosmotropic anion and a nonspecific cation, that is, NaF (Scheme 1, picture c), the  $\Psi_0$  value would be higher because anions would be repelled from the surface yielding a local excess of cations. If salts are made of nonspecific anion but chaotropic or kosmotropic cations, that is,  $\text{NH}_4\text{Cl}$  or  $\text{CaCl}_2$ , respectively, the ion distribution would be similar to that shown in Scheme 1, pictures d and e, respectively. (It should be noted that figures have been only depicted for 1:1 electrolytes but not for 2:1 species). Therefore, the effect induced by a chaotropic anion on the  $\Psi_0$  value may be similar to that provoked by a kosmotropic cation. Likewise, a kosmotropic anion would behave as a chaotropic cation. Just compare Scheme 1, pictures b and e, or Scheme 1, pictures c and d. A hydrophilic surface would reorganized the ions just in the opposite way that a hydrophobic surface does. Anyway, the molecular mechanism is similar, although now kosmotropic ions tend to accumulate near the surface, because the water adjacent to a hydrophilic surface has an increased density instead, and chaotropic ions would be located far from this high-density water region.

(2) On the other hand, there is a second mechanism that can be considered to explain Hofmeister effects in which no ion adsorption considerations are taken into account. As an example, we can analyze the surface potential of an air–water interface. It has been argued<sup>14–16</sup> that the water molecules at the air–water interface have a preferential orientation with the oxygen atoms outermost. A result of this orientation is the establishment of an electrical double layer at the surface with the outermost

portion of the double layer being negative and the innermost part being positive. Then, an electrical potential difference ( $\Delta\Psi$ ) can be measured across the air–water interface. If water contains an electrolyte, the surface potential can be modified if the solvated ions specifically disrupt the water organization at the interface. It is also assumed that there is deficiency of electrolytes in the surface layer, obtaining a pure water layer about 4 Å thick.<sup>17–19</sup> The way that Hofmeister ions rearrange the interface water dipoles is explained by a cooperative mechanism. Local changes in water structure are transmitted cooperatively by water–water hydrogen bonding<sup>6</sup> through several molecular layers. Collings and Washabaugh<sup>3</sup> purposed different models that took into account at least three water layers. Scheme 2 shows how this molecular mechanism would act. Nonspecific electrolytes would not modify the structure of pure water, either in bulk or at the interface, and then a reference  $\Delta\Psi$  value is obtained. If a chaotropic anion is added, the local water restructuring is transmitted to the interface water molecules, partially changing their dipole orientations and then modifying the surface potential. Experimental measurements<sup>20</sup> have shown that chaotropic anions reduce  $\Delta\Psi$ . Kosmotropic anions rearrange local water molecules in the opposite way that chaotropic anions do, despite having identical sign of charge. This could be understood by remembering that Hofmeister ions restructure the water molecules not only by means of charge and size but also by its Lewis base or acid character. So, a kosmotropic anion would lead to an increase of the  $\Delta\Psi$  value (Scheme 2c). The effects induced by cations are just on the contrary of the anions, because of their different charge sign.



**SCHEME 2. Modifications in the Surface Potential Induced by Changes in the Average Dipole Orientation of the Water Molecules Located at the Interface<sup>a</sup>**


<sup>a</sup> The free ion layer is denoted by \*. Dark gray circles represent chaotropic ions, light gray circles represent kosmotropic ions, clear circles with a charge inside ( $\ominus$ ) represent nonspecific anions, and totally empty circles are the water molecules. The dipoles of some water molecules have been drawn as arrows. Picture (a) represents the situation for nonspecific anions and cations. Picture (b) depicts the effect of chaotropic anions and nonspecific cations. Picture (c) depicts the effect of kosmotropic anions and nonspecific cations. Picture (d) depicts the effect of chaotropic cations and nonspecific anions. Picture (e) depicts the effect of kosmotropic cations and nonspecific anions. More details are provided in the main text.

This has been reflected in Scheme 2d,e. This explanation given for an air–water interface could be extended to any hydrophobic material immersed in water, for example, polystyrene.

**Goals of the Paper.** Although there exist numerous references in the literature that use Hofmeister ions to study many systems, few papers can be found presenting a systematic analysis of Hofmeister series using latex particles. This paper is the first part of a broader study centered on the colloidal stability of polystyrene latex particles in the presence of different salts related to the HS. There are three important aspects that have been analyzed, namely, (i) the hydrophobic/hydrophilic degree, (ii) the charge sign, and (iii) the surface charge density ( $\sigma_0$ ) of the immersed surfaces, to elucidate how they affect ranking of the chosen Hofmeister ions. The work presented in this paper is actually concerned with two of these items, namely, the analysis of the charge sign and the  $\sigma_0$ , because the hydrophobic character of the latex particles has been kept almost constant. The influence of the hydrophobic/hydrophilic character has been extensively evaluated in a second part,<sup>21</sup> in which the hydrophobic surface of latex particles was changed to hydrophilic by adsorbing a protein. The Hofmeister salts selected for the study are listed below. On one hand, the salts  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ , and  $\text{NaSCN}$  were chosen to analyze the effects of four anions with different positions in the HS. On the other hand,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$ , and  $\text{NH}_4\text{NO}_3$  were selected for comparing cations. In addition, three different latexes have been employed in this work. All of them were synthesized using styrene as the unique or major monomer, and their main differences are related to their surface ionic groups. Two of them were anionic with different acid groups at the surface, and the other one presents

a positive surface charge having a weak base character. These latex pools allow us to test independently the effect of charge sign and  $\sigma_0$  of the surfaces on ordering the Hofmeister ions by means of their destabilizing properties. As will be shown, the interaction pair potential between the latex particles is specifically modified by each of these Hofmeister ions, which is reflected on reliable differences regarding the colloidal stability of the latex samples. This is why stating a theoretical model that accounts for the Hofmeister effects would be advisable.

The paper has been structured as follows. First, a complete characterization of the latex particles is described. Then, an extensive study on the aggregation patterns of the latex particles is presented. Subsequently, the electrophoretic mobility behavior of our samples is evaluated, which can help to corroborate some conclusions arising from the colloidal stability studies. Finally, the paper finishes with a theoretical section in which a modification in the electrical term of the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory is proposed to include in such a theory the Hofmeister effects.

**Materials and Methods**

**Reagents.** Styrene and sodium styrene sulfonate (NaSS) monomers were obtained from Merck and Fluka, respectively, and they were used without further purification. The initiators used in this work were 4,4'-azobis(4-cyanopentanoic acid) (ACPA) purchased from Aldrich and azo-*N,N'*-dimethyleisobutyramidine hydrochloride (AMDBA), which was kindly donated by Dr. J. W. S. Goossens from Bayer, A.G. A cationic lipid, distearoyl dimethylammonium bromide (DSDMA) from Fluka, was also employed in this study. The rest of the salts

TABLE 1: Synthesis Conditions of the Latexes<sup>a</sup>

latex	H <sub>2</sub> O (ml)	st (g)	NaSS (mg)	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mg)	NaHSO <sub>3</sub> (mg)	NaHCO <sub>3</sub> (mg)	ACPA (mg)	ADMBA (mg)	NaOH (mg)	HCl (μL)	stirring rpm	T (°C)	time (h)
ABJ2	567	90	775	820	320	508					250	45	14
AMJ5	720	25					300		225		350	80	20
AMJ10	720	35						200		390	350	60	15

<sup>a</sup> Abbreviations: st, styrene; NaSS, sodium styrene sulfonate; ACPA, 4,4'-azobis(4-cyanopentanoic acid); ADMBA, azo-*N,N'*-dimethyleisobutyramidine hydrochloride.

were of analytical grade and purchased from different firms: Sigma, Panreac, and Scharlau. Double-distilled and deionized (DDI) water was used throughout.

**Preparation and Characterization of Latex Particles.** Three different polystyrene latexes have been used in this work. All of them were synthesized in our laboratories. There are two anionic latexes, namely, **ABJ2** and **AMJ5**. The former has strong acid groups (sulfonate) in the surface, and the latter possesses weak acid groups (carboxyl). The third latex, **AMJ10**, is cationic, and the nature of its surface-charged group is amidine, a weak base group. All of them were prepared by emulsifier-free polymerization in a discontinuum reaction. The sulfonate latex is a styrene/NaSS copolymer, and the surface-charged groups come from both the initiator molecules and the NaSS comonomer. **AMJ5** and **AMJ10** were synthesized using styrene as the only monomer. For both latexes, the surface-charged groups come from the initiators. ACPA initiator provides carboxyl groups to the **AMJ5** latex, and the cationic groups of **AMJ10** latex derive from the ADMBA molecules. The reactor was a spherical vessel (maximum volume = 1 L), and solutions were stirred with a palette located at 2 cm over the bottom of the vessel. Synthesis conditions were established following studies of different authors,<sup>22–24</sup> and they are summarized in Table 1.

