Cationic Hofmeister Series of Wettability Alteration in Mica–Water–Alkane Systems

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Supporting Information

ABSTRACT: The specific interaction of ions with macromolecules and solid–liquid interfaces is of crucial importance to many processes in biochemistry, colloid science, and engineering, as first pointed out by Hofmeister in the context of (de)stabilization of protein solutions. Here, we use contact angle goniometry to demonstrate that the macroscopic contact angle of aqueous chloride salt solutions on mica immersed in ambient alkane increases from near-zero to values exceeding 10°, depending on the type and concentration of cations and pH. Our observations result in a series of increasing ability of cations to induce partial wetting in the order Na⁺, K⁺ < Li⁺ < Rb⁺ < Cs⁺ < Ca²⁺ < Mg²⁺ < Ba²⁺. