Specific Ion Effects on Particle Aggregation Induced by Monovalent Salts within the Hofmeister Series

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ABSTRACT: Ion specific effects of monovalent salts on charging and aggregation for two types of polystyrene latex particles were investigated by electrophoresis and time-resolved light scattering. The chemical composition of the electrolytes was systematically varied in the experiments. Accordingly, NaH₂PO₄, NaF, NaCl, NaBr, NaNO₃, and NaSCN were used to vary the anions and (CH₃)₄NCl, NH₄Cl, CsCl, KCl, NaCl, and LiCl for the cations. The salt concentration dependence of the electrophoretic mobilities indicates that the surface charge was screened by the counterions when their concentrations increased. For the SCN⁻ ions, adsorption on positively charged particles leads to charge reversal. The aggregation rates are small at low electrolyte concentrations indicating stable dispersions under these conditions, and they increase with the salt concentration. When viscosity corrections are taken into account, no ion specific effects in the fast aggregation regime can be established. The slow and fast aggregation regimes are separated by the critical coagulation concentration (CCC). Within the experimental error, the CCCs are the same in systems containing different co-ions but the same counterions, with the exception of ammonium salts. However, the variation of counterions leads to different CCC values due to specific interaction of the counterions with the surface. These values follow the Hofmeister series for negatively charged sulfate latex particles, while the reversed order was observed for positively charged amine latex. Comparison between experimental CCCs and those calculated by the theory of Derjaguin, Landau, Verwey, and Overbeek reveals that variations in the surface charge due to ionic adsorption are mainly responsible for the ion specific effects in the aggregation process.

INTRODUCTION

While the Hofmeister series has been known for more than a century, the molecular mechanisms governing this characteristic sequence in the ionic specificities are still not fully clarified.³⁻⁵ The Hofmeister series was discovered in protein precipitation experiments, and this series classifies ions according to their increasing stabilization power of protein solutions, namely,

\[ \text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{F}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^- < \text{SCN}^- \]

\[ \text{(CH}_3\text{)}_4\text{N}^+ < \text{NH}_4^+ < \text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} \]

This sequence states that solutions of negatively charged proteins remain stable even at high salt concentrations in solutions containing the ions appearing in the right, while they precipitate already at lower salt concentrations containing the ions appearing on the left. Numerous other phenomena can be ordered according to the same sequence, for example, surface tensions or viscosities of electrolyte solutions, dissolution heats of salts, binding of ligands, and charging of proteins or polyelectrolytes.²⁻¹³

Here, we focus on the relation between the Hofmeister series and colloidal particle aggregation.¹⁴⁻²⁷ This question has also been pursued for quite some time, whereby that community rather used the term lyotropic series. Particle aggregation is known to be fast at high salt concentrations or for weakly charged particles, while it slows down at low salt concentrations or highly charged particles.¹⁵,²⁸ The transition between these two regimes is denoted as the critical coagulation concentration (CCC). The ionic valence induces an important dependence, which is referred to as the Schulze–Hardy rule.¹⁵⁻²³,²⁶,²⁹ This rule states that the CCC strongly decreases with an increase in the valence of the counterions. Thereby, multivalent cations are relevant for negatively charged particles, while multivalent anions, for positively charged ones.

However, even ions of the same valence may lead to different CCCs.¹⁷⁻²⁵ The respective shifts can be normally classified according to the Hofmeister series. Negatively charged particles typically follow the direct Hofmeister series quoted earlier. Thereby, the ions on the left induce lower CCCs, while the ions on the right, higher ones. On the other hand, positively charged particles follow the indirect Hofmeister series. The latter series maintains the same sequence of ions, but ions on the left induce higher CCCs, while the ions on the right, a lower one. However, ions of higher valence quoted within the Hofmeister...
series should be excluded from this reasoning, since they primarily follow the Schulze–Hardy rule. Therefore, we only focus on monovalent ions here.

The classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) of colloidal aggregation surmises that the interactions between particles are described by a superposition of attractive van der Waals forces and repulsive double layer forces across an indifferent electrolyte solution. The fast aggregation regime is governed by an attractive interaction potential, while the slow regime is characterized by a thermally activated energy barrier crossing. The DLVO theory suggests that the CCC is a sharp transition between these two regimes. A strong decrease of the CCC with ionic valence is equally predicted, in accordance to the Schulze–Hardy rule. Aggregation rates calculated with DLVO theory show reasonable agreement with experimental data, especially for weakly charged particles.

However, this classical theory cannot directly rationalize any trends in particle aggregation rates within the Hofmeister series, as it considers no other ionic properties than the valence. Ionic specificity can be introduced into DLVO theory by assuming that ions are no longer indifferent. This picture supposes that ions adsorb specifically to the particle surfaces, thereby modifying the surface charge and thus the double layer force. This simple approach qualitatively rationalizes the observed dependencies of the CCC. The Hofmeister series also reflects the size and hydration of ions. Small and strongly hydrated anions, such as F⁻ and Cl⁻, appear on the left, while large and poorly hydrated ones, such as SCN⁻ and I⁻, on the right. The cations are arranged in the opposite way. On the left, one finds large and poorly hydrated cations, such as N(CH₃)₄⁺ and Cs⁺, while strongly hydrated ones, such as Na⁺ and Li⁺, are situated on the right. Suppose that the particle surface is hydrophobic and poorly hydrated. Poorly hydrated ions will adsorb to such surfaces more strongly than well hydrated ones (i.e., like-seeks-like). Binding of cations to a negatively charged surface will neutralize the surface charge and thus leads to a decrease of the CCC. Adsorption of anions will increase the magnitude of the surface charge and lead to a larger CCC. Analogous reasoning applies to positively charged particles. Adsorption of anions will neutralize the surface, while adsorption of cations will lead to an increase of surface charge. Therefore, negatively charged hydrophobic particles follow the direct Hofmeister series, while positively charged ones, the indirect series. Similar arguments can be put forward for particles with a hydrophilic or well hydrated surface. Well hydrated ions will adsorb more strongly on such a hydrated substrate than poorly hydrated ions, and the situation is reversed. Stability of negatively charged hydrophilic particles should rather follow the indirect Hofmeister series, while positively charged ones, the direct series. This picture may be further complicated by additional forces induced by the adsorbed ions. Such short-ranged forces are normally not included in the DLVO theory. These forces are typically introduced into a modified treatment of the electric double layer where one introduces additional ion–substrate interactions (e.g., hydration, van der Waals, and image charges). While such additional forces may modify the sequences within the series, the qualitative picture remains similar.

Particle surface charge density has often been found to vary systematically with the type of ions, as one would expect for a hydrophobic surface. The charge of positively charged alumina decreased in the Cl⁻ > Br⁻ > I⁻ order following the indirect Hofmeister series. The same trend was reported for positively charged latex particles as revealed by electrophoresis. The charge density of negatively charged alumina particles would decrease from Cs⁺ to Na⁺ with the direct Hofmeister series. Similar trends were observed for negatively charged hematite, titania, and silica. However, the behavior of the mentioned silica sample seems atypical, since other authors reported the charge density of silica to follow the indirect Hofmeister series as one would expect for a hydrophilic substrate. Analogous behavior was reported for silver halide.

Many trends in the observed CCCs are also consistent with the fact that surfaces of colloidal particles are hydrophobic. Negatively charged polystyrene and clay mineral particles follow the direct Hofmeister series, while positively charged metal oxides and polystyrene particles follow the indirect one. While the same trend was observed for negatively charged silver halide particles, the behavior of this system seems atypical, since the surface charge densities follow the reverse trend. For polystyrene particles, however, only a few cations were investigated so far. The opposite dependence was observed for protein-coated latex or calcined titania, as one would expect for hydrophilic surfaces. However, ion specific effects on particle aggregation were absent for weakly charged iron oxide, titania, and carboxylated latex particles.

A transition between the direct and indirect Hofmeister series was observed for CCCs of titania after a heat treatment. The native particles followed the indirect series in basic conditions, as one would expect for a hydrophilic surface. After heat treatment, the surface becomes hydrophobic, and the direct series is observed. A similar transition between the direct and indirect Hofmeister series was also evidenced for the water–silica interface upon pH variations through electric surface potentials obtained from direct force measurements. In acidic conditions, the silica surface is more hydrophobic and thus follows the direct series. In basic conditions, the surface becomes more hydrophilic due to the ionization of the silanol groups and, therefore, reflects the indirect Hofmeister series. The observations that the charge density of silica may follow the direct or the indirect Hofmeister series could also be related to this hydrophobic to hydrophilic transition. In some situations, partial reversal of Hofmeister series was equally reported, and this possibility was confirmed by computer simulations.

The present work investigates how the position of monovalent ions within the Hofmeister series affects the aggregation of negatively and positively charged polystyrene latex particles. Absolute aggregation rate coefficients were measured by combining time-resolved static light scattering (SLS) and dynamic light scattering (DLS). Similar light scattering techniques were used to study particle aggregation earlier. The surface charging properties were investigated by electrophoresis. The present study explores a larger number of ions than the previous investigations, especially cations. Moreover, the use of the indifferent chloride allows addressing the specific effect of different cations unequivocally. In addition, the variation of the absolute aggregation rate constant in the fast aggregation regime with the type of salt and particles is studied for the first time.
**EXPERIMENTAL SECTION**

Materials. Polystyrene latex particles that were functionalized with amidine or sulfate groups on their surface were purchased from Invitrogen Corp. The particle size and the surface charge density of the particles were determined by the manufacturer by transmission electron microscopy (TEM) and conductometric titration. The sulfate latex has a mean radius of 265 nm, a polydispersity expressed as a coefficient of variation (CV) of 2.0%, and a surface charge density of $-77$ mC/m$^2$. In the case of the amidine latex, the corresponding quantities are 110 nm, 4.3%, and +132 mC/m$^2$. The suspensions needed for the measurements were prepared by mixing the appropriate salt solutions with a particle stock suspension, while for the amidine particles a polyvinylidene fluoride membrane was used. The particle concentrations of the dialyzed stock solution, which is a mixture of concentrated H$_2$SO$_4$ and 30% H$_2$O$_2$ at a concentration. The concentration of the sulfate latex stock suspension was 65 g/L, while the one of amidine latex, around 7 g/L. Analytical grade NaCl, KCl, CsCl, NH$_4$Cl, NaSCN (Sigma-Aldrich), LiCl, NaH$_2$PO$_4$ (Acros Organics), NaF, NaBr, NaNO$_3$, and N(CH$_3$)$_4$Cl (Pluka) were dissolved in pure water, adjusted to pH 4.0 with HCl and filtered with a 0.1 µm syringe filter (Millipore). All experiments were performed in a thermostated environment at a temperature of 25.0 °C. Milli-Q water (Millipore) was used throughout.

Electrophoretic Mobility. ZetaSizer Nano ZS (Malvern) equipped with a He/Ne laser operating at 633 nm as a light source and an avalanche photodiode as a detector was used to measure the electrophoretic mobility of the particles in an electric field of 4 kV/m. The suspensions needed for the measurements were prepared by mixing the appropriate salt solutions with a particle stock suspension, with final particle concentration of 50 mg/L for the sulfate latex and 5 mg/L for the amidine latex. The suspensions were equilibrated for 1 min prior to the measurements. Five runs were performed for each sample, and averaged.