A comprehensive cleaning process was followed after the synthesis. It is well-known that the diverse methods to prepare clean latexes could provide polymer colloids with quite different electrokinetic and stability properties. For this reason, to clean our latexes, we have followed the recommendations given by Wilkinson et al.<sup>25</sup> in their extensive paper dedicated to reviewing a wide range of cleaning and characterization techniques. After synthesis, the latexes were filtered through glass wool, and then they underwent repeated cycles of centrifugation–decantation–redispersion (except for **ABJ2** latex, because of its small size). Subsequently, serum replacement was employed in several steps: first with DDI water until the electrical conductivity of the samples was below 2 μS cm<sup>−1</sup>. Then, a strong acid solution was added to serum replacement to replace the cations with protons. Finally, DDI water was added to remove the excess acid until the electrical conductivity was, again, below 2 μS cm<sup>−1</sup>.

The average particle diameter was obtained by transmission electron microscopy (TEM) using a H-7000 FA Hitachi microscope. The mean diameter of each latex sample was obtained averaging over 500 individual particles (automatically analyzed with Bolero software, AQ Systems).

Surface charge densities of the latexes were determined by conductometric and potentiometric automatic titrations employing a pH-meter (Crison Instruments, model 2002) and a conductimeter (Crison Instruments, model 525) and a Dosimat 665 (Mettrom) to add the tritane agent.

**Electrophoretic Mobility.** Electrophoretic mobility measurements were performed with a Zeta-Sizer IV (Malvern Instruments). Latex particles were diluted in the desired electrolyte solution, and data were obtained from the average of six

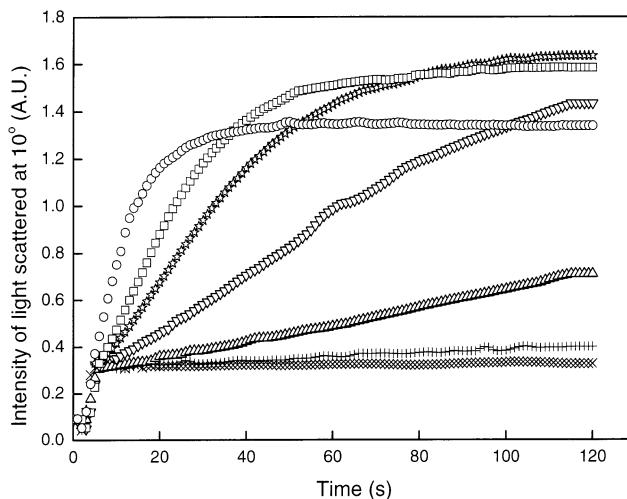


Figure 1. Aggregation kinetic of **ABJ2** particles for increasing NaCl concentration: (x) 100; (+) 150; (Δ) 200; (▽) 250; (☆) 300; (□) 400; (○) 625 mM.

measurements at the stationary level in a cylindrical cell. Standard deviations were always lower than 5%. It should be noted that no buffered solutions were used in both mobility and coagulation experiments to avoid the presence of other salt species different from the chosen Hofmeister ions.

**Colloidal Stability.** Particle aggregation studies were carried out using a low-angle light-scattering technique. Scattering light intensity was observed at 10° for 120 s. The scattering cell was rectangular with a 2 mm path length. The cell was thoroughly cleaned with chromic acid, rinsed with distilled water, and then dried using an infrared lamp. Equal volumes (1 mL) of salt and latex solutions were mixed and introduced into the cell by an automatic mixing device. Aggregation analyses were performed in two nonbuffered solutions at pH 4 (HCl 10<sup>−4</sup> M) and pH 10 (NaOH 10<sup>−4</sup> M) freshly prepared.

The latex dispersions used for such coagulation experiments were diluted enough to minimize multiple scattering effects. The light scattered at 10° behaves linearly for the first steps of the coagulation. However, linearity was rapidly lost in the aggregation kinetics in which aggregates of large size were formed quickly. A typical coagulation experiment is shown in Figure 1.

The stability ratio, also called Fuch's factor (*W*), is a criterion broadly used to study the stability of colloidal systems. It can be obtained by the following expression

$$W = \frac{k_r}{k_s} \quad (1)$$

in which the rate constant *k<sub>r</sub>* corresponds to rapid coagulation kinetic and *k<sub>s</sub>* is the rate constant for slow coagulation regime. The ratio of both constants is equal to that of the ratio of the initial slopes in our coagulation experiments (see Figure 1). The critical coagulation concentration (CCC), that is, the minimum salt concentration needed to rapidly aggregate the colloidal

**TABLE 2: Some Characteristics of Latex Particles<sup>a</sup>**

latex	mean diameter (nm)	PDI	$\sigma_0$ at pH 4 ( $\mu\text{C}/\text{cm}^2$ )	$\sigma_0$ at pH 10 ( $\mu\text{C}/\text{cm}^2$ )
<b>ABJ2</b>	$138 \pm 7$	1.007	$-9.6 \pm 0.4$	$-9.6 \pm 0.4$
<b>AMJ5</b>	$364 \pm 13$	1.004	$-6.1 \pm 0.3$	$-20.5 \pm 0.8$
<b>AMJ10</b>	$320 \pm 15$	1.007	$+18.3 \pm 1.2$	$+4.0 \pm 0.6$

<sup>a</sup> Abbreviations: PDI, polydispersity index;  $\sigma_0$ , surface charge density.

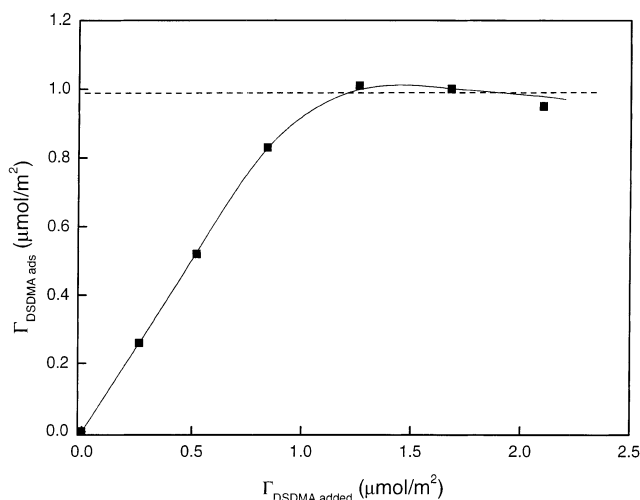
system, can be easily obtained by plotting the logarithm of  $W$  versus the logarithm of the salt concentration and locating that point where  $\log W$  reduces to zero.

## Results and Discussions

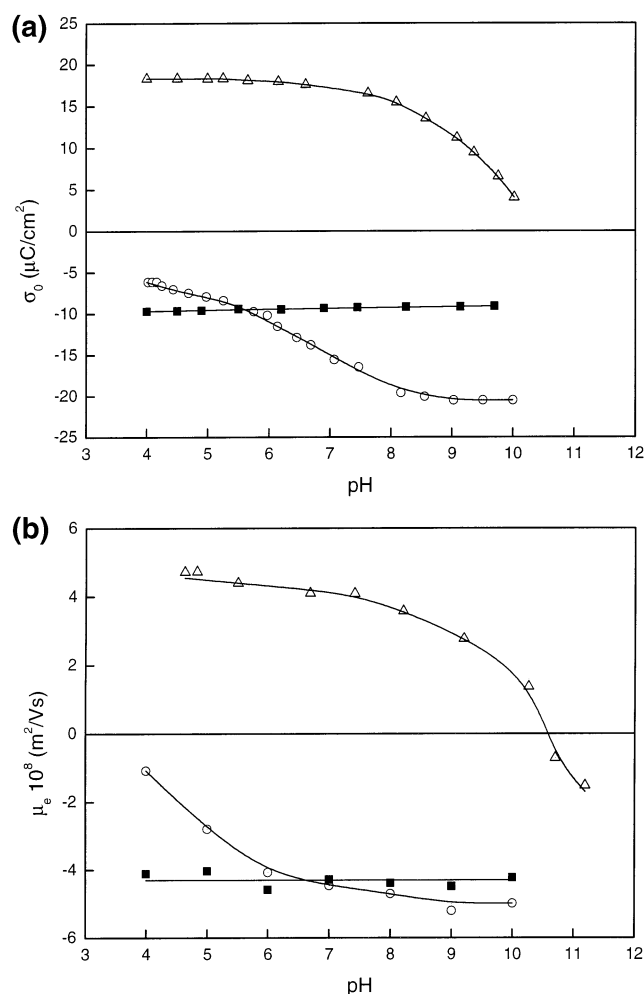
**Surface Characterization of Latex Particles.** A complete surface characterization of latex particles were performed to quantify the surface charge density and its dependence on pH. Strong acidic and weak acidic and basic characters of surface groups were also corroborated measuring the electrophoretic mobility as a function of pH. First, the mean diameter of the particles was measured by TEM. The obtained results are shown in Table 2. The three latex samples were highly monodisperse, their polydispersity index (PDI) being extremely close to unity.

