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Smith, Alexander; Maroni, Plinio; Trefalt, Gregor; Borkovec, Michal

Unexpectedly Large Decay Lengths of Double Layer Forces in Solutions of Symmetric, Multivalent Electrolytes

Alexander M. Smith, Plinio Maroni, Gregor Trefalt, Michal Borkovec*

Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II,

30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

*Corresponding author: michal.borkovec@unige.ch (email)

Abstract

Double layer forces acting between micron-sized silica particles are measured with the atomic force microscope (AFM) in solutions of symmetric, multivalent electrolytes. In particular, the following 2:2 electrolytes, $CuSO_4$, $MgSO_4$, and the 3:3 electrolyte $LaFe(CN)_6$ were investigated. For the multivalent electrolytes, the measured decay lengths are substantially larger than the ones expected on the basis of simple Debye-Hückel (DH) theory. These deviations can be explained quantitatively by the formation of neutral ion pairs. The measured surface charge density decreases in magnitude with increasing valence. Both effects are caused by ion-ion correlations, which are not included in the classical DH theory. However, this theory remains applicable provided one considers the formation of ion pairs in solution and an effective surface charge density. This effective charge is substantially smaller in magnitude than the one of the bare surface. This reduction results from adsorption of counter-ions, which becomes stronger with increasing valence. These observations reveal that DH theory is applicable even in the presence of multivalent ions, provided the effective parameters are chosen appropriately.

Introduction

Derjaguin, Landau, Verwey, and Overbeek (DLVO) stressed the importance of forces acting between solid surfaces across aqueous solutions already long time ago.[1-3] However, reliable measurements of such forces had to await the development of the surfaces forces apparatus (SFA).[4] More recently, the tools for such direct force measurement could be substantially expanded with total internal reflection microscopy (TIRM)[5,6], optical tweezers combined with video microscopy[7,8], and the colloidal probe technique based on the atomic force microscope (AFM).[9-13]

Early measurements between mica surfaces have already demonstrated that at lower salt levels such forces are normally dominated by double layer interactions, which lead to a characteristic exponential decay at larger separation distances.[4,14-16] Thereby, the range of this interaction decreases with increasing electrolyte concentration. This behavior can be rationalized with Debye-Hückel (DH) theory, which represents a linearized version of the Poisson-Boltzmann (PB) theory. In agreement with experiment, these theories predict that these forces decay exponentially at larger distances.[3] The corresponding decay length turns out to be identical to the Debye length, which indeed decreases with increasing electrolyte concentration.

However, recent theoretical work has cast doubt on the validity of the classical DH and PB theories, especially in systems containing multivalent ions.[17-20] These theories are based on a mean-field approximation, thereby neglecting correlations between the ions. Such ion-ion correlations have been claimed to be especially important near interfaces, but also in the bulk in the vicinity of highly charged ions. For example, such correlations may manifest itself by formation of fluid-like or crystalline ionic phases near interfaces.[19,21]

In spite of these reservations, numerous experiments have confirmed that double layer forces agree with DH or PB theories even in the presence of multivalent ions.[6,11,15,16,22-25] Moreover, the measured decay lengths match the expected Debye lengths too. In these systems, however, effects of ion-ion correlations should be important and mean-field DH or PB should not be necessarily applicable. This apparent contradiction calls for an explanation. This article sheds new light on this question through force measurements in symmetric, multivalent electrolytes.

Experimental

Materials. Silica particles with diameter 5.2 μm (Bangs Laboratories Inc., USA) were attached to tipless cantilevers (MicroMash) using epoxy glue. Similar particles were also sprinkled over quartz substrates and together with cantilevers then heated to 1150 °C for 3 hours to firmly attach the particles. As previously reported, this sintering process also shrinks the particles to 4.4 μm, and significantly reduces their surface roughness.[26] Immediately prior to experiment, substrates and cantilevers were rinsed thoroughly with

