Forces between silica particles in the presence of multivalent cations

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Abstract

Forces between negatively charged silica particles in aqueous electrolyte solutions were measured with the colloidal probe technique based on atomic force microscope (AFM). The present study focuses on the comparison of monovalent and multivalent counterions, namely K^+ , Mg^{2+} , and La^{3+} . The force profiles can be well described with the theory Derjaguin, Landau, Verwey, and Overbeek (DLVO) down to distances of about 4 nm. At smaller distances, the forces become strongly repulsive due to additional non-DLVO repulsion. In the presence of La^{3+} , one observes an additional attractive force with a range of about 1 nm at intermediate salt concentrations. This force is probably related to ion-ion correlations, but could also be influenced by surface charge heterogeneities or charge fluctuation forces.

Graphical Abstract

Keywords

Atomic force microscope; colloidal probe technique; direct force measurement; water-silica interface; multivalent ion;

Introduction

Multivalent metal ions strongly modify forces acting between charged interfaces in aqueous solutions. Such interactions have broad implications in mineral processing, water purification, and subsurface transport [1-3]. The simplest framework to address such interactions is the classical theory developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO) [4]. This theory suggests that forces between charged interfaces are governed by two principal contributions, namely the van der Waals attraction and double layer repulsion. The strength of the van der Waals force is related to the electronic properties of the bulk materials, but the surface roughness may also contribute [5-8]. Double layer force is principally influenced by the surface charge density and the ionic composition of the electrolyte solution [9-14]. The surface charge or, more precisely, the diffuse layer potential determine the magnitude of this force, while dissolved ions the range of the interactions through screening. Multivalent metal ions may adsorb strongly to negatively charged interfaces, and thereby they reduce the magnitude of the diffuse layer potential [15-19]. However, theoretical studies suggest that the presence of multivalent ions may induce additional short-ranged attractive forces due to ion-ion correlation effects [20-23].

Due to recent technical progress, interactions between charged surfaces across electrolyte solutions can be investigated routinely. Forces between macroscopic surfaces can be measured with the surface forces apparatus (SFA) or the thin film balance [24-26]. These techniques have the advantage that the surface separation can be extracted independently, whereby the SFA offers an excellent distance resolution, typically down to few Angstroms. Forces involving colloidal particles can be probed with the colloidal probe technique, which is based on the atomic force microscope (AFM) [6,9-12,27], total internal reflection microscopy (TIRM) [28,29], or optical tweezers combined with video-microscopy [30,31]. All these techniques currently reach pN force resolution or better and thus can be used to probe interaction forces for particles down to few μm in diameter. TIRM has the best force resolution among those, but can only be used to measure forces between a colloidal particle and a planar substrate. The optical tweezers technique allows one to access forces between two particles, while the colloidal probe technique can be used in the sphere-plane as well as sphere-sphere geometry.

Several studies report force measurements between charged solid substrates in the presence of multivalent cations. Early studies were carried out with the SFA [15,16]. At longer distances, they report double layer forces that are governed by diffuse layer potentials of lower magnitude, especially for trivalent La^{3+} cations. Later studies confirmed that the decay length of the double layer force is in good agreement with DLVO predictions [32,33]. More recently, direct force measurements did provide

evidence of charge reversal of silica and mica by trivalent cations [18,34]. A similar charge reversal of anionic latex particles induced by trivalent cations was equally reported with direct force measurements [17] and electrophoresis [35-37]. This charge reversal is induced by adsorption of the multivalent ions, and therefore affects the diffuse layer potential of the surfaces involved. Comparison of direct force measurements with DLVO theory suggests that this theory captures these force profiles well even in the presence of multivalent ions, definitely at distances larger than few nm. At shorter distances, additional attractive forces were reported, especially in the presence trivalent cations [17-19]. The latter attractive component could be related to ion correlation effects, surface charge heterogeneities, charge fluctuations, or image charges [20-22,38-41].