The surface charge density ( $\sigma_0$ ) of latexes **AMJ5** and **AMJ10** was obtained by conductometric back-titration. The  $\sigma_0$  calculation for latex particles with weak acid or base groups must not present any difficulty, and details on how it can be obtained are described in ref 26. However, the calculus of  $\sigma_0$  for a sulfonate latex by means of conductometric titration may become unreliable because the strong acid groups on the surface are not possible to determine directly. What is evaluated is the concentration of  $\text{H}_3\text{O}^+$  ions that act as counterions. Hence, correlating the  $\text{H}_3\text{O}^+$  concentration to the surface charge density may become a difficult task because the usual counterions,  $\text{Na}^+$  or  $\text{K}^+$  (which arise from those electrolytes used in the particle synthesis), must previously be completely replaced by protons. Whatever the method used to replace the cations (usually incubation with ion-exchange resins or, as in our case, by addition of a strong acid to the serum replacement device), it is really difficult to ensure a total exchange of protons. Therefore, a shadow of a doubt always remains when  $\sigma_0$  values of sulfonate latexes are calculated. This is why the surface charge density of the **ABJ2** was obtained in an alternative way: adsorbing a cationic lipid, namely, DSDMA, in a 50% (v/v) ethanol/water mixture. Details are given elsewhere,<sup>27</sup> and what is shown is that in 50% ethanol/water solutions the adsorption of DSDMA on a polystyrene latex with sulfonate groups is mainly led by pure electrostatic attraction. At maximum DSDMA coverage, latex–lipid complexes are totally unstable because a complete charge cancellation takes place. Obtaining  $\sigma_0$  is immediate knowing the number of lipid molecules adsorbed per unit area, assuming that each sulfonate group is balanced by one DSDMA. Such a DSDMA adsorption onto the **ABJ2** particles is shown in Figure 2.

The surface charge density of latexes with weak acid or base groups depends on pH. This dependence can be analyzed by potentiometric titrations, as also described in ref 26. The  $\sigma_0$  values versus pH for the three latexes are plotted in Figure 3a. In addition, the  $\sigma_0$  dependence on pH has been corroborated by electrophoretic mobility ( $\mu_e$ ) measurements, shown in Figure 3b. It can be observed that for sulfonate latex the  $\mu_e$  remains constant in all of the pH range studied, while for carboxyl and cationic latexes, a decrease in  $\mu_e$  values is perceived when their



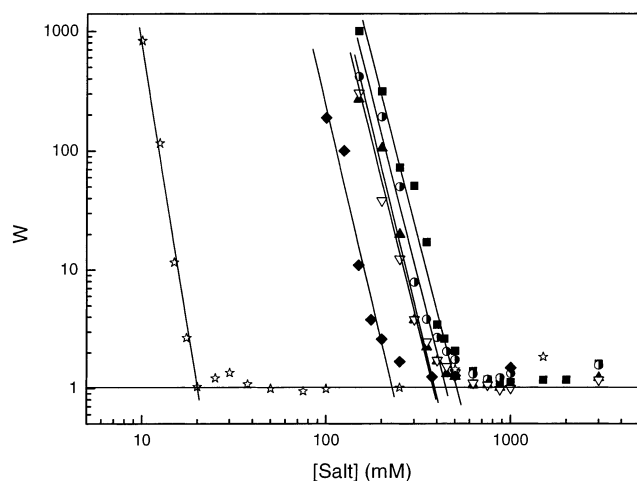
**Figure 2.** Adsorption isotherm of DSDMA in 50% ethanol/water solutions (v/v) for the **ABJ2** latex.



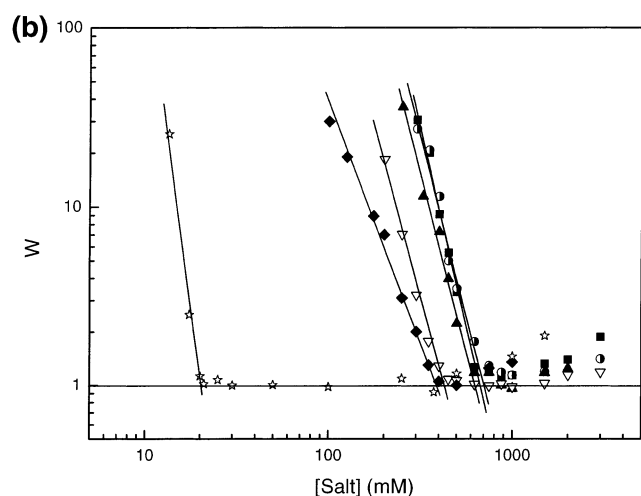
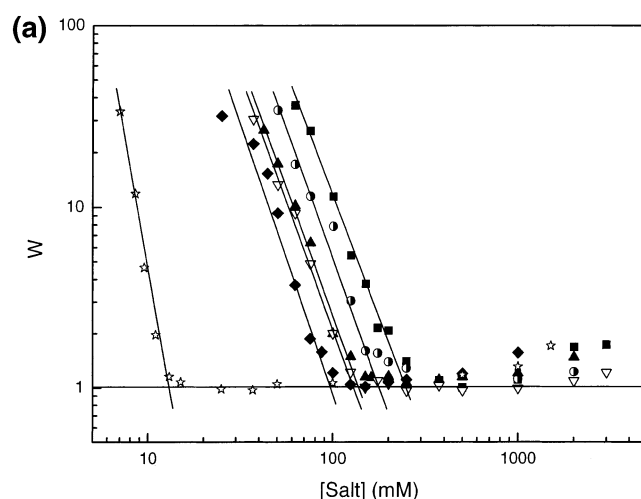
**Figure 3.** Dependence of (a) the surface charge density and (b) the electrophoretic mobility on pH for the (■) **ABJ2**, (○) **AMJ5**, and (Δ) **AMJ10** latexes.

$\sigma_0$  values diminish. From these measurements, it is easy to identify the weak acidic and basic character of the latexes, although it should be noted that there is not an exact correspondence between  $\sigma_0$  and  $\mu_e$  data because mobility is related to  $\zeta$  potential and not to the surface potential.

**Colloidal Aggregation Results.** Because **AMJ5** and **AMJ10** latexes change their  $\sigma_0$  values with pH, the stability studies were

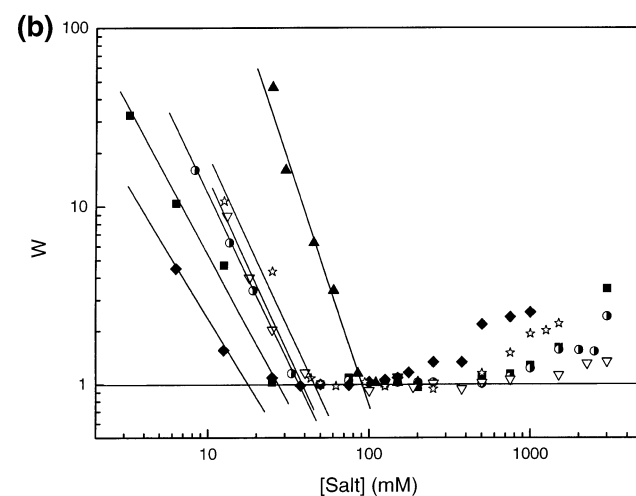
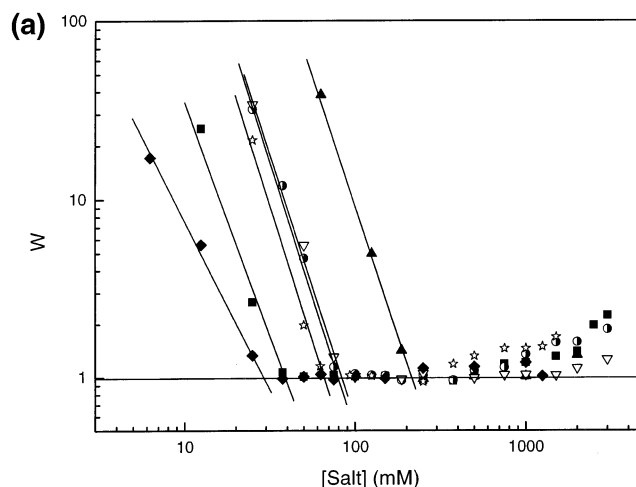


**Figure 4.** Stability ratio (Fuch's factor) versus electrolyte concentration for the **ABJ2** latex at pH 4: (■) NaSCN; (○) NaNO<sub>3</sub>; (▲) NaCl; (◆) Na<sub>2</sub>SO<sub>4</sub>; (▽) NH<sub>4</sub>NO<sub>3</sub>; (☆) Ca(NO<sub>3</sub>)<sub>2</sub>.