ethanol and ultrapure water. After drying in a stream of nitrogen, they were placed in air plasma for at least 15 minutes. Electrolyte solutions were prepared from NaCl, CsCl, $CuSO_4 \cdot 5H_2O$ (Sigma-Aldrich, >99.9%) and $MgSO_4$ (Acros Organics, 97% anhydrous) with ultrapure Milli-Q water (Millipore). $LaFe(CN)_6$ was prepared by precipitation reaction as described by Bhat et al.[27] In brief, concentrated solutions of $LaCl_3$ and $K_3Fe(CN)_6$ (Sigma-Aldrich ⧠99%) were mixed together in equimolar amounts. The $LaCl_3$ solution was added dropwise with constant stirring at 25 °C. The mixture was then left in the dark overnight, and the resulting precipitate was washed with ultrapure water over a Buchner funnel to remove any traces of KCl. The red-brown crystals were stored in a desiccator over silica gel for several weeks before use. X-ray powder diffraction confirmed that the salt was $LaFe(CN)_6 \cdot 4 H_2O$. The amount of crystal water was also confirmed with thermal gravimetric analysis (TGA). The concentrations of all solutions used were verified by atomic absorption spectroscopy (AAS) or complexometric titrations. The measured concentrations agreed with the nominal ones within <2%. The solution pH in the experiments was 5.8±0.3.

Direct Force Measurements. Forces between silica particles were measured using a closed-loop AFM (MFP-3D, Asylum Research) mounted on an inverted optical microscope (Olympus IX 73). The particle on the cantilever was aligned above a particle deposited on the substrate to within 50 nm using the horizontal scanner of the AFM. After centering a pair of particles, at least 200 approach-retraction cycles were measured at velocity 300 nm/s. For each pair the diffuse layer potential was verified to lie within about 10% of the average of the sample. This method assures that the particle pair is close to symmetric. The deflection signal was converted to force-separation profiles by subtracting the baseline in the absence of any forces, and by fitting the constant compliance region where the particles are in intimate contact at high forces. The spring constant of the cantilever was measured using the method described by Sader et al.[28], which relies on the lateral dimensions of the cantilever and its frequency response. The forces obtained from repeated approach curves between a particular pair of particles were averaged, typically leading to a force resolution of about 2 pN and down to distances of about 0.2 nm.

Results and Discussion

We use the AFM to study forces between silica particles of about 5 µm in diameter. A scheme of the experiment is shown in Fig. 1a. In particular, we investigate 2:2 electrolytes, namely $CuSO_4$ and $MgSO_4$, and the 3:3 electrolyte $LaFe(CN)_6$ at pH 5.6. While the exponential decay of the double layer force is observed in all these systems, the decay length is substantially larger than the one expected from the DH theory. This behavior can be explained quantitatively by the formation of ion-pairs. In fact, formation of ion pairs is a consequence of ion-ion correlations.
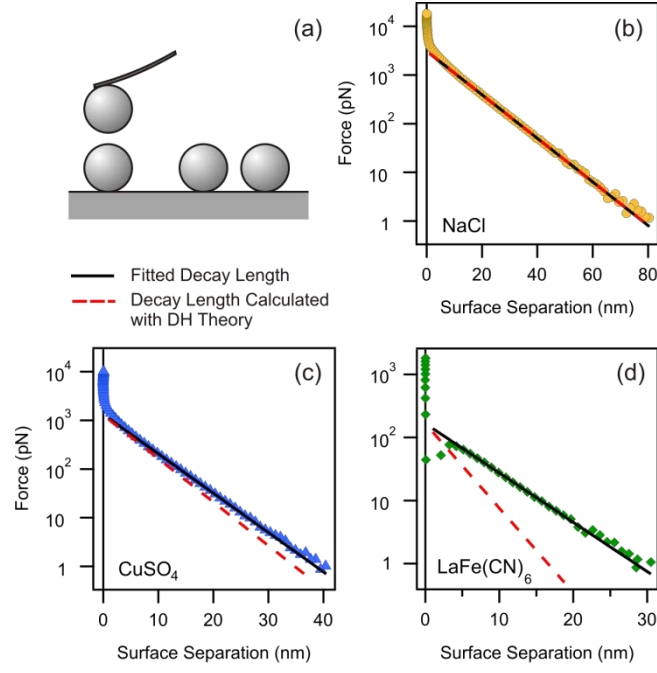
Figure 1. (a) Scheme of direct force measurements with the AFM. Representative force profiles at 1.0 mM salt concentrations acting between silica particles in symmetric (b) 1:1, (c) 2:2 and (d) 3:3 electrolytes. The profiles are close to exponential, as expected from DH theory, but this theory substantially underestimates the decay length in multivalent electrolytes.