Aggregation Rates by Light Scattering. Absolute aggregation rates were determined in 1.0 M KCl by combined time-resolved SLS and DLS on the multiangle goniometer (ALV/CGS-8F). This goniometer uses eight fiber-optic detectors and solid state laser of a wavelength of 532 nm. Quartz cuvettes were first cleaned in piranha mixture, which is a mixture of concentrated H$_2$SO$_4$ and 30% H$_2$O$_2$ at a volume ratio of 3:1, then rinsed with water, and dried in a dust-free oven at 60 °C. The particle concentration was 4 mg/L (4.9 × 10$^{13}$ m$^{-3}$) for the sulfate latex, and 1 mg/L (1.7 × 10$^{14}$ m$^{-3}$) for the amidine latex. The stable stock particle suspension was injected into the salt solution in the cuvette, mixed, and immediately monitored by light scattering. The intensity and the correlation function were accumulated for 20 s, and the apparent hydrodynamic radius was calculated from the second order cumulant fit. This quantity was recorded as a function of time until the initial radius increased by about 40%. To determine the absolute aggregation rate coefficient, the SLS intensity $I(q,t)$ and the apparent hydrodynamic radius $r_h(t)$ were followed with time, $t$, at different magnitudes of the scattering vector, $q$. For short times, relative change of the scattering intensity can be written as:

$$\Sigma = \frac{1}{I(q, 0)} \left| \frac{dI(q, t)}{dt} \right|_{t=0} = kN_f \left( \frac{I_1(q)}{2I_2(q)} - 1 \right)$$

where $k$ is the aggregation rate coefficient and $N_f$ is the initial particle number concentration while $I_1(q)$ and $I_2(q)$ are the scattering intensities of the monomers and dimers, respectively.

Corresponding expression for the relative rate of change of the hydrodynamic radius is:

$$\Delta = \frac{1}{\eta(q, 0)} \left| \frac{d\eta(q, t)}{dt} \right|_{t=0} = kN_f \left( 1 - \frac{1}{a} \frac{I(q)}{2I(q)} \right)$$

where $\alpha = r_h^2/r_i^2$, with $r_i$ and $r_h$ being the hydrodynamic radii of the monomer and the dimer. Combining eqs 1 and 2, one obtains

$$\Sigma = \left( 1 - \frac{1}{a} \right)^{-1} \Delta - kN_f$$

A scatter plot of the relative rates $\Sigma$ and $\Delta$ gives a straight line, whereby the slope yields the hydrodynamic factor $a$ and the absolute aggregation rate coefficient follows from the intercept. The respective experimental results obtained in 1.0 M KCl solutions are shown in Figure 1. The aggregation rate coefficient for the sulfate latex was (3.3 ± 0.2) × 10$^{-14}$ m$^3$/s and for the amidine latex (3.0 ± 0.2) × 10$^{-14}$ m$^3$/s. These aggregation rate coefficients agree within experimental error with our previous measurements with time-resolved SLS for the same particles at pH 5.0 in 1.0 M KCl. The hydrodynamic factors $a$ were for the sulfate latex 1.37 ± 0.02 and for the amidine 1.31 ± 0.02. These values compare reasonably well with the theoretical value of 1.39, which can be calculated from low Reynolds number hydrodynamics.

For other conditions, the aggregation rate was measured by time-resolved DLS with the compact single-angle goniometer (ALV/CGS-3) with a He/Ne laser of a wavelength of 633 nm. The hydrodynamic radius was monitored at a scattering angle of 90° in the same fashion as described previously. The particle concentration was chosen in the range of 50–200 mg/L for the sulfate latex and in the range of 2–10 mg/L for the amidine latex. The relative rate coefficient was obtained from the relative increase of the hydrodynamic radius. Absolute rate coefficients were obtained by dividing the apparent rate coefficient by the apparent rate coefficient in 1.0 M KCl at the same particle concentration and by multiplying this ratio by the absolute aggregation rate coefficient in 1.0 M KCl.