In this article, we present direct force measurements between negatively charged silica particles in the presence of multivalent cations, namely K^+ , Mg^{2+} , and La^{3+} . The advantage of the present sphere-sphere geometry is that the two interacting surfaces are very similar. This aspect is not always obvious for the frequently used sphere-plane geometry. The present results confirm that DLVO theory is capable of capturing the interaction forces in this system over a wide concentration range and further suggests the presence of additional non-DLVO attractive force in solutions containing La^{3+} ions.

Experimental

Materials. Experiments were carried out with silica particles obtained from Bangs Laboratories Inc., USA. The particle size was measured with a scanning electron microscope (SEM, JSM-6510LV, JEOL). Particles were spread on a silicon wafer of about $5 \times 5 \text{ mm}^2$ in area and sintered at 1150°C for 3 hours. Once cooled down, the silicon wafer was attached to the SEM support, gold coated at a pressure of 10 Pa during 30 s, and imaged. The images of about 50 particles were collected, and the diameter of each particle was extracted with ImageJ software [42]. The scale of the images was calibrated with $1 \text{ }\mu\text{m}$ standard calibration grid (Ted Pella, Redding, USA). From the size distribution, one obtains the average particle diameter of $4.39 \text{ }\mu\text{m}$ with a polydispersity characterized by the coefficient of variation of 1.3%. The manufacturer reports an average diameter of $5.0 \text{ }\mu\text{m}$, and a coefficient of variation of 10%. The smaller particle size measured by the SEM is likely caused by shrinkage of the particles during heating. The same heating procedure is used for all subsequent experiments.

The root mean square (RMS) roughness of the particles was measured by AFM imaging. The particles were sintered onto a quartz slide in the same way as described above. The particles were imaged in 10 mM KCl solution adjusted to pH 4.0 with the AFM (MFP-3D, Asylum Research) in the amplitude modulation mode. Silicon cantilevers (OMCL-AC240TS, Olympus) with a nominal tip radius < 10 nm and a resonance frequency of about 110 kHz in air were used. Images were acquired with a scan rate of $0.2 \mu\text{m/s}$, a free oscillation amplitude (FOA) of about 10 nm, and a set point to around 90% of the FOA. The roughness was determined for an area of $1 \times 1 \mu\text{m}^2$ and averaged over 5 particles.

All force experiments were carried out at room temperature of $22 \pm 2^\circ\text{C}$ in solutions of KCl, MgCl_2 , and LaCl_3 prepared in Milli-Q water. Subsequently, pH 4.0 was adjusted by addition of HCl. In these solutions, we expect that K^+ , Mg^{2+} , and La^{3+} represent the principal cationic species. While the formation of the LaCl^{2+} complex is possible, it should only become important higher salt concentrations [17,43].

Direct Force Measurements. Forces between the silica particles were measured in electrolyte solutions by the colloidal probe technique. The particles were attached to tip-less cantilevers and to the substrate as follows. The cantilevers (MikroMasch, Tallin, Estonia) were cleaned in air plasma (PDC-32G, Harrick, New York) for 5 minutes. Few silica particles were placed on a glass slide and tiny drops of about $5 \mu\text{L}$ of glue (Araldite 2000+) were deposited in their proximity. The cantilever was mounted in the AFM, brought in contact with the drop of the glue with the translation stage, and a particle was picked up in this fashion.

The glass slide sealing the AFM fluid cell and a 19 mm square quartz slide (Edmund Optics) were cleaned for 2 hours in piranha solution, which consists of a 3:1 mixture of H_2SO_4 (98%) and H_2O_2 (30%), then rinsed with pure water, and dried under a stream of pure nitrogen. The particles were then spread onto the quartz slide. The cantilever with the silica particles and the quartz slide were sintered in an oven at 1150°C for 3 hours. This procedure leads to a firm attachment of the particle to the cantilever or to the quartz plate. The heating further removes the glue used completely.

For the measurements, a closed-loop AFM (MFP-3D, Asylum Research) mounted on an inverted optical microscope (Olympus IX70) was used. Prior to the measurements, the quartz slide and the probes with the attached particles were rinsed in pure water, then in ethanol, dried in air, and finally treated in air plasma for 20 min. The reverse side of the slide with the sintered particles was glued (Pattex 100% Repair Gel) onto the glass slide sealing the AFM cell. The AFM fluid cell was mounted with the slide and the cantilever, thoroughly flushed with the respective electrolyte solution, and then closed. The attached

particle was centered above another particle on the substrate, and a precise alignment was achieved to an accuracy of about 100 nm by horizontal adjusting the AFM-piezoes and by observing the interface fringes with the optical microscope. The forces were obtained by averaging of about 150 approach and retraction cycles, which were accumulated with sampling rate of 5 kHz, a cycling frequency of 0.5 Hz, and approach-retraction velocities of 300 nm/s. The constant compliance region is not easily defined for the present particles, and therefore we assume zero separation when the load reaches 5 nN/m for repulsive force curves, and 1 nN/m for the attractive ones. The separation distance has a precision of about 0.3 nm for each individual force curve, which is similar to procedures used earlier [44,45]. The cantilever deflection was converted to force with the spring constant of the cantilever. The cantilever spring constants were in the range of 0.1–0.3 N/m, and they were obtained from resonance frequency, quality factor, and lateral dimensions of the cantilever [46]. The spring constant determined in this fashion agreed with those determined from thermal fluctuations of the cantilever within 10%. The measured forces were finally normalized with the effective radius. At low salt levels, forces are repulsive down to contact. Attraction was observed at higher salt levels, but forces remained repulsive down to short distances. Upon retraction, no adhesion was observed in KCl and MgCl₂ solutions, and the force curves are identical upon approach and retraction. Only in LaCl₃ solutions, jump-in instabilities and adhesion forces of 0.8±0.1 mN/m were observed at salt concentrations in the range 1–10 mM. Forces measured between different particle pairs were typically reproducible within 10–20%. This fact confirms that the measurement geometry is close to perfectly symmetrical. The same particles were used in a previous study [47], and that study used the average size reported by the manufacturer. This assumption leads to an underestimation of the normalized force by about 10%.

Data Analysis. The forces were analyzed within the Derjaguin approximation, which stipulates that the force F acting between two particles is given by

$$F = 2\pi R_{\text{eff}} W \quad (1)$$

where R_{eff} is the effective radius and W is the interaction free energy per unit surface area in the plate-plate geometry. In the symmetric sphere-sphere geometry, $R_{\text{eff}} = R/2$ where R is the particle radius. Since the sample is rather monodisperse, the average particle radius was taken.

The forces are initially represented by DLVO theory. The underlying expression is

$$F = F_{\text{vdW}} + F_{\text{dl}} \quad (2)$$

where F_{vdW} is the van der Waals force and F_{dl} is the double layer contribution. For the former, the following non-retarded expression is used

$$\frac{F_{\text{vdW}}}{R_{\text{eff}}} = -\frac{H}{6(h + \delta)^2} \quad (3)$$

where H is the Hamaker constant, h is the surface separation, and δ is the shift of the plane of origin of the van der Waals force with respect to the contact point.

The double layer force is calculated by solving the PB equation between two equally charged plates [4,48-50]. Thereby, one calculates the electric potential $\psi(x)$ profile as a function of the position x . The origin of x is taken at the mid-plane, while the two plates are located at $x = \pm h/2$. For a solution containing different ions of number concentrations c_i and valence z_i the PB equation reads [48,49]

$$\frac{d^2\psi}{dx^2} = -\frac{q}{\varepsilon_0\varepsilon} \sum_i z_i c_i e^{-z_i \beta q \psi}, \quad (4)$$

where q is the elementary charge, ε_0 is the dielectric permittivity of vacuum, ε is the dielectric constant, and $\beta = 1/(kT)$ is the inverse thermal energy. The latter relation defines T as the absolute temperature and k as the Boltzmann constant. We use $\varepsilon = 80$ as appropriate for water at room temperature. As two identical surfaces are considered here, the symmetry of the systems implies that the PB equation can be solved in the half-space $0 \leq x \leq h/2$. The boundary conditions are