Figure 1 illustrates these deviations by comparing the measured force profiles in 1:1, 2:2 and 3:3 electrolytes at concentrations of 1 mM. Under these conditions, double layer forces dominate. In the semi-logarithmic representation used, the force profile appears as a straight line, which indicates that the force decays exponentially. The PB theory suggests that at larger distances the forces induced by the overlap of the double layers follow the DH-like expression[3]

$$F_{dl}(h) = 2\pi R \varepsilon_0 \varepsilon \kappa_{eff} \psi_{eff}^2 \exp(-\kappa_{eff} h) \tag{1}$$

where h is the smallest surface separation, R the particle radius, ε_0 is the permittivity of vacuum, ε the dielectric constant, ψ_{eff} is the effective surface potential, and κ_{eff} is the effective inverse decay length. The latter parameter is normally assumed to be identical to the inverse Debye length κ_D, which can be evaluated for a symmetric $z{:}z$ electrolyte from the relation[3]

$$\kappa_D^2 = \frac{2z^2 \beta e^2 N_A c_{tot}}{\varepsilon_0 \varepsilon} \tag{2}$$

whereby e is the elementary charge, c_{tot} is the total molar concentration of the electrolyte, N_A the Avogadro's number, and $\beta = 1/kT$ whereby k is the Boltzmann constant and T the absolute

temperature. We use $\varepsilon = 80$ as appropriate for water at 25°C. We have fitted the profiles shown in Fig. 1 to eq. (1) by adjusting the effective surface potential ψ_{eff} and the effective inverse decay length κ_{eff}. At larger distances, the fits are excellent. For the multivalent electrolytes, however, one finds substantial discrepancies when comparing the calculated Debye length κ_D^{-1} from the known electrolyte concentration with eq. (2) with the decay lengths extracted from the measured force profiles, see Fig. 1b,c. For the 2:2 and 3:3 electrolytes, the best fit of the data yields decay lengths of 5.4±0.2 nm and 5.6±0.4 nm, while the DH expression yields 4.9 nm and 3.2 nm, respectively. The measured decay lengths are systematically larger than the calculated ones. These deviations are clearly beyond any experimental error, especially since the electrolyte concentrations were verified with independent analytical techniques. Moreover, the observed decay length agrees with the Debye length for the 1:1 electrolyte. In this case, the best fit shown in Fig. 1b yields a decay length κ_{eff}^{-1} of 9.7±0.2 nm, and DH theory predicts the same value.

Given these discrepancies, we have studied the concentration dependence of the force profiles in these systems in detail. Such data sets are shown in Fig. 2. Qualitatively, one observes the typical behavior of interaction forces between identical charged interfaces. At low salt concentrations, the forces are repulsive and long-ranged, as they are dominated by repulsive double layer forces. This mechanism leads to the exponential dependence discussed above. Two effects modify the situation at higher salt concentrations. First, the range of the repulsive double layer forces decreases, as one expects due to increasing screening. Second, the presence of the attractive van der Waals force becomes apparent, mainly through an intermediate minimum occurring at larger distances. The van der Waals force can be well approximated by the non-retarded expression[3]

$$F_{vdW}(h) = -\frac{HR}{12} \cdot \frac{1}{h^2} \tag{3}$$

where *H* is the Hamaker constant. Since a power law decays more slowly than an exponential, the van der Waals force dominates the force profile at larger distances. At very high salt concentrations, the repulsive double layer force disappears completely, and the force profile is entirely dominated by the attractive van der Waals force, see Fig. 3.