**RESULTS**

Charging and aggregation of negatively charged sulfate latex particles and positively charged amidine particles were investigated in monovalent electrolyte solutions at pH 4.0 by electrophoresis and time-resolved DLS. The solution composition was systematically varied, whereby Na(CH$_3$)$_3$Cl, NH$_4$Cl, CsCl, KCl, NaCl, and LiCl were used to vary cations, while the anions were varied by mixing Na$_2$HPO$_4$, NaF, NaCl, NaBr, NaNO$_3$, and NaSCN. In this way, the influence of both counter- and co-ions could be addressed. Since these ions are situated within the Hofmeister series, the relation between particle aggregation rates and the position within this series will be clarified.
**General Trends.** The electrophoretic mobility of the particles is shown versus the salt concentration for the sulfate particle in Figures 2a and 3a, while for the amidine particles, in Figures 4a and 5a. The magnitude of electrophoretic mobility typically decreases with the salt concentration due to screening of the surface charge. At low salt concentrations, negative and positive mobilities were observed for the sulfate and amidine latex particles, respectively. This sign reflects the charge of the ionized surface functional groups at pH 4.0. The actual values of the electrophoretic mobilities depend on the type of ions, and these trends will be discussed later.

Absolute particle aggregation rate coefficients are shown versus the salt concentration for the sulfate particle in Figures 2b and 3b and for the amidine particles in Figures 4b and 5b. At low salt concentration, the absolute aggregation rates are small. This behavior is referred to as the slow or reaction controlled regime, and the rate coefficients increase with the salt concentration strongly. At higher salt concentrations, the aggregation rate coefficients become large. Here, one has the fast or diffusion controlled regime, and the rate coefficients are almost independent of the salt level. The critical coagulation concentration was identified as the transition point between the slow and fast aggregation regimes. While the CCC depends sensitively on the type of ion present, no systematic trends concerning the aggregation rates in the slow regime could be established.

**Fast Aggregation Regime.** When investigating eventual ion specific effects on aggregation rates at high electrolyte concentrations, one must realize that viscosities of concentrated electrolyte solution may significantly deviate from the one of pure water. The rate coefficients in the diffusion controlled regime may therefore vary, since the diffusion coefficient of the particles depends on the solution viscosity. In order to take this effect into account, known dynamic viscosities, \( \eta \), of the salt solutions investigated here were considered. \(^{57,58}\) To simplify the data analysis, the experimental viscosity data were represented with the relation

\[
\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2
\]

(4)

where \( \eta_0 = 8.90 \times 10^{-4} \) Pa·s is the dynamic viscosity of water at 25 °C while A, B, and D are constants. The constant A was calculated from the Debye–Hückel theory,\(^ {10}\) while B and D were obtained by least-squares fits to the experimental viscosity data. The resulting constants are reported in Supporting Information Table S1. To compare the experimental aggregation rates, the aggregation rate coefficients were normalized with the diffusion controlled aggregation rate coefficient, \( k_0 \), obtained from Smoluchowski’s theory\(^ {15,28}\)

\[
k_0 = \frac{8k_BT}{3\eta} = 1.23 \times 10^{-17} \text{ m}^3/\text{s}
\]

(5)

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and the numerical value refers to water at 25 °C.

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**Figure 2.** Charging and aggregation of negatively charged sulfate latex particles as a function of the concentration of various monovalent chloride salts of different cations: (a) electrophoretic mobilities and (b) aggregation rate coefficients. The gray region represents an envelope of all experimental data points.

**Figure 3.** Charging and aggregation of negatively charged sulfate latex particles as a function of the concentration of various monovalent sodium salts of different anions: (a) electrophoretic mobilities and (b) aggregation rate coefficients. The gray region represents an envelope of all experimental data points.
The averaged normalized rate coefficients $k/k_S$ above the CCC are shown in Figure 6a. These normalized rates are independent of the type of ions within the experimental error. Moreover, these normalized coefficients are very similar for the two types of particles used, namely, $0.26 \pm 0.01$ for the sulfate latex and $0.23 \pm 0.01$ for the amidine latex. However, this normalized coefficient may depend on the type of particle used. This point was established by reanalyzing fast aggregation rates of latex particles in nine different salt solutions, which include multivalent ions, which were published earlier by us. These data include carboxyl and sulfate latex particles. The latter sulfate latex particles are different from the one used here. When the aggregation rate coefficients are normalized by Smoluchowski's rates including the correct viscosities, we find again no dependence on the type of ions present. However, the normalized rate coefficients differ from the values reported earlier. For the carboxyl latex particles, one finds $0.16 \pm 0.01$, while for the latter sulfate particles $0.29 \pm 0.01$. The fact that the normalized aggregation rates vary with the particle type somewhat is probably related to their variable polymeric compositions, which originates from the differing conditions during synthesis. Differences in surface roughness may equally contribute. However, when the same type of particles is considered, the normalized fast aggregation rate coefficients are independent of the type of salt. This observation suggests that attractive forces acting in the fast aggregation regime are not influenced by the nature of the ions present. These experimental results should be contrasted with earlier reports, where a modest variation of the fast aggregation rate on the type of salt was reported. In our view, however, these results are hardly conclusive, since viscosity corrections were not considered in these studies.