$$\left. \frac{d\psi}{dx} \right|_{x=0} = 0, \quad (5)$$

and the constant regulation (CR) approximation at the surface implies

$$\varepsilon_0\varepsilon \left. \frac{d\psi}{dx} \right|_{x=h/2} = \sigma - C_1 [\psi(h/2) - \psi_D], \quad (6)$$

where ψ_D and s are the diffuse layer potentials and surface charge density of the isolated surface, and C_1 their inner layer capacitance. The inner layer capacitance can be viewed as the Stern capacitance in first

approximation, but it may also contain contributions from ions adsorption processes [14,50]. While charge regulation effects can also be treated by means of surface complexation models [13,14,48], the constant regulation approximation represents a much simpler way to quantify these effects within a theoretical description of double layer forces.

The PB equation is solved numerically subject to these boundary conditions. The diffuse layer potential of an isolated surface is related to the surface charge density by

$$\sigma = \pm \left[2kT\epsilon_0\epsilon \sum_i c_i \left(e^{-z_i\beta q\psi_D} - 1 \right) \right]^{1/2}, \quad (7)$$

where the $\pm$ signs reflect the sign of the electric potential. The surface charge density represents the surface charge within the inner layer, namely the one that is neutralizing the charge of the diffuse layer. Instead of the inner layer capacitance, we report the regulation parameter defined as [14,50]

$$p = \frac{C_D}{C_D + C_1}, \quad (8)$$

where C_D is the diffuse layer capacitance, which is given by

$$C_D = \frac{\partial \sigma}{\partial \psi_D} = \pm \left(\frac{q^2 \epsilon_0 \epsilon}{2kT} \right)^{1/2} \frac{\sum_i z_i c_i \left(e^{-z_i\beta q\psi_D} - 1 \right)}{\left[\sum_i c_i \left(e^{-z_i\beta q\psi_D} - 1 \right) \right]^{1/2}} \quad (9)$$

The regulation parameter provides a more intuitive interpretation of the boundary conditions, since $p=1$ refers to constant charge (CC) conditions, while $p=0$ to constant potential (CP) conditions. The constant regulation approximation given in (6) is exact at larger separation distances, while it may become less accurate close to contact [14,48]. However, it was shown that this approximation is excellent for many realistic situations. The swelling pressure is then calculated from the electric potential at the mid-plane $\psi_M = \psi(0)$, namely [4,49]

$$\Pi = kT \sum_i c_i \left(e^{-z_i\beta q\psi_M} - 1 \right). \quad (10)$$

The interaction free energy is then obtained by integrating the pressure profile

$$W_{\text{dl}} = \int_h^{\infty} \Pi(h') dh' \quad (11)$$

The PB calculations are carried out numerically [49]. The solution is modeled either as a monovalent electrolyte with the concentration that corresponds to the added amount of KCl and HCl, or as a mixed electrolyte containing the appropriate concentrations of MgCl_2 or LaCl_3 and HCl. From these concentrations, one can evaluate the respective ionic concentrations c_i entering in eq. (4).

Results and discussion

Forces between pairs of similar silica particles are measured by the colloidal probe technique based on the AFM. These systems are investigated in aqueous solutions of KCl, MgCl_2 , and LaCl_3 adjusted to pH 4.0. The silica particles used have a diameter of about 4.4 μm . The particles are attached to the cantilever and the substrate by sintering at 1150°C. Figure 1 shows the scheme of the experiment and various images of these particles. One observes that these particles do have moderate surface asperities. The surface roughness was determined by quantitative analysis of the AFM images and has a root mean square (RMS) value of about 0.8 ± 0.1 nm. This small roughness results from the sintering of the particles.

Forces in the Presence of Monovalent Counterions. Force profiles in monovalent KCl solutions are shown in Fig. 2. At low salt concentration, the surfaces interact with a soft and long-ranged repulsive force. The range and the magnitude of this force decreases with increasing salt level, which is typical for double layer forces. At higher salt levels, these forces become attractive at larger distances, suggesting the onset of the van der Waals force. At short distances, however, the forces are always repulsive. This short-range non-DLVO force is probably due to overlap of hairy layers of polysilicic acid or hydration of the silica surface [51-56].