**Figure 5.** Stability ratio (Fuch's factor) versus electrolyte concentration for the **AMJ5** latex at (a) pH 4 and (b) pH 10: (■) NaSCN, (○) NaNO<sub>3</sub>, (▲) NaCl, (◆) Na<sub>2</sub>SO<sub>4</sub>, (▽) NH<sub>4</sub>NO<sub>3</sub>, and (☆) Ca(NO<sub>3</sub>)<sub>2</sub>.

carried out at two of them, pH 4 and pH 10, to check whether Hofmeister effects could also depend on different surface charge densities. Table 2 collects the  $\sigma_0$  values obtained by titration at these pHs. As it was previously commented, the **ABJ2** latex does not modify its  $\sigma_0$  value, and thus stability of this sulfonate latex can be studied at only one pH. We chose pH 4 for its



**Figure 6.** Stability ratio (Fuch's factor) versus electrolyte concentration for the **AMJ10** latex at (a) pH 4 and (b) pH 10: (■) NaSCN, (○) NaNO<sub>3</sub>, (▲) NaCl, (◆) Na<sub>2</sub>SO<sub>4</sub>, (▽) NH<sub>4</sub>NO<sub>3</sub>, and (☆) Ca(NO<sub>3</sub>)<sub>2</sub>.

analysis. It is broadly assumed that NaCl is an inert electrolyte with regard to its interaction with polystyrene surfaces. Therefore, experiments of colloidal aggregation performed with such a salt have been taken as a reference for comparing the specific effect of the rest of the salts. Aggregation results are shown in Figures 4 (**ABJ2**), 5a,b (**AMJ5** at pH 4 and 10, respectively), and 6a,b (**AMJ10** at pH 4 and 10, respectively). The CCC values obtained from these figures are indicated in Table 3. Some conclusions can be extracted from this vast set of experiments. The most relevant of them are listed in the following.

(1) First, the stability patterns obtained by NaCl are discussed. The CCC values are practically in the same order as those of the  $\sigma_0$  values, the most stable latex being the most charged. There is, however, a slip in such ranking. The cationic latex (**AMJ10**) at pH 4 presents a quite low stability (CCC being equal to 210 mM with NaCl), while its surface charge density is high ( $18.3 \mu\text{C}/\text{cm}^2$ ), that is, actually near the carboxyl latex when it is totally charged ( $20.5 \mu\text{C}/\text{cm}^2$ ). Besides, the mobility data shown in Figure 3b would prompt the thought that **AMJ10** should show a higher stability at acid pH than that obtained. At least, electrostatic arguments would aim to this conclusion. Some authors,<sup>28</sup> however, have found flocculation phenomena in situations in which measured  $\zeta$ -potential was still sufficient to ensure electrostatic repulsion between colloidal particles. Such a coagulation was justified by means of hydrophobic attraction. In principle, this reasoning should not be applied to our latexes



**TABLE 3. Critical Coagulation Concentration for the Latexes at pH 4 and 10<sup>a</sup>**

ABJ2 Latex at pH 4						
Hofm. ion	CCC (mM)	$\Psi_0$ (mV)	$\Delta\Psi_0$ (mV)			
SCN <sup>-</sup>	505	-27.0	-1.8			
NO <sub>3</sub> <sup>-</sup>	445	-26.1	-0.9			
Cl <sup>-</sup>	390	-25.2	0			
SO <sub>4</sub> <sup>2-</sup>	225	-29.2	-4.0			
NH <sub>4</sub> <sup>+</sup>	385	-25.1	+1.0			
Na <sup>+</sup>	445	-26.1	0			
Ca <sup>2+</sup>	20	-14.6	+11.5			

AMJ5 Latex						
Hofm. ion	pH 4			pH 10		
	CCC (mM)	$\Psi_0$ (mV)	$\Delta\Psi_0$ (mV)	CCC (mM)	$\Psi_0$ (mV)	$\Delta\Psi_0$ (mV)
SCN <sup>-</sup>	240	-22.7	-3.0	675	-29.6	-0.7
NO <sub>3</sub> <sup>-</sup>	170	-20.8	-1.1	700	-29.9	-1.0
Cl <sup>-</sup>	140	-19.7	0	610	-28.9	0
SO <sub>4</sub> <sup>2-</sup>	100	-24.0	-4.3	370	-33.5	-4.6
NH <sub>4</sub> <sup>+</sup>	130	-19.4	+1.4	430	-26.3	+3.6
Na <sup>+</sup>	170	-20.8	0	700	-29.9	0
Ca <sup>2+</sup>	13	-14.1	+6.7	21	-15.4	+14.5

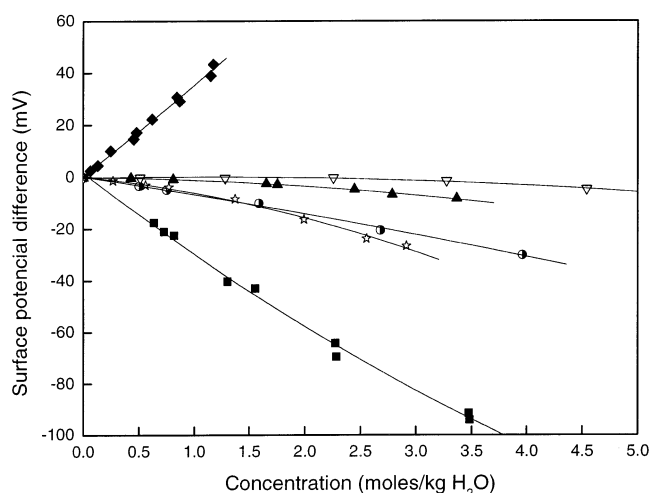
AMJ10 Latex						
Hofm. ion	pH 4			pH 10		
	CCC (mM)	$\Psi_0$ (mV)	$\Delta\Psi_0$ (mV)	CCC (mM)	$\Psi_0$ (mV)	$\Delta\Psi_0$ (mV)
SCN <sup>-</sup>	40	14.2	-7.6	27	12.6	-4.9
NO <sub>3</sub> <sup>-</sup>	80	17.0	-4.8	35	13.6	-3.9
Cl <sup>-</sup>	210	21.8	0	90	17.5	0
SO <sub>4</sub> <sup>2-</sup>	30	17.6	-4.2	18	15.3	-2.2
NH <sub>4</sub> <sup>+</sup>	85	17.1	+0.1	40	14.1	+0.5
Na <sup>+</sup>	80	17.0	0	35	13.6	0
Ca <sup>2+</sup>	72	22.0	+5.0	45	19.5	+5.9

<sup>a</sup>  $\Psi_0$  is the corresponding surface potential obtained by application of the DLVO theory.  $\Delta\Psi_0$  is the surface potential difference with regard to that obtained for chloride when anions are compared and that obtained for sodium when cations are compared.

because all them are made of polystyrene and, thus, no important differences in the hydrophobic character among their surfaces should be expected. Nevertheless, it has been demonstrated<sup>24,29,30</sup> that cationic polystyrene particles synthesized with the AMBDA initiator present a more hydrophobic surface. Justification lies in the fact that their charged groups (amidine) are placed in an organic heterocycle, and then they are embedded in a more apolar environment than sulfonate or carboxyl groups. Therefore, this more hydrophobic character of the **AMJ10** latex would make particles less stable than predicted by their  $\sigma_0$  value.

(2) Another important feature is that the stability of the latexes is specifically influenced by the nature of the electrolyte used. Whatever latex was chosen, the CCC values differ for different salts. The DLVO theory, extensively used to explain the stability of colloidal particles, does not account the specificity effect of ions, and it predicts the same CCC for 1:1 electrolytes. Likewise, no CCC differences should be obtained between different 2:1 salts. Actually, no classical theory of colloid science can explain quantitatively the experimental results that we have obtained.

(3) In relation to the stability sequence obtained with the Hofmeister ions employed in our latexes, we have found the following results: (i) for negative latexes, **ABJ2** and **AMJ5** at both pH values, the CCC values obtained can be ranked as (more stable) SCN<sup>-</sup>  $\geq$  NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> (more unstable) and (more stable) Na<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > Ca<sup>2+</sup> (more unstable) (with the only exception being carboxyl latex at pH 10 for which the



**Figure 7.** Surface potential difference versus solution concentration of the electrolytes (■) NaSCN, (○) NaNO<sub>3</sub>, (▲) NaCl, (◆) Na<sub>2</sub>SO<sub>4</sub>, (▽) NH<sub>4</sub>Cl, and (☆) Ca(NO<sub>3</sub>)<sub>2</sub> for an air/water interface at 20 °C. Data obtained from ref 16.

CCC value of NO<sub>3</sub><sup>-</sup> was higher than that of SCN<sup>-</sup>) and (ii) for the positive latex, **AMJ10**, the order can listed as (more stable) Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > SCN<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> (more unstable) and (more stable) NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup> > Ca<sup>2+</sup> (more unstable) (with the exception of pH 10 at which Ca<sup>2+</sup> showed a slightly higher stability than Na<sup>+</sup>).