**Specific Ion Effects on Negatively Charged Sulfate Latex.** The electrophoretic mobility at given salt concentrations decreases with the type of cation from $N(CH_3)_4^+$ to $Li^+$. This sequence reflects the expected direct Hofmeister series; namely, $N(CH_3)_4^+ < NH_4^+ < Cs^+ < K^+ < Na^+ < Li^+$ (Figure 2a). This trend in the electrophoretic mobility reflects the affinity of the different cations to the surface. Therefore, poorly hydrated $N(CH_3)_4^+$ ion adsorbs most strongly to the hydrophobic latex particle surface and, hence, reduces the magnitude of the surface charge and of the mobility. The strongly hydrated $Li^+$ ion adsorbs weakly on the particle surface, or not at all, and the magnitudes of the surface charge and of the mobility are therefore the largest.

The CCC, which reflects the transition between the fast and slow regime, systematically varies with the type of cation (Figure 2b). The CCC shifts from low to high values following the direct Hofmeister series; namely, $N(CH_3)_4^+ < NH_4^+ < Cs^+ < K^+ < Na^+ < Li^+$ (Figure 6b). This trend is expected for a negatively charged hydrophobic surface. The poorly hydrated $N(CH_3)_4^+$ ion adsorbs strongly to the surface, thereby reducing the magnitude of surface charge, and therefore the CCC. On the other hand, well hydrated $Li^+$ ion induces the highest CCC,
since the surface charge is high due to weak adsorption of this ion. These results are in agreement with molecular dynamic simulations at hydrophobic surfaces.40 One further observes that the CCCs for Li⁺ and Na⁺ are almost identical, suggesting that these two ions do not adsorb to the surface at all. Similar trends in the CCCs following the direct Hofmeister series as a typical for a negatively charged hydrophobic substrate were previously reported for various systems, including montmorillonite, silver iodide, and heat-treated titania.21,24,25 The same trend was also documented for negatively charged polystyrene latex, but with Na⁺ and NH₄⁺ ions only.18,20 When the particles are weakly charged, there are no ion specific effects on the charging and aggregation behavior in the presence of Na⁺, K⁺, and Cs⁺ for iron oxide, titania, and carboxylate latex.21,23,26 In this situation, the cations do not interact with the surface specifically.

Co-ions have no effect on the charging and aggregation of the sulfate latex particles (Figure 3). The electrophoretic mobilities are similar for all ions investigated, with the exception of F⁻, which induces somewhat lower mobilities. The CCCs are identical within experimental error, and they have the value of 400 ± 10 mM (Figure 6b). One might expect that the CCCs also follow the direct Hofmeister series H₂PO₄⁻ > F⁻ > Cl⁻ > Br⁻ > NO₃⁻ > SCN⁻, reflecting the indirect Hofmeister series (Figure 4a). This trend in the electrophoretic mobility was also found for other positively charged latex particles17,19,20 and reflects the affinity of the different anions to the surface. Strongly hydrated anions, such as H₂PO₄⁻ or F⁻, interact weakly with the hydrophobic latex particle surface. The poorly hydrated anions, such as NO₃⁻ or SCN⁻, interact more strongly with the surface, and their adsorption reduces the surface charge. The adsorption of SCN⁻ is so pronounced that a charge reversal is induced. Such charge reversal has been observed for highly charged multivalent ions60,61 but also for other strongly adsorbing monovalent ions.19,43