At larger distances, these force profiles can be quantitatively explained by DLVO theory, which includes the non-shifted non-retarded van der Waals contribution ($\delta = 0$) and the double layer force. The latter force is modeled within the full PB theory for two planar charged surfaces, whereby the boundary conditions are treated within the constant regulation approximation. As Fig. 2 indicates, however, the repulsion at short distances is inconsistent with DLVO theory. This interaction can be modeled as a short-ranged repulsive exponential force, leading to the force profile

$$\frac{F}{R_{\text{eff}}} = \frac{F_{\text{vdW}}}{R_{\text{eff}}} + \frac{F_{\text{dl}}}{R_{\text{eff}}} + A_s e^{-q_s h} \quad (12)$$

where A_s is the amplitude, and q_s^{-1} is the decay length of the repulsive non-DLVO force. To remove the divergence of the van der Waals force at small distances, we introduce a shift $\delta > 0$ of the plane of origin of the van der Waals force defined in eq. (3). This shift can be interpreted as originating from surface roughness. To determine this contribution, the model was fitted to the experimental data at high salt concentrations, where the double layer force is negligible. The following parameters were found. The van der Waals force is characterized by a Hamaker constant of $H = (2.8 \pm 0.5) \times 10^{-21}$ J and a shift $\delta = 0.70 \pm 0.04$ nm, while the non-DLVO repulsive force by a decay length $q_s^{-1} = 0.26 \pm 0.03$ nm and an amplitude $A_s = 0.91 \pm 0.03$ mN/m. Indeed, the shift is comparable to the measured roughness of 0.8 ± 0.1 nm.

Once these parameters were determined, the double layer force was added and force profiles at all salt levels were refitted. At low KCl concentrations, the salt concentrations and regulation parameters could be determined from the force curves to good accuracy. The salt concentrations were fixed to the nominal values, but when fitted, they would always fall within 15% of the nominal values. The regulation parameters did not show any clear trend, yielding an average value of $p = 0.58 \pm 0.04$. For this reason, this parameter was fixed to that value, and the force curves were refitted to obtain the diffuse layer potentials. This regulation parameter is also given in Table 1.

The resulting diffuse layer potentials are shown in Fig. 3. While the sign of the diffuse layer potential cannot be determined from force measurements in the present symmetric setting, the negative sign was introduced since silica is known to develop a negative surface charge due to the dissociation of the surface silanol groups [57]. The magnitude of the diffuse layer potential decreases with increasing salt concentration. The observed potentials are similar to the values obtained by direct force measurements involving silica surfaces in monovalent salt solutions [9,10,47,58-60]. The diffuse layer potential can be rationalized with the charge-potential relationship given in eq. (7) for a fixed surface charge density σ . The resulting charge density is approximately -6.5 ± 0.3 mC/m² (Table 1). The magnitude of this value is somewhat larger, but well comparable to previous studies of silica surfaces in monovalent salt solutions [9,10,47,59]. These authors report charge densities ranging between -4 and -2 mC/m². These values are also comparable with charge densities obtained from electrokinetic techniques for similar silica samples [9,55]. A charge density that is independent of the salt concentration is actually incompatible with the

regulation parameter of $p = 0.58$ reported above. A value of $p < 1$ indicates that the surface charge may regulate upon changes of the surface separation or salt concentration [14]. However, the actual fit of the experimental data is far from perfect, and the remaining discrepancies may reflect the presence of charge regulation effects, which could be caused by exchange of protons and potassium ions.

The Hamaker constant of $H = (2.8 \pm 0.5) \times 10^{-21}$ J obtained here agrees well with the value of $H = 2.2 \times 10^{-21}$ J that was measured in a similar setting by Dishon et al. [10]. These values are rather close to the currently best theoretical estimate of 1.6×10^{-21} J, which is based on accurate spectra over a wide frequency range [5]. Earlier calculations based on simplified spectra seem to lead to unrealistically large values [5,61]. A substantially smaller Hamaker constant of $(2.5 \pm 0.5) \times 10^{-22}$ J was reported in a similar system recently [45]. A value comparable to the previous one was also measured for the same particles as used here, but sintered at a lower temperature [47]. We suspect that this reduction of the Hamaker constant is mainly caused by a larger surface roughness of the particles used in those studies. While the Hamaker constant is expected to be a weak function of the salt concentration [4], this dependence cannot be established due to the limited accuracy of the direct force measurements.