In order to analyze the experimental data quantitatively, we rely on classical DLVO theory. This theory surmises that the overall force *F* can be approximated by the sum of the contributions of the van der Waals and double layer forces, namely[3]
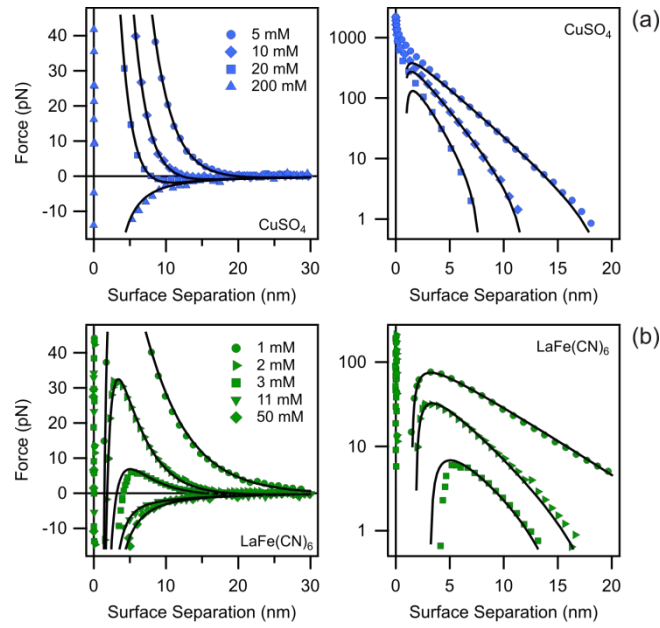
Figure 2. Forces between two micro-meter sized silica particles in (a) $CuSO_4$ and (b) $LaFe(CN)_6$ solutions of different concentrations. Solid lines are best fits with DLVO theory. Left column shows the data in linear representation and the right column the repulsive forces in semi-logarithmic representation.
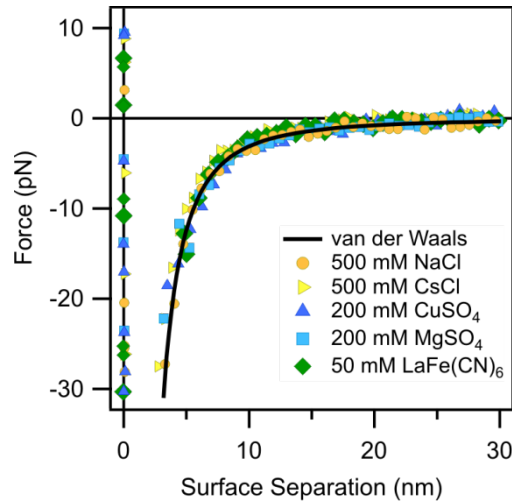

Figure 3. Van der Waals force between two micro-meter sized silica particles in different electrolyte solutions of high concentrations. The solid line is the best fit with eq. (3) with a Hamaker constant of $(1.7\pm0.1)\times10^{-21}$ J.

$$F(h) = F_{vdW}(h) + F_{dl}(h) \tag{4}$$

Thereby, we express the van der Waals force with eq. (3), while the double layer force is approximated with the DH-like expression given in eq. (1). This description further relies on the Derjaguin approximation, but this approximation is expected to be highly accurate as the size of the colloidal particles is much larger than the range of the interactions.[3]

The Hamaker constant is evaluated from the force profiles at high salt concentrations. As shown in Fig. 3, these profiles are independent of the type of salt. They follow the dependence suggested by eq. (3) very well. From the best fit one obtains the Hamaker constant $H = (1.7\pm0.1)\times10^{-21}$ J. This value compares well to the value of 2.1×10^{-21} J measured by Sivan and coworkers[29] and to the theoretical estimate of 1.6×10^{-21} J calculated from accurate reflectance spectra.[30]

By fixing the Hamaker constant to the above value, we are left with two unknown parameters characterizing the double layer force, namely the effective inverse decay length κ_{eff} and the effective potential ψ_{eff}. This DLVO model is able to fit the measured force profile very well down to certain cut-off distances, see Fig. 2. These distances were chosen to be about 2 nm for the 1:1 electrolytes, 3 nm for the 2:2 and 6 nm for the 3:3. Provided the cut-off distance is chosen to be sufficiently large, the fitted parameters are independent of this choice. The reason for the choice of a larger cut-off distance for the 3:3 electrolyte is the presence of an additional attractive non-DLVO force. This attraction is most evident in the measured force profile in $LaFe(CN)_6$ electrolyte at 3 mM in the semi-logarithmic representation, see Fig. 2b. While such non-DLVO forces were observed in systems containing multivalent ions earlier[12,24], their effects can be eliminated in the present analysis by introducing an appropriate cut-off. On the other hand, including the van der Waals force is essential to obtain satisfactory fits, especially for higher salt concentrations. The present approach allows interpreting double layer forces with simple DH theory. At the same time, however, no information about the regulation properties and its capacitance can be obtained. This information would be accessible at shorter distances only, where the use of the more complicated PB theory would be necessary.