It can be concluded that the order in stability is practically reversed for the cationic latex in comparison to the anionic ones. Moreover, taking into account the rank of HS given in the Introduction, it can be seen that for 1:1 electrolytes the sequence coincides with that obtained with our cationic latex and it is opposite for the anionic ones. For divalent anions, it can be observed that they always induce the most destabilizing effects. To clarify as much as possible the discussion of the results, the monovalent ions analysis will first be presented. The inversion found in our Hofmeister series when the sign of the surface changes has been also obtained in studies of crystallization of proteins and in the stability of inorganic colloids, despite polystyrene and protein or inorganic surfaces presenting interfacial characteristics that are totally different. On one hand, Riès-Kautt and co-workers showed that a positive protein ordered anions in agreement with HS<sup>31</sup> but a negative one reversed the order of HS.<sup>32</sup> On the other hand, Franks<sup>33</sup> observed that  $\zeta$  potential of negative silica evaluated with different Hofmeister cations showed an ion ordering that was inverted for positive materials such as alumina, hematite, or zirconia. All of these patterns can be understood if the presence of Hofmeister ions modifies the surface potential, whatever microscopic mechanism takes place. Jarvis and Scheiman<sup>20</sup> showed numerous experimental data in which the air/water interface potential changed for different added salts. A representative selection of those results obtained with the same ions used by us is shown in Figure 7. As can be seen, SCN<sup>-</sup> reduces the surface potential compared to Cl<sup>-</sup>, which practically does not change it. NO<sub>3</sub><sup>-</sup> also diminishes it, although not as much as SCN<sup>-</sup>. If the behavior of NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> cations is compared, the ammonium ion slightly increases the surface potential. These features are also observed in our polystyrene/water interface. Compared to Cl<sup>-</sup>, the presence of SCN<sup>-</sup> ions reduces the surface potential (making it more negative) and thus generates more stable systems if latex particles are negatively charged and less stable ones if they are positively charged. NO<sub>3</sub><sup>-</sup> behaves as SCN<sup>-</sup>, although its effect is not as drastic. The opposite effect is shown



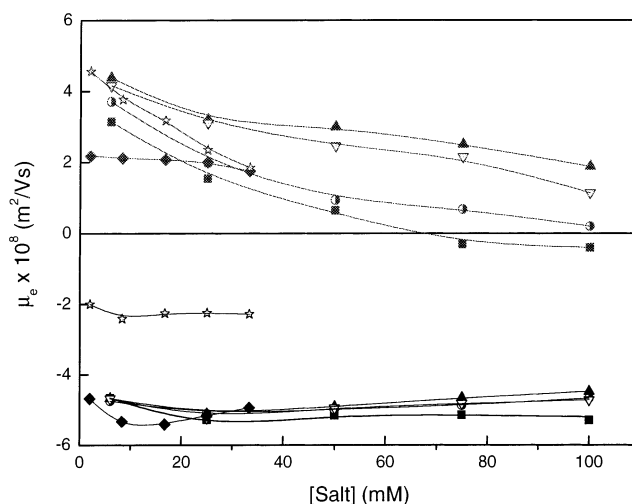
by the ammonium ion when compared to sodium, as it slightly increases the potential, improving the stability of cationic latex particles and diminishing that of anionic ones. As shown, monovalent ions seem to induce similar effects in both the air/water and the polystyrene/water interface. Anyway, this behavior should not be extrapolated to any hydrophobic surface in contact with an aqueous solution because an oil/water interface behaves differently from the air/water interface with regard to the Hofmeister effects.<sup>34</sup>

In relation to the influence of surface charge densities on the stability order, it seems that the sequence was not exceptionally affected when pH, and hence  $\sigma_0$ , was varied because only few exceptions have been found with this variation.

The analysis of the instability induced by divalent ions is not as simple as that previously discussed for the monovalent ions. In this case, the valency of sulfate or calcium ions is more important by means of the reduction of the electric potential associated with the diffuse layer than the modification induced by these ions in the surface potential by means of their "Hofmeister" effect. What is clear is that both ions destabilize dramatically the system when they act as counterions. It would be possible to give a plausible explanation of this phenomenon, at least qualitatively. The concentration of divalent ions near a surface of opposite charge must be much higher than that of those interfaces having the same sign. Then, their divalent nature would considerably reduce the electrical potential in the proximity of the surface, facilitating the approximation of the particles and thus triggering aggregation for much lower salt concentrations compared to 1:1 electrolytes or to situations in which the divalent species acts as co-ion. The strong Hofmeister effect shown by these two ions in other systems seems to be a little masked in the coagulation of polystyrene particles. At least, it would not be possible to predict whether the Hofmeister effect of these divalent ions could imply a reduction or an increment of the surface potential, as shown by the monovalent species. According to the air/water experiments (see Figure 7), sulfate should increase the potential and calcium would reduce it. Nevertheless, a more rigorous analysis must be done prior to stating such a conclusion with our latex particles. That analysis will be shown in the next section.

(4) A general feature of the HS is that they are dominated by anion effects, instead of cation effects.<sup>3,4</sup> Our results aim in the same direction. Comparing our cations, only clear differences among CCC values are obtained when they act as counterions, and thus their local concentration near the surface is high. Differences become questionable, however, when they act as co-ions. This does not happen with the anions, which show significant differences however they act, as counterions or co-ions. In fact, even for anionic latexes when the local concentration of anions in the proximity of the surface is supposed to be low, nonnegligible variations in the CCC values are obtained.

**Electrophoretic Mobility.** The major effect of the anions has also been demonstrated measuring the electrophoretic mobility ( $\mu_e$ ) of the particles versus different salts concentrations. These measurements were performed to support the stability results, although technical limitations of our mobility instrument made it impossible to exactly reproduce the CCC conditions because reliable data can only be obtained for ionic strengths lower than 100 mM (that is, 33 mM for a 2:1 electrolyte). Additionally, much lower concentrations of particles than those used in the stability experiments were used in the mobility measurements. These  $\mu_e$  data are shown in Figure 8. Mobility is plotted versus salt concentration for **ABJ2** and **AMJ10** latexes at pH 4. Results obtained with the **AMJ5** sample gave very



**Figure 8.** Electrophoretic mobility versus electrolyte concentration for the **ABJ2** latex (negative region) and **AMJ10** latex (positive region) at pH 4: (■) NaSCN; (●) NaNO<sub>3</sub>; (▲) NaCl; (◆) Na<sub>2</sub>SO<sub>4</sub>; (▽) NH<sub>4</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup>; (☆) Ca(NO<sub>3</sub>)<sub>2</sub>.

similar patterns to those obtained with the other anionic latex. For the sake of clarity, the mobility of this carboxylated latex has not been shown in this Figure 8. From these  $\mu_e$  data, it is worth highlighting three points that will be independently commented on: (1) The cationic latex shows significant differences among the several salts analyzed even at low salt concentration. For the anionic latexes, although these differences exist, they are much less important. (2) In general terms, the differences in the  $\mu_e$  data observed between cationic and anionic latexes cannot be explained in the basis on their  $\sigma_0$  values previously obtained. (3) For all of the latexes studied, the divalent ions, when acting as counterions, depicted constant  $\mu_e$  values in all range of concentrations tested, despite their very low CCC values.

In relation to the first point, it can be clearly observed that differences are more significant in the cationic latex, where variations of even 3 mobility units are obtained between NaCl and NaSCN salts. The  $\mu_e$  data corroborate that SCN<sup>-</sup> and NO<sub>3</sub><sup>-</sup> make the surface potential of the polystyrene/water interface more negative, always compared to the Cl<sup>-</sup> results. As can be also checked in these mobility experiments, the potential reduction induced by the SCN<sup>-</sup> ion (which even produces an inversion in the sign of the mobility at high concentrations) is sharper than that of nitrate. This feature also appears in the anionic latexes, although the differences are not as clear as those for the cationic latex for which anions act as counterions. Anyway, in the anionic latexes as the SCN<sup>-</sup> concentration becomes higher, the difference with regard to the  $\mu_e$  data of other monovalent ionic species becomes more significant. If NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> cations are compared, nitrate being the common anion, mobility data also reflect the stability patterns, that is, the ammonium increases (makes more positive) the polystyrene surface potential, independently of its charge sign. However, differences between monovalent ions are not as noticeable in the anionic latexes. Probably, major differences would be obtained if mobility data could be taken at salt concentrations proximate to the corresponding CCC values. It can also be observed that, as a general feature, the mobility decreases (in absolute value) as the electrolyte concentration becomes higher because of the compression of the electrical double layer. This behavior is more pronounced for the cationic latex, which presents much lower CCC values than the anionic one. Curiously, no zero mobility was exactly obtained when measured

at the corresponding CCC values. The different method used to obtain the mobility, in which particle concentrations are more diluted than those used in the aggregation experiments, could justify these discrepancies. In addition, to obtain the  $\mu_e$  values, the particles are forced to move in an external field. This field could influence and modify somehow the interaction and the structure of the electric double layer depending on the type of ions surrounding the particles.