The presence of a short-ranged repulsive non-DLVO force acting between silica surfaces was also reported in previous studies [9,44,52,54]. The range of the short-ranged force is similar to values found earlier [44,47,52]. This force was suggested to originate from the overlap of hairy or gel layers of polysilicic acid [54-56]. Other researchers argue that this repulsion is a hydration force and is due to the structuring of water close to the surface [51-53].

Forces in the Presence of Multivalent Counterions. Forces were studied in MgCl_2 and LaCl_3 solutions at pH 4.0 in a similar fashion as in KCl, and they are summarized in Fig. 4. Both situations resemble the results found for KCl, except the relevant salt concentrations are lower. This fact can be understood since the decay of the force profiles is dictated by the ionic strength, which is larger for salt solutions containing ions of higher valence for a given salt concentration. Moreover, the forces in LaCl_3 solutions are more attractive at intermediate salt levels than for the two other salts.

The measured force profiles in MgCl_2 are shown in Fig. 4a. The force could be successfully fitted with same model as used in KCl solutions. At high salt levels, the data are consistent with the same parameters for the van der Waals force and the non-DLVO short range force. In particular, the Hamaker constant and the short-ranged repulsive force remain unchanged. Figure 5 illustrates this feature more clearly. The double layer force can be rationalized with a constant regulation parameter of $p = 0.96 \pm 0.03$. The force profile is well described by fixing the salt concentration to its nominal value. When the salt

concentrations were fitted, they were typically lower, but remained within 20% of the nominal value. The resulting diffuse layer potentials are shown in Fig. 3. These potential were fitted with the PB model, and the corresponding surface charge density was found to be $-3.5 \pm 0.2 \text{ mC/m}^2$ (Table 1). The magnitude of the surface charge is substantially lower in KCl, which suggests that Mg^{2+} ions adsorb to the silica surface, and neutralize the surface charge more extensively than K^+ ions.

The force profiles in LaCl_3 solutions shown in Fig. 4b resemble the ones in the other electrolytes. However, they show a stronger attraction at intermediate salt concentrations. This feature becomes more obvious when inspecting Fig. 5, which compares the attractive force profiles in different salt solutions and at different concentrations. Indeed, the minima in the force profiles measured in LaCl_3 solutions at intermediate concentrations are about 3-times deeper than in KCl and MgCl_2 solutions. At high salt levels, however, this additional attraction disappears, and the minima have the same depth in 30 mM LaCl_3 solution as in 500 mM KCl and MgCl_2 electrolytes. When the electrolyte concentrations are increased further, the attractive profile remains the same.

To capture this additional attractive interaction quantitatively, we have modified the force profile by introducing an additional attractive exponential force, namely

$$\frac{F}{R_{\text{eff}}} = \frac{F_{\text{vdW}}}{R_{\text{eff}}} + \frac{F_{\text{dl}}}{R_{\text{eff}}} + A_s e^{-q_s h} - A_p e^{-q_p h} \quad (13)$$

where $A_p > 0$ is the amplitude and q_p^{-1} is the decay length of the attractive non-DLVO force. At high salt concentrations, the forces are consistent with same van der Waals force and short-range repulsion as determined for the KCl system. The fitted range of the additional attraction remains relatively constant, and can be therefore fixed to its average value of $q_p^{-1} = 1.3 \text{ nm}$. Good description of the force curves can be achieved by fixing the salt concentrations to their nominal values. However, when one attempts to fit these concentrations, one would systematically obtain values that were 20–30% lower than the nominal ones. We suspect that formation of LaCl^{2+} complexes might be responsible for this behavior [43]. The force curves can be described with a constant regulation parameter of $p = 0.97 \pm 0.03$. The diffuse layer potentials are shown in Fig. 3. They can be reasonably well interpreted with a surface charge density of $-1.0 \pm 0.2 \text{ mC/m}^2$ within the PB model (Table 1). The lower magnitude of the surface charge density again illustrates that the multivalent ions neutralize the surface charge more effectively than the monovalent ones. The fact that the surface is negatively charged was verified by measuring the forces at very low La^{3+}

concentrations down to about 10^{-8} M. When decreasing the La^{3+} concentration, the magnitude of the force would increase, and approach the values observed in the background monovalent electrolyte.

Monovalent versus Multivalent Counterions. We would like to point out several characteristic features concerning forces between silica surfaces in the presence of multivalent metal ions, especially in Mg^{2+} and La^{3+} electrolytes. They address the reduction of the surface charge, modification of the regulation parameters, and the occurrence of additional attractive non-DLVO forces.

The first aspect is related to the substantial reduction of the surface charge in the presence of multivalent counterions. The measured magnitude of the surface charge density decreases about by a factor of 6 within the series K^+ , Mg^{2+} , and La^{3+} (Table 1). A similar reduction of the surface charge density was observed in electrophoresis experiments with silica particles in the presence of La^{3+} in solutions at low pH [62]. At neutral and higher pH, the same study reports that the particles undergo charge neutralization and a charge reversal due to extensive adsorption La^{3+} ions to the negatively charged silica surface. A similar charge reversal was also observed with force measurements at neutral pH [18,34]. Streaming potential studies reveal a charge reversal of silica at neutral conditions in the presence of divalent Ca^{2+} and Mg^{2+} cations, albeit at relatively high salt concentrations [63]. The charge of carboxylated and sulfate latex particles does also reverse even in acidic conditions in the presence of La^{3+} , and to a lesser extent with Ca^{2+} and Mg^{2+} [17,37]. We suspect that the adsorption of the multivalent ions is more extensive in the latter systems, probably due to the hydrophobicity of the latex particle surface.

The second aspect concerns the substantially higher regulation parameters in the presence of the multivalent ions than for the monovalent ones (Table 1). The former systems basically obey the CC boundary conditions. This finding is actually in agreement with the simple model given in eqs. (8) and (9). The diffuse layer capacitance C_D increases with increasing valence of the counterions, and in such systems the regulation parameter should be higher, and approach the CC conditions. However, the high regulation parameters reported here are in contrast with recent force measurements between charged polystyrene latex particles in the presence of multivalent ions [17,64,65]. These studies demonstrate that the presence of multivalent ions lead to small regulation parameters, typically close to CP boundary conditions. A possible explanation of the decrease of the regulation parameter for the latex particles could be related to the extensive adsorption of the multivalent ions. Upon approach, the adsorption equilibrium might shift substantially, which could lead to an increase of the inner layer capacitance C_1 .

The third aspect worthy discussion is the emergence of an additional attractive force in the presence of multivalent counterions. Figure 5 illustrates that the attraction is substantially stronger at lower concentration of La^{3+} ions than in the presence of cations of lower valence or at higher concentrations of La^{3+} . Similar attractive non-DLVO force trends were reported for silica in the presence different trivalent cations by Dishon et al. [18], and for sulfate latex in the presence of multivalent oligomeric aliphatic amines [65]. In all these cases, the additional attractive force profile can be rationalized with an additional exponential attraction with a range of about 1.0 nm. In the present system, the maximum magnitude of the amplitude is about 1.8 mN/m, while Dishon et al. [18] report a comparable magnitude of 1.2 mN/m. In the sulfate latex system, the attraction is stronger and features a maximum amplitude of about 10 mN/m. Similar attractive forces induced by multivalent ions with somewhat larger range of 2–3 nm were also reported with other types of latex particles [14,17,66]. These additional attractive non-DLVO forces might be related to ion-ion correlation effects, even though theoretical studies predict these interactions to be shorter ranged, typically in the sub-nm range [21,22,67]. The experimentally observed larger range of these interactions could possibly originate from additional contributions of surface charge heterogeneities and charge fluctuation forces [39,68,69]. The charge heterogeneities may induce further attractive forces, which are expected to be screened at elevated salt concentrations. This feature would be in line with the decrease of the attractive forces at higher salt concentrations, as observed experimentally. Charge fluctuation forces represent another interesting scenario. This force is related to the regulation properties of the interfaces, and it is proportional to the square of the inner layer capacitance. However, the present systems are close to CP conditions, and therefore we do not expect this contribution to be very important.