The fitted effective inverse decay length κ_{eff} is shown in Fig. 4a, where it is plotted relative to the inverse Debye length κ_D given by eq. (2). This ratio is unity within experimental error for both 1:1 electrolytes investigated, namely NaCl and CsCl. For multivalent electrolytes, however, this ratio is substantially below unity, and gets as low as 0.7 for the 2:2 electrolytes, and even 0.3 for the 3:3 electrolyte. This ratio decreases with increasing salt concentration. Interestingly, analogous deviations were revealed by TIRM in 2:2 electrolytes, albeit only mM concentrations were investigated.[6] The authors of the latter study ascribed these deviations, probably incorrectly, to experimental noise. No

deviations in the decay length were reported in earlier force measurements in 2:2 electrolytes[22], but this conclusion was possibly justified given the lower force resolution in these experiments. In asymmetric 1:z and z:1 electrolytes, measured decay length agreed reasonably well with the expected ones.[6,11,15,16,22-25] Deviations in the decay length were equally reported in highly concentrated electrolytes and ionic liquids containing monovalent ions.[31-33] In dilute electrolytes, the deviations seem to be most pronounced in multivalent, symmetric electrolytes studied here.
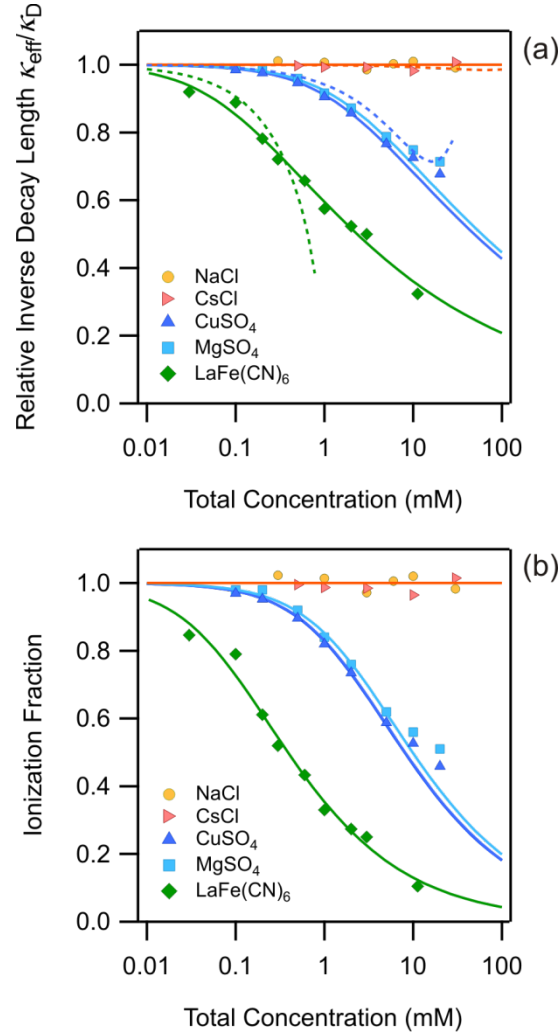

Figure 4. Parameters characterizing decay length of the double layer forces obtained from best-fits the experimental force profiles with DLVO theory for different symmetric electrolytes versus the total electrolyte concentration c_{tot}. Solid lines are obtained with the chemical equilibrium model that considers formation of neutral ion pairs. The association constants are given in Table 1. (a) Inverse decay length relative to inverse Debye length $\kappa_{\text{eff}} / \kappa_{\text{D}}$. (b) Ionization fraction of the electrolyte $c_{\text{ion}} / c_{\text{tot}}$. Dotted lines in (a) are the predictions of eq. (7) proposed by Kjellander and Mitchell.[34]

In the present situation, we interpret these deviations as follows. Multivalent ions in symmetric electrolytes are known to form ions pairs, which form according to the chemical equilibrium[35,36]

$$\mathrm{M}^{z+} \quad + \quad \mathrm{X}^{z-} \quad \rightleftharpoons \quad \mathrm{MX} \tag{5}$$
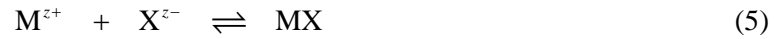
where M^{+z} represents the cation, X^{-z} the anion, and MX the neutral ion pair. According to this equilibrium, the electrolyte will be fully dissociated at low concentrations only, while at higher concentrations the neutral ions pairs MX form. Since only ions contribute to screening, this equilibrium reaction explains why larger decay lengths are observed.