A short discussion is now presented to clarify why the mobility patterns of the cationic latex are quite different from that shown by the anionic one. It has been demonstrated<sup>22,26</sup> that polystyrene latex particles with surface charge density values in the 10–20  $\mu\text{C}/\text{cm}^2$  range and sulfonate or carboxyl groups on the surface show identical  $\mu_e$  data despite their  $\sigma_0$  difference. Therefore, changes in mobility are only detectable if changes in  $\sigma_0$  values take place below (approximately) 10  $\mu\text{C}/\text{cm}^2$ . This feature is related to the ion condensation mechanism explained by Maning<sup>35</sup> for linear particles and extended by Belloni,<sup>36</sup> Robert and co-workers<sup>37,38</sup> and Levin<sup>39</sup> to spherical geometric. Both experimental events, the significant differences found in  $\mu_e$  data of **AMJ10** latex as a result of small changes in surface potential induced by the Hofmeister ions (which were almost negligible in the **ABJ2** and **AMJ5** samples) and the low CCC value shown by the cationic latex compared to the other two, question the validity of the  $\sigma_0$  value obtained for the former by titration, despite titration results being repeatedly confirmed.

Anyway, the most striking result shown in Figure 8 is the apparent lack of sensitivity in mobility when divalent ions act as counterions. That is, the mobility of calcium for the **ABJ2** latex behaves as  $\text{SO}_4^{2-}$  for the cationic one, given an approximately constant  $\mu_e$  value in the concentration range tested. Surprisingly, in both cases the mobility values at concentrations beyond their corresponding CCC are not zero. We have not found any plausible explanation for this behavior, although a similar feature was obtained by Wu et al.<sup>28</sup> after adsorbing  $\text{Ca}^{2+}$  on montmorillonite because coagulation took place in situations in which mobility data showed sufficient electrostatic repulsion to keep stable the colloidal system. They argued that such a lack of stability was due to hydrophobic attraction, because these authors consider the surface interaction to be constituted by three terms: an electrical contribution, which arises from the overlapping of two electrical double layers, a London–van der Waals term, and an interaction potential the origin of which lies on the donor/acceptor electron properties of the surface with the surrounding water. This third contribution is responsible for the (in)stability related to the overlap of solvent shell structured layers and thus is what originates such a non-DLVO attraction between hydrophobic surfaces.

## A Theoretical Approach

As commented previously, the elaboration of a novel theory about surface interactions that explains properly and quantitatively the role played by each of the ions of the Hofmeister series is actually a utopia. Water cooperativity yields spatial orientations in which hydrogen bonds are structured leading to either low- or high-density water layers. This depends on several properties of the surface and ions, such as those related to donor/acceptor electron, charge, and hydrophobic/hydrophilic character, and on the ability of ions to be adsorbed or excluded from interfaces. Nowadays, no theory can undertake these considerations. Because of the complexity discussed above about the establishment of a new theory and for the sake of simplicity, we have chosen to use a DLVO model in which a modification will be introduced to consider the salt specificity of the

Hofmeister series. This *modus operandi* can be criticized because this simple theory usually fails because of its own numerous limitations and approximations.<sup>34</sup> Despite this handicap, “extra-DLVO” forces are commonly included when DLVO theory breaks down, as can be checked after perusing the literature. As an example, Molina-Bolívar et al.<sup>40–42</sup> have recently published in prestigious journals a modification on the DLVO theory with the goal of including the effect of hydrated cations on the restabilization of hydrophilic colloids at high salt concentrations. Independently, Franks<sup>33</sup> and Lyklema<sup>43</sup> also had to modify the potential that appears in the repulsive electrostatic term of the DLVO theory to account for the Hofmeister effects of monovalent cations on the stability and mobility of inorganic colloids. Changes in the surface or  $\zeta$  potential or both were explained by these authors considering an ion adsorption mechanism. Concretely, Lyklema justified this specific adsorption on changes in the configurational entropy of the water molecules adjacent to the solid surface after binding of the ion to the surface sites. Tardieu et al.<sup>44</sup> also used the DLVO theory in protein crystallization studies, and they were obeyed to vary either the charge or the potential attraction to account the salt series. Our strategy aims in the same direction because DLVO interactions will be somehow modified by the presence of specific cations and anions. We have clearly seen in the aggregation experiments that the specificity of the HS modifies the pair potential. Whatever microscopic mechanisms takes place, reorientation of water dipoles at the interface or ion adsorption or exclusion, Hofmeister ions change the electrostatic term of the total interaction potential. The inclusion of the ionic specificity in the DLVO theory can be done as follows.

**Fitting Strategy.** The total potential energy ( $V_T$ ) of the interaction that determines the colloidal stability between two identical particles is defined by the DLVO theory as a sum of two terms:

$$V_T = V_A + V_E \quad (2)$$

The  $V_A$  term corresponds to the energy of interaction caused by the van der Waals dispersion forces, which is attractive between identical materials, and can be expressed for spherical particles as<sup>45</sup>

$$V_A = -\frac{A}{6} \left[ \frac{2a^2}{H(4a+H)} + \frac{2a^2}{(2a+H)^2} + \ln \frac{H(4a+H)}{(2a+H)^2} \right] \quad (3)$$

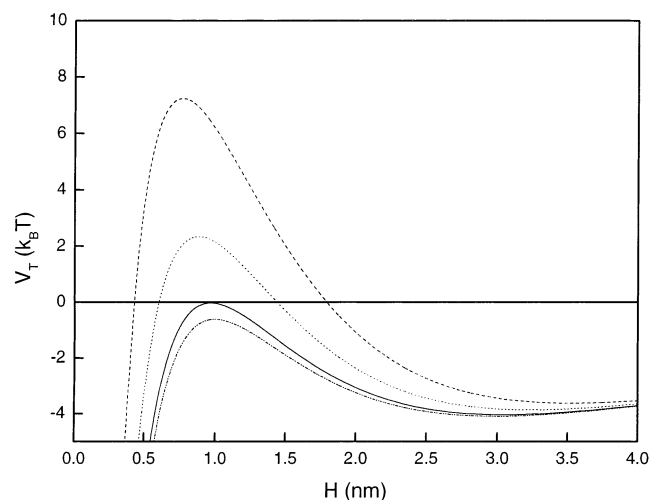
where  $A$  is the Hamaker constant for the interacting particles immersed in a medium,  $a$  is the particle radius, and  $H$  is the distance between the surfaces of both particles.

The  $V_E$  term represents the repulsive interaction created by the overlap of the electrical double layers of the particles. According to the constant surface potential model and assuming moderate potential (that is, lower than 50 mV), the following approximated expression can be used:<sup>46</sup>

$$V_E = 2\pi\epsilon_0\epsilon_r a \Psi_0^2 \ln[1 + \exp(-\kappa H)] \quad (4)$$

$\epsilon_r$  being the relative permittivity of the electrolyte solution,  $\epsilon_0$  the permittivity of the vacuum,  $\Psi_0$  the surface potential (or the Stern potential, if Stern model is considered), and  $\kappa$  the Debye parameter given by

$$\kappa = \left( \frac{\sum_i \rho_i e^2 z_i^2}{\epsilon_r \epsilon_0 k_B T} \right)^{1/2} \quad (5)$$



**Figure 9.** DLVO total interaction potential ( $V_T$  in  $k_B T$  units) versus distance. Concentration of the 1:1 electrolyte is 390 mM, and the Hamaker constant is equal to  $5.5 \times 10^{-21}$  J. Surface potential was used as the fitting parameter: (---)  $\Psi_0 = 27.0$  mV; (···)  $\Psi_0 = 26.1$  mV; (—)  $\Psi_0 = 25.2$  mV; and (— · —)  $\Psi_0 = 25.1$  mV.

where  $\rho_i$  is the concentration of ion “ $i$ ” in the bulk,  $e$  the elementary electric charge,  $z_i$  the ion valency,  $k_B$  the Boltzmann constant, and  $T$  the temperature. In fact, eq 4 is applicable in the case of large particle radii and small surface separations, that is,  $\kappa a \gg 1$  and  $H \ll a$ .

As known, CCC is defined by the DLVO theory as that salt concentration at which both the maximum value of  $V_T$  and its derivative  $dV_T/dH$  are equal to zero. Starting from this, surface potential was taken as the fitting parameter to fit the theoretical CCC to that obtained by experiments. Other parameters were set at fixed values. The relative permittivity of pure water was selected for  $\epsilon_r$ , and the Hamaker constant for the polystyrene–water–polystyrene (PS–W–PS) interface was taken from literature, being equal to  $5.5 \times 10^{-21}$  J.<sup>47</sup> The exactitude of this  $A$  value may be questionable because a plethora of Hamaker constant values (both experimental and theoretical) for the PS–W–PS interaction can be found in the literature. Anyway, what must be pointed out is that whatever its value was, it must be practically the same for our three polystyrene latexes. Then, differences in stability will never be originated by variations in  $A$  but by changes in the electrical term.