The CCCs decrease in the same sequence reflecting the expected indirect Hofmeister series (Figures 4b and 6c). However, a pronounced decrease of the CCC is only observed in the series Cl⁻ > Br⁻ > NO₃⁻ > SCN⁻, while in the presence of H₂PO₄⁻, F⁻, and Cl⁻ the CCC remains practically constant. This constancy indicates that the latter ions are basically indifferent and do not adsorb on the particle surface. Similar specificities involving Cl⁻, NO₃⁻, and SCN⁻ ions were also reported for the CCCs for sulfate latex particles earlier.17,18,20 However, the indifference for the other ions was not reported for latex so far, but only for weakly charged titania.21 The observed trends in the CCCs agree with the ones predicted theoretically based on the ionic polarizability, except that the positions of Br⁻ and NO₃⁻ are reversed.41

In the presence of various co-ions, namely, Cs⁺, K⁺, Na⁺, and Li⁺, the measured electrophoretic mobilities and CCCs were very similar (Figures 5 and 6c). Since the affinity of these ions toward the surface decreases in the same sequence, one would expect that the CCCs follow the indirect Hofmeister series. However, no systematic dependence could be established, and the CCC remains constant at 200 ± 10 mM. We suspect that these ions interact with the highly positively charged surface too weakly. Nitrogen-containing ions, namely, N(CH₃)₄⁺ and NH₄⁺, behave irregularly. The indirect Hofmeister series would suggest higher CCCs, but the measured values are substantially lower than for the remaining cations within the series. This discrepancy could be probably related to a specific interaction between the amine groups on the particle surfaces and the nitrogen-containing ions (e.g., hydrogen bonding). These findings are similar to previous measurements of the CCCs for positively charged latex particles, where small shifts between Na⁺ and NH₄⁺ were reported.18,20

Origin of Interparticle Forces. A simplified form of DLVO theory was used to clarify ion specific effects on the CCCs. Electrophoretic mobilities, \( u \), were converted to diffuse layer potentials, \( \psi_{DL} \), with the Smoluchowski equation15

![Figure 6. Characteristics of the latex particle aggregation versus the position in the Hofmeister series. The effect of cations is shown in the left column, while of the anions, in the right column. (a) Aggregation rate coefficients in the fast regime normalized by the Smoluchowski value. The error bars represent three times the standard deviation. CCCs for (b) sulfate particles and (c) amidine particles. The arrows indicate the expected trends from direct or indirect Hofmeister series. The lines serve to guide the eye only.](image-url)
where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon$ is the dielectric constant. We have $\varepsilon = 80$ for water at room temperature. The accuracy of the Smoluchowski equation was checked with the standard electrokinetic model. For the particles and concentration range considered, both models agreed within 3%. The surface charge density $\sigma$ was determined by fitting $\psi_D$ at different salt levels with the Derjaguin–Hückel charge-potential relationship:

$$\sigma = e \epsilon_0 \psi_D$$

(7)

where $\kappa$ is the inverse Debye length defined by

$$\kappa^2 = \frac{2N_Ae^2c}{\epsilon\epsilon_0k_B T}$$

(8)

where $c$ is the molar concentration of the monovalent electrolyte, $N_A$ the Avogadro number, and $e$ the elementary charge. While the resulting charge densities reflect the extent of the ion adsorption, an eventual influence of the variation of the position of the shear plane with the type of ions is neglected. The CCC was estimated from DLVO theory, which assumes that the total interaction energy can be written as a superposition of electrostatic double layer energy, $V_{dd}$, and the van der Waals energy, $V_{vdW}$, namely,

$$V = V_{dd} + V_{vdW}$$

(9)