The argument can be made quantitative by considering the respective mass actions law, which reads[35,36]

$$K = \frac{[\mathrm{MX}]}{[\mathrm{M}^{z+}][\mathrm{X}^{z-}]} \tag{6}$$

where K is the association constant and square brackets [...] denote the molar concentration of the respective species. The concentration of the free ions c_{ion} can be obtained by realizing that one has $c_{\mathrm{ion}} = [\mathrm{M}^{z+}] = [\mathrm{X}^{z-}]$ due to electroneutrality, and that the concentration of the ion pairs is given by $[\mathrm{MX}] = c_{\mathrm{tot}} - c_{\mathrm{ion}}$ where c_{tot} is the total salt concentration. The latter relation follows from mass balance. Based on these relations one can evaluate the ionization fraction $c_{\mathrm{ion}} / c_{\mathrm{tot}} = \kappa_{\mathrm{eff}}^2 / \kappa_{\mathrm{D}}^2$. The latter relation follows by assuming that the effective inverse decay length can be evaluated from the classical DH expression eq. (2) by inserting the concentration of the free ions c_{ion}. We neglect effects of activity coefficients and of higher order ionic clusters (i.e., ion triplets). These effects may become important at higher concentrations[35,36], but they are expected to be minor in the concentration range considered.

The results of these calculations are compared with the relative effective inverse decay length in Fig. 4a, while the corresponding ionization fractions are shown in Fig. 4b. Indeed, the simple chemical equilibrium given in eq. (5) accounts for the observed dependence very well. Thereby, the value of the association constant K has to be fitted to the experimental data. The respective values are given in Table 1. The two measured values for the 2:2 electrolytes are identical within experimental error. One also observes that the values extracted from the force measurements compare favorably with earlier studies, which were based on conductivity, dielectric spectroscopy, or osmotic measurements.[35-42] While effects of ion pairing were also discussed in 1:1 electrolytes[43], we cannot detect any deviations of this kind through force measurements in the present system. Ion pairing was also invoked to explain deviations in the decay lengths highly concentrated monovalent electrolytes and ionic liquids,

albeit solvent structuring could also be involved.[31-33] Formation of ions pairs is also less pronounced in asymmetric z:1 and 1:z electrolytes[36], and for this reason, deviations from the expected Debye lengths were not reported in these systems, or they were minor.[6,11,15,16,22-25]

Table 1. Ion pair association constants and surface charge densities for the systems investigated.

Electrolyte	Valence	Association constant lg K (L/mol)			Surface charge density[a] (mC/m^2)
		Fitted[a]	Literature	Bjerrum[e]	
NaCl	1:1	<0.3	−0.09[b,43]	<0	−8.4±0.4
CsCl	1:1	<0.3	−0.21[b,43]	<0	−7.2±0.6
CuSO$_4$	2:2	2.39±0.02	2.40[b,37], 2.40[c,38], 2.40[d,35]	2.68	−4.6±0.3
MgSO$_4$	2:2	2.31±0.04	2.20[b,39], 2.22[c,40], 2.38[d,35]	2.69	−5.3±0.3
LaFe(CN)$_6$	3:3	3.71±0.04	4.20[b,41], 3.73[b,42]	4.08	−1.1±0.2

[a]Present results obtained from the measured force profiles. The literature values of the association constants were determined with [b]conductivity, [c]dielectric spectroscopy, and [d]osmotic pressure measurements. [e]Association constant calculated with Bjerrum theory.

Recently, several authors have suggested that ion-ion correlation effects may induce a variation of the effective inverse decay length κ_{eff} with the concentration.[34,44,45] For a symmetric z:z electrolyte, Kjellander and Mitchell proposed that at sufficiently low concentrations the leading correction is[34]

$$\frac{\kappa_{\mathrm{eff}}^2}{\kappa_{\mathrm{D}}^2} = 1 + \frac{z^4}{6}\Lambda^2 \ln \Lambda + ... \tag{7}$$

where κ_{D} is the inverse Debye length given by eq. (2) and $\Lambda = \kappa_{\mathrm{D}} L_{\mathrm{B}}$ where $L_{\mathrm{B}} = \beta e^2 / (4\pi\varepsilon_0\varepsilon)$ denotes the Bjerrum length. The predictions of this formula are also shown in Fig. 4a. Indeed, at sufficiently low concentrations, this relation agrees with the experimental data quite well. However, the ion-pairing equilibrium discussed above leads to a different lower order correction, namely

$$\frac{\kappa_{\mathrm{eff}}^2}{\kappa_{\mathrm{D}}^2} = 1 + a\Lambda^2 + ... \tag{8}$$

where $a = -K / (8\pi z^2 N_A L_B^3)$. Similar corrections as given in eq. (8) were also proposed in the literature.[44,45] However, the latter approaches predict $a > 0$, which is in obvious disagreement with experiment. Note that the chemical equilibrium treatment does not lead to the correction given in eq. (7).