Conclusion

Direct force measurements were performed with negatively charged silica particles in dilute aqueous electrolyte solutions containing multivalent counterions, namely K^+ , Mg^{2+} , and La^{3+} . The perfect symmetry of the sphere-sphere geometry can be confirmed through measurements with between different pair of similar particles. The force profiles can be well described with DLVO theory down to distances of about 4 nm. Deviations are observed at smaller distances for all types of metal ions, whereby the forces become strongly repulsive. This additional non-DLVO force is likely related to the hairy or gel layers of polysilicic acid or to the strong hydration of the silica surface. In the presence of La^{3+} , one observes an additional attractive non-DLVO force with a range of about 1 nm. This force is probably due to ion-ion

correlation effects, which are possibly magnified by surface charge heterogeneities [20-22,38]. However, charge fluctuation or image charge effects could equally contribute [39,40]. Multivalent counter-ions lead to a substantial reduction of the magnitude of the surface charge density, which is related to the adsorption of these ions to the silica surface.

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Table 1. Parameters used to describe the measured force profiles.

Salt	Surface charge density ^a σ (mC/m ²)	Regulation parameter p	Range of repulsion q_s^{-1} (nm) ^c	Range of attraction q_p^{-1} (nm) ^d
KCl	-6.5 ± 0.3	0.58 ± 0.04^b	0.26 ± 0.04^b	–
MgCl ₂	-3.5 ± 0.2	0.96 ± 0.03^b	0.26^e	–
LaCl ₃	-1.0 ± 0.2	0.97 ± 0.03^b	0.26^e	1.3 ± 0.1^b

^aObtained by fitting the measured diffuse layer potentials. ^bAverage value from fits at different concentrations. ^cShort-range repulsive exponential non-DLVO force fitted in the KCl system. ^dShort-range attractive exponential non-DLVO force fitted in the LaCl₃ system. ^eValue fixed during the fit.

Figure 1. Colloidal probe experiment and the particles used. (a) Scheme of the experiment. (b) AFM image of the silica particles after sintering at 1150°C. (c) Side view of the cantilever with the attached particle. (d) Top view of the particles attached to the substrate.

Figure 2. Force profiles between silica particles in KCl solution at pH 4.0 compared with calculations. DLVO theory (left) is compared to results where an additional non-DLVO exponential repulsion was added (right). These calculations are based on the constant regulation (CR) approximation. For 5 mM, these calculations also compared with constant charge (CC) and constant potential (CP) conditions, which are enclosing the grey region. (a) Lower and (b) higher salt concentrations. The slopes of the triangles in (b) indicate the spring constant of the cantilever.

Figure 3. Diffuse layer potentials of silica particles versus the salt concentration as obtained from direct force measurements. The solid lines are calculations based on the PB theory with fixed surface charge densities given in Table 1.

Figure 4. Force profiles between silica particles in the presence of multivalent cations at pH 4.0 compared with calculations. (a) MgCl_2 and (b) LaCl_3 . The solid lines correspond to best fits of DLVO theory, which includes a short-range exponential repulsion and, for LaCl_3 also a longer-ranged exponential attraction. The slopes of the triangles in indicate the spring constant of the cantilever.

Figure 5. Attractive force profiles in different salt solutions indicated. The stronger attraction in the LaCl_3 solution of intermediate concentrations can be rationalized with an additional exponential non-DLVO attraction.

Figure 6. Amplitude of attractive non-DLVO forces in LaCl_3 solution at pH 4.0. The solid line serves to guide the eye only.