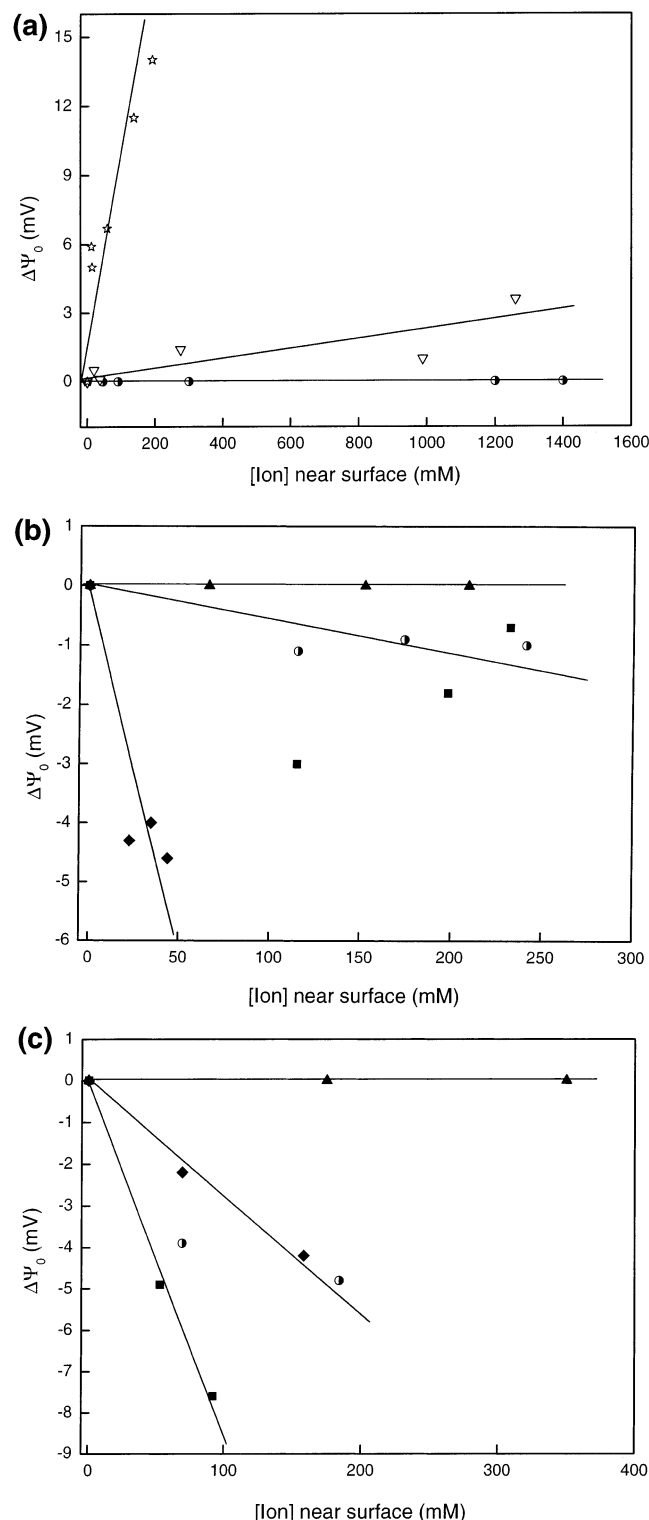
Figure 9 shows the DLVO potential versus distance for a salt concentration of a 1:1 electrolyte equal to 390 mM. A surface potential of 25.2 mV (in absolute value) fits such a concentration as the CCC. Because that is the experimental CCC of the **ABJ2** latex in a NaCl solution, the  $\Psi_0$  value so obtained will be assigned for such a latex in the presence of that salt. In the same way, different  $\Psi_0$  values have been obtained for each of our experiments and results are shown in Table 3. Taking  $\text{Cl}^-$  as a reference ion because of its position in the HS, changes in the surface potential induced by the presence of other anions with specific effects can be evaluated. These surface potential differences ( $\Delta\Psi_0$ ) are also shown in Table 3. The same strategy has been followed for comparing cations using sodium as the reference ion.

Most of the Hofmeister effects on different systems present linear dependences with the salt concentrations. Protein solubility,<sup>48</sup> protein melting temperature,<sup>49</sup> the  $B_2$  virial coefficient of the osmotic pressure in protein solutions,<sup>50</sup> or even the air/water interface potential<sup>20</sup> shown in Figure 7 behaves linearly. Therefore, a linear dependence of the polystyrene/water surface potential on the concentration of Hofmeister salts could also

be expected. Our surface potential differences,  $\Delta\Psi_0$  (with regard to  $\text{Cl}^-$  and  $\text{Na}^+$  ions), as a function of salt concentration are depicted in Figure 10a–c. Surprisingly, some linear tendencies arise despite the roughness of the fitting strategy employed. It should be noted, however, that the problem of fitting this kind of curve is doubled because it is necessary to know not only the effective surface potential but also the concentration of ions near the interface at the CCC. Bulk concentration is used in noncharged surfaces,<sup>20</sup> but charged surfaces distribute ions heterogeneously. The experimental results have shown how the specific influence of the Hofmeister ions is different depending on whether they act as co-ions or counterions. This is why in Figure 10a–c the shown ion concentration is that obtained at the proximity of the surface after performing a Boltzmann distribution.<sup>11</sup> No ion size consideration or electric charge correlations between ions have been taken into account. Therefore, the lack of linearity could also have its origin in the calculus of the local ion concentration instead of errors in obtaining the surface potential. The best results were obtained for cations (Figure 10a). In this figure, the data obtained for the anionic and cationic latexes are plotted together and a rough linearity was obtained, which implies that cations have a similar behavior acting as co- or counterions and, therefore, independently of the surface nature of the latex. But when anions are compared (Figure 10b,c) the tendencies are not as clear. First, it is not possible to represent in one single linear plot both type of latexes. There is no correlation between the surface potential differences,  $\Delta\Psi_0$ , obtained for cationic and anionic latexes. A possible explanation could be that, as it was previously commented, the cationic latex (**AMJ10**) presents a more hydrophobic surface than the anionic particles. This difference could make Hofmeister ions behave in such a way that anions present patterns in the **AMJ10** sample that are different from that shown for the anionic latexes. Such a difference in hydrophobicity would explain the marked potential reduction induced by the most chaotropic anion,  $\text{SCN}^-$ , in the **AMJ10** latex. It should be noted that the  $\Psi_0$  reduction is even more drastic than that given by  $\text{SO}_4^{2-}$  ions, despite the fact that the valency of the latter doubles that of the former. This feature also supports the experimental fact that says that chaotropic ions (i.e.,  $\text{SCN}^-$ ) tend to accumulate into the low-density water layer at hydrophobic surfaces, while kosmotropic ions (i.e.,  $\text{SO}_4^{2-}$ ) are usually excluded from it. Cations seem not to distinguish this hydrophobic difference among our cationic and anionic latexes. Once more, the Hofmeister effect of cations seems to be less specific than that shown by anions. Only a couple of exceptions were found regarding the observed linear tendencies and only for anions, the  $\text{SCN}^-$  ion for anionic latexes (Figure 10b) and the  $\text{NO}_3^-$  ion for the cationic particles (Figure 10c). Concretely, the  $\text{SCN}^-$  ion acting as co-ion gave an opposite tendency to the rest of the ions (anion or cations) showing an increase of  $\Delta\Psi_0$  for increasing ion concentration. Again, this most extreme ion in the HS seems to show a major sensitivity to any possible change in surface characteristics.

All of the data shown in this paper support the previous ideas that a modification on the DLVO theory should be done to be able to consider the Hofmeister effects. From the experimental results, a linear dependence of surface potential on the salt concentration ( $C_0$ ) could be proposed, that is,  $\Psi_0 = a + bC_0$ , as in the case of air/water interface (Figure 7). If linear dependence was accepted, keeping in mind that this model is rather simplistic and that there are some experimental exceptions, the surface potential should change in such a way that the slope of the linear behavior of the surface potential should





**Figure 10.** Surface potential difference obtained by using DLVO theory (see the fitting strategy in the text) (a) for polystyrene/water interfaces in which only effects of cations are evaluated, the common anion being  $\text{NO}_3^-$  ((●)  $\text{Na}^+$ , (▽)  $\text{NH}_4^+$ , and (☆)  $\text{Ca}^{2+}$ ), (b) for negatively charged polystyrene/water interfaces in which only effects of anions are evaluated, the common cation being  $\text{Na}^+$  ((■)  $\text{SCN}^-$ , (●)  $\text{NO}_3^-$ , (▲)  $\text{Cl}^-$ , and (◆)  $\text{SO}_4^{2-}$ ) and (c) for positively charged polystyrene/water interfaces in which only effects of anions are evaluated, the common cation being  $\text{Na}^+$  ((■)  $\text{SCN}^-$ , (●)  $\text{NO}_3^-$ , (▲)  $\text{Cl}^-$ , and (◆)  $\text{SO}_4^{2-}$ ).

depend on (at least) two factors: (i) On one hand, the slope depends on one term that accounts for the nature of the interface and that would take different positive or negative values

depending on the hydrophobic/hydrophilic character of the surface. The capital letter  $S$  can be assigned for such a factor. (ii) On the other hand, the slope also depends on the ion nature, patterns being different for identical interfaces if the ion is changed. The capital letter  $I$  can be then assigned. Therefore, the surface potential  $\Psi_0$  in eq 4 could be changed by this expression:

$$\Psi_0 = \Psi_{0\text{NaCl}} + SIC_0 \quad (6)$$

where  $\Psi_{0\text{NaCl}}$  is the surface potential of the interface in the presence of a nonspecific electrolyte (i.e.,  $\text{NaCl}$ ) and  $C_0$  is the concentration of a Hofmeister ion at the proximity of the surface.  $C_0$  could be assumed to be the bulk concentration only for uncharged surfaces, such as air/water or oil/water interfaces. Equation 6 should be only used for salts having  $\text{Na}^+$  or  $\text{Cl}^-$ ; that is, when the cation is sodium, the salt would be  $\text{NaX}$  (where  $X$  can be any anion and  $i$  its valency); electrolytes with chloride as the common anion would be  $\text{YCl}_j$ .

The main problem in applying eq 6 is that both factors,  $S$  and  $I$ , become fitting parameters with the additional handicap that an arbitrary value must be assigned to  $S$  for a given surface to be able to analyze the values of  $I$  for different ions.

## Conclusions

The dependence on colloidal stability of different latex particle using several ions of Hofmeister series has been analyzed. The results show that the positive or negative nature of the surface is important to determine the stability sequence. We have found that for 1:1 electrolytes the positive particles rank ions (from high to low stabilizing properties) in agreement with HS while negative particles reverse this order. Anyway, divalent ions have always shown the most destabilizing results. Thus, it can be concluded that for these systems, when  $\text{SO}_4^{2-}$  or  $\text{Ca}^{2+}$  act as counterions, the effect of double layer compression is more important than any possible water structure effect. The sign of charge does exert an important influence on ranking the Hofmeister ions. The HS order, however, seems not to depend significantly on the surface charge density of the immersed surfaces. Another conclusion that can be stated is that the cationic latex surface is more hydrophobic than that of negative latexes. This is supported by both the CCC values and the electrophoretic mobility results obtained. Mobility measurements have been also useful to corroborate that the effectiveness on changing the surface potential is more pronounced for the most chaotropic anion and kosmotropic cation. Finally, an extension of DLVO theory has been proposed, modifying the electrical term where the surface potential appears to include the Hofmeister effects.

**Acknowledgment.** We appreciate the financial support from the Projects MAT99-0662-C03-02 and MAT2000-1550-C03-01 given by the Comisión Interministerial de Ciencia y Tecnología (CICYT).

## References and Notes

- (1) Lewith, S. *Arch. Exp. Pathol. Pharmacol.* **1888**, 24, 1.
- (2) Hofmeister, F. *Arch. Exp. Pathol. Pharmacol.* **1888**, 24, 247.
- (3) Collins, K. D.; Washabaugh, M. W. *Q. Rev. Biophys.* **1985**, 18, 323.
- (4) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. *Q. Rev. Biophys.* **1997**, 30, 241.
- (5) Pay, N. G. M.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 2417.
- (6) Barnes, P.; Finney, J. L.; Nicholas, J. D.; Quinn, J. E. *Nature* **1979**, 282, 459.



- (7) Wiggins, P. M. *Physica A* **1997**, 238, 113.
- (8) Lumry, R.; Battistel, E.; Jolicoeur, C. *Faraday Symp. Chem. Soc.* **1982**, 17, 93.
- (9) Wiggins, P. M. *Langmuir* **1995**, 11, 1984.
- (10) Wiggins, P. M. *Cell Biol. Int.* **1996**, 20, 429.
- (11) Israelachvili, J. *Intermolecular & Surface Forces*, 2nd ed.; Academic Press: London, 1991; Chapter 12.
- (12) Kim, J.; Cremer, P. S. *Chem. Phys. Chem.* **2001**, 8/9, 543.
- (13) Ninham, B. W.; Yaminsky, V. *Langmuir* **1997**, 13, 2097.
- (14) Weyl, W. A. *J. Colloid Sci.* **1951**, 6, 389.
- (15) Good, R. J. *J. Chem. Phys.* **1957**, 61, 810.
- (16) Fletcher, N. H. *Philos. Mag.* **1962**, 7, 255.
- (17) Langmuir, I. *J. Am. Chem. Soc.* **1917**, 39, 1848.
- (18) Harkins, W. D.; McLaughlin, H. M. *J. Am. Chem. Soc.* **1925**, 47, 2083.
- (19) Harkins, W. D.; Gilbert, E. C. *J. Am. Chem. Soc.* **1926**, 48, 604.
- (20) Jarvis, N. L.; Scheiman, M. A. *J. Phys. Chem.* **1968**, 72, 74.
- (21) López-León, T.; Jódar-Reyes, A. B.; Ortega-Vinuesa, J. L.; Bastos-González, D. Hofmeister effects on the un-stabilisation and re-stabilisation of a cationic latex covered by IgG. *J. Chem. Phys.*, submitted for publication, 2002.
- (22) Bastos, D.; de las Nieves, F. J. *Colloid Polym. Sci.* **1993**, 271, 860.
- (23) Guthrie, W. H. New free radical initiators and their use in the preparation of polystyrenes polymer colloids. Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1985.
- (24) Ortega-Vinuesa, J. L.; Gálvez-Ruiz, M. J.; Hidalgo-Álvarez, R. *Langmuir* **1996**, 12, 3211.
- (25) Wilkinson, M. C.; Hearn, J.; Steward, P. *Adv. Colloid Interface Sci.* **1999**, 81, 77.
- (26) Bastos-González, D.; Ortega-Vinuesa, J. L.; de las Nieves, F. J.; Hidalgo-Álvarez, R. *J. Colloid Interface Sci.* **1995**, 176, 232.
- (27) Ortega-Vinuesa, J. L.; Gálvez-Ruiz, M. J.; Hidalgo-Álvarez, R. *J. Mater. Sci.: Mater. Med.* **1995**, 6, 754.
- (28) Wu, W.; Giese, R. F.; van Oss, C. J. *Colloids Surf., A* **1994**, 89, 241.
- (29) Holgado, J. A.; Martín, A.; Martínez, F.; Cabrerizo, M. A. In *Proceedings of the Solid/Fluid Interfaces Capillarity and Wetting Congress*, Arnhem, The Netherlands, September 1–6, 1992.
- (30) Martín-Rodríguez, A.; Cabrerizo-Vílchez, M. A.; Hidalgo-Álvarez, R. *Colloids Surf., A* **1996**, 108, 263.
- (31) Riès-Kautt, M.; Ducruix, A. *J. Biol. Chem.* **1989**, 264, 745.
- (32) Carbonnaux, C.; Riès-Kutt, M.; Ducruix, A. *Protein Sci.* **1995**, 4, 2123.
- (33) Franks, G. V. *J. Colloid Interface Sci.* **2002**, 249, 44.
- (34) Ninham, B. W. *Adv. Colloid Interface Sci.* **1999**, 83, 1.
- (35) Manning, G. S. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, 100, 909.
- (36) Belloni, L. *Colloid Surf., A* **1998**, 140, 227.
- (37) Roberts, J. M.; Sierzputowskagracz, H.; Stejskal, E. O.; Osteryoung, J. G. *J. Phys. Chem. B* **1998**, 102, 7735.
- (38) Aoki, K.; Roberts, J. M.; Osteryoung, J. G. *Langmuir* **1998**, 14, 4445.
- (39) Levin, Y.; Barbosa, M. C.; Tamashiro, M. N. *Europhys. Lett.* **1998**, 41, 123.
- (40) Molina-Bolívar, J. A.; Galisteo-González, F.; Hidalgo-Álvarez, R. *Phys. Rev. E* **1997**, 55, 4522.
- (41) Molina-Bolívar, J. A.; Galisteo-González, F.; Hidalgo-Álvarez, R. *Colloids Surf., B* **1999**, 14, 3.
- (42) Molina-Bolívar, J. A.; Ortega-Vinuesa, J. L. *Langmuir* **1999**, 15, 2644.
- (43) Lyklema, J. Specificity in the statics and dynamics of surface confined ions. *Mol. Phys.*, in press.
- (44) Tardieu, A.; Le Verge, A.; Malfois, M.; Bonete, F.; Finet, S.; Riès-Kautt, M.; Belloni, L. *J. Cryst. Growth* **1999**, 196, 193.
- (45) Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*, 3rd ed.; Marcel Dekker: New York, 1997; Chapter 10.
- (46) Ohshima, H. In *Electrical Phenomena at Interfaces: Fundamentals, Measurements, and Applications*; Ohshima, H., Furusawa, K., Eds.; Surfactant Science Series, Vol. 76; Marcel Dekker: New York, 1998, Chapter 3.
- (47) Gregory, J. *Adv. Colloid Interface Sci.* **1969**, 2, 397.
- (48) Setschenow, J. Z. *Phys. Chem.* **1889**, 4, 117.
- (49) von Hippel, P. H.; Wong, K.-Y. *Science* **1964**, 145, 577.
- (50) Piazza, R.; Pierno, M. *J. Phys.: Condens. Matter* **2000**, 12, 443.