By invoking the Derjaguin and superposition approximations, one has

$$V_{dd} = 2\pi \epsilon \epsilon_0 \psi_D^2 \exp(-\kappa h)$$

(10)

where $r$ is the particle radius and $h$ is the separation distance between particle surfaces. The van der Waals interaction energy is approximated with the nonretarded expression

$$V_{vdW} = -\frac{Hr}{12h}$$

(11)

where $H$ is the Hamaker constant. The CCC can be located by assuming that the energy barrier just vanishes

$$V(h_{max}) = 0 \quad \text{and} \quad \frac{dV}{dh}_{h = h_{max}} = 0$$

(12)

where $h_{max}$ is the separation at the energy barrier. Combining eqs 9–12, one can express the CCC as

$$\text{CCC} = \frac{0.365}{N_A L_B} (H\varepsilon_0 e)^{-2/3} \sigma^{4/3}$$

(13)

where $L_B = e^2/(4\pi \varepsilon \varepsilon_0 k_B T)$ is the Bjerrum length, which is 0.72 nm at room temperature in water. Note that the preceding relation is only approximate, since accurate DLVO calculations show that the energy barrier does not quite vanish at CCC.

The calculated and experimental data given in Supporting Information Table S2 and Figure 7 show indeed a good correlation between the CCCs and the surface charge density. The straight line obtained from DLVO theory agrees with the correlation between the CCCs and the surface charge density. Information Table S2 and Figure 7 show indeed a good agreement with the value of 1.0 $\times$ 10$^{-20}$ J that is obtained from the full Lifshitz calculation. However, these values are factors of 3–5 larger than the Hamaker constants of similar latex particles that were actually measured with the colloidal probe technique. The reduction of these values is probably due to surface roughness. When one assumes that the presently used latex particles have comparably smaller Hamaker constants, the observed values of the CCCs indicate the presence of additional attractive non-DLVO forces. The substantial scatter of the data points in Figure 7 also points toward possible variation of the distance of the shear plane with the nature of the ion, or the importance of additional forces, which are most probably of hydrophobic nature.

### CONCLUSION

Surface charge and aggregation of anionic and cationic polystyrene latex particles were investigated in the presence of various monovalent electrolytes by electrophoresis and time-resolved light scattering. Sodium salts of H$_3$PO$_4^-$, F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, and SCN$^-$ were used to probe the effect of anions, while with chloride salts of N(CH$_3$)$_4^+$, NH$_4^+$, Cs$^+$, K$^+$, Na$^+$, and Li$^+$ the cations were varied. These ions interact with oppositely charged particle surfaces specifically. They normally adsorb, and thereby modify, the surface charge and the CCC. Poorly hydrated counterions, such as N(CH$_3$)$_4^+$ and SCN$^-$, adsorb to

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**Figure 7.** Comparison of experimental CCC values for the sulfate and amidine latex particles with DLVO theory. The data are plotted versus the magnitude of surface charge density, which was estimated from the electrophoretic mobility. The DLVO theory uses the superposition approximation to calculate the double layer interactions.

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the oppositely charged surfaces more strongly, and they lower the magnitude of the surface charge and the CCC substantially. Strongly hydrated counterions, such as Li+ or F−, do not adsorb, and lead to high magnitudes of the surface charge and high CCCs. For some well hydrated counterions, the CCC remains independent of the type of ions. In this regime, we suspect that these ions do not adsorb to the particle surface at all. On the other hand, these ions interact only weakly with equally charged surfaces, and the CCCs are basically independent of the nature of the co-ion. Moreover, we have demonstrated that the aggregation rate in the fast regime does not depend on the type of ions present but only on the type of particles.

DLVO theory can be used to confirm that the principal mechanism responsible for the shifts of the CCCs originates from modification of the surface charge. The dependence of the CCC on the surface charge density obtained from electrophoresis agrees well with DLVO theory. However, the Hamaker constant obtained by fitting the experimental CCC data is probably somewhat high, indicating the presence of additional non-DLVO forces.

**ASSOCIATED CONTENT**

Supporting Information

Tables S1 and S2 with viscosity coefficients and experimental CCCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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