Let us now discuss the measured effective potentials, which were converted to the more commonly used diffuse layer potential ψ_{dl} . For a symmetric electrolyte, the respective relation reads[3]

$$\psi_{eff} = \frac{4}{z\beta e} \tanh\left(\frac{z\beta e \psi_{dl}}{4kT} \right)$$
(9)

Thus, by knowing the effective potential ψ_{eff} one can obtain the diffuse layer potential ψ_{dl} by inverting eq. (9). The diffuse layer potential reflects the electric potential at the origin of the diffuse layer. From force experiments in symmetric geometries, one can only extract the magnitude of the potential. The negative sign follows from the fact that silica is negatively charged through the dissociation of the surface silanol groups. This fact is also well established by independent methods, such as electrophoresis or streaming potential measurements.[46,47] The resulting diffuse layer potentials ψ_{dl} versus the total electrolyte concentration are shown in Fig. 5.
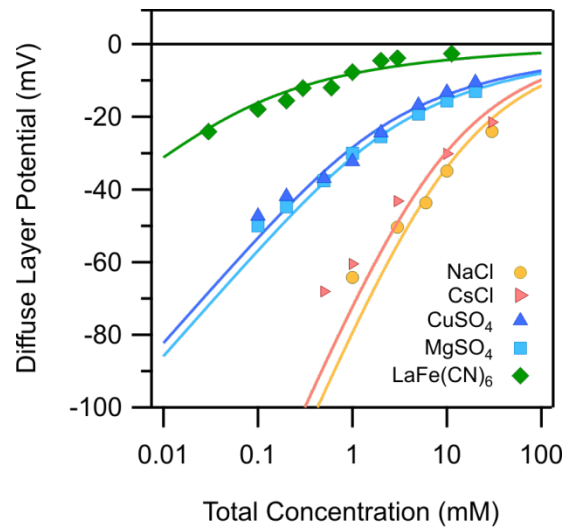

Figure 5. Diffuse layer potential extracted from the best fits with DLVO theory. The solid lines were calculated with eq. (10) by considering the finite degree of dissociation and constant charge densities given in Table 1.

One observes that the diffuse layer potential increases with increasing salt, which results from progressive screening. This trend can be quantified with the Grahame equation[3]

$$\sigma = (8\varepsilon_0\varepsilon N_A c_{ion} / \beta)^{1/2} \sinh\left(\frac{z\beta e\psi_{dl}}{2}\right) \qquad (10)$$

where σ is the surface charge density compensating the diffuse layer charge. In this expression, one must use the concentration of the free ions, which can be calculated by means of the mass action law and the fitted association constants given in Table 1. The resulting charge densities are also given in this table. Their increase with increasing valence can be explained as follows. Cations adsorb to the negatively charged water-silica interface, and the tendency for adsorption becomes stronger with increasing valence. The fact that these values are only determined by the type of the cation is confirmed by the fact that similar charge densities were found with force measurements between silica surfaces in $MgCl_2$ and $LaCl_3$ electrolytes.[25] Analogous trends of diffuse layer potentials with concentration and valence were also reported for positively and negatively charged latex particles in the presence of divalent, trivalent, and tetravalent counterions.[11,24] For ions of higher valence, the adsorption can be so important that a charge reversal is induced.[11,12,24] However, such a charge reversal is not observed here. Under present conditions, the bare charge density of the water-silica interface is about -30 mC/m^2, as can be estimated by potentiometric titrations.[46,48,49] The magnitude of the latter value is substantially larger than the magnitude of the surface charge densities obtained from the present force measurements (Table 1). This difference originates from the charge compensation by the adsorbed and condensed counter-ions close to the interface.

In the light of the present results, let us now address the question why the DH or PB theories remain applicable to systems containing multivalent ions, in spite of the fact that such mean-field approach is expected to fail.[17-19] Levine and coworkers have already answered this question by analyzing their Monte Carlo simulation results.[20] They have investigated the concentration profiles around charged macroions in electrolyte solutions containing multivalent ions interacting through Coulombic and hard-sphere forces only. These results were compared with PB theory. It was found that the PB theory fails seriously, if the electrolyte is assumed to be fully dissociated and if the bare surface charge is used. However, PB theory was found to work well, provided two modifications were introduced. First, the formation of ion pairs in solution was considered. Second, a renormalized surface charge density was introduced, which was chosen such that the large distance behavior of the concentration profiles was reproduced. The latter aspect was already pointed out earlier.[50] Since their model does not introduce any other interactions than electrostatic, ion pairing and charge renormalization are caused by ion-ion correlation effects.

Our approach to interpret our experimental data is not any different. By fitting an effective decay length, one considers the formation of ion pairs. The respective association constants are found to agree with independent reports. The fitted effective charge density is nothing but a renormalized charge density, which is chosen such that the long distance decay of the force profile is reproduced. These charge densities vary with the type of ions, which clearly indicates their effective character. Close to the interface, the ionic concentration is substantial, and ion-ion correlation effects will be important.

For these reasons, the DH or PB theories remain applicable, provided ion pairing and effective charge densities are taken into account. The formation of ion pairs in solution and differences between effective and bare charge densities are effects of ion-ion correlations. The only difference to the situation discussed by Levine and coworkers[20] is that they only consider Coulombic and hard-core interactions, while in the real situation, other types of interactions are equally present. The adsorption of ions to interfaces will be equally influenced by additional interactions, such as, dispersion and solvation forces. However, these interactions are short-ranged, and can also be included by choosing an appropriate association constant and an effective surface charge density.

The extent of ion pair formation due to Coulombic and hard-sphere interactions can be estimated by Bjerrum's theory.[20,51] He expressed the association constant introduced in eq. (6) as

$$K = 4\pi N_{A} \int_{r_{min}}^{r_{max}} e^{-\beta u(r)} r^2 \, dr \tag{11}$$

where $\beta u(r) = -z^2 L_B / r$ is the Coulomb interaction potential between the oppositely charged ions, r_{min} the distance of closest approach between the ion centers, and r_{max} the largest possible ionic distance within the ion-pair. While Bjerrum chose $r_{max} = z^2 L_B / 2$, the precise choice of this cut-off is unimportant, provided the ion-pairs are sufficiently stable. Exactly the same relation as given in eq. (11) can also be obtained from a statistical mechanical evaluation of the association constant in the classical approximation. Since ions are predominantly in direct contact, a situation that is referred to as contact ion pairs, the distance of closest approach r_{min} can be estimated from the sum of the ionic radii that are known from X-ray and neutron diffraction.[52,53] The relevant ionic radii are summarized in Table 2. With these distances, one can use Bjerrum's theory to calculate the association constants, and which are given in Table 1. Indeed, this theory predicts the right trend of the measured constants with valence, albeit the calculated constants are about factor of 2 larger than the experimental ones. This discrepancy could be due to the fact that not only contact ion pairs are present, but some of these pairs are separated by water molecules, leading to the formation of solvent-separated or solvent-shared ion pairs.[36] The distance between ions in these ion pairs is larger, which leads to a lower

binding constant. Moreover, ions are not just charged hard-spheres, and the assumed Coulomb law will become inaccurate close to contact, especially since the dielectric continuum picture is no longer appropriate and other forces are equally present, particularly, dispersion and solvation interactions. In spite of its simplicity, the predictions of the Bjerrum theory are most reasonable, and they confirm that Coulombic forces and, thus, ion-ion correlations are indeed important in the formation of these pairs.

Table 2. Ionic radii (in nm) of selected ions taken from Marcus.[52]

Cations		Anions	
Na^+	0.097	Cl^-	0.180
Cs^+	0.173	SO_4^{2-}	0.242
Mg^{2+}	0.070	$Fe(CN)_6^{3-}$	0.479^a
Cu^{2+}	0.072		
La^{3+}	0.114		

[a]Taken from Buchner et al.[53]

Conclusion

To conclude, we have presented results of direct force measurements between negatively charged micron-sized silica particles in solutions of symmetric, multivalent electrolytes, in particular, 2:2 and 3:3 electrolytes. We find that the measured force profiles can be quantitatively interpreted with DLVO theory, by taking van der Waals and double layer interactions into account. The latter can be accurately modeled with the DH theory, provided two effects are taken into account. First, the formation of ion pairs must be considered, as their presence increases the decay length of the electrostatic interactions substantially. Second, the diffuse layer potential of the interface must be properly adjusted, as this value is influenced by effects of ion adsorption. Both modifications are a consequence of ion-ion correlations, which become especially important in multivalent symmetric electrolytes.

Acknowledgement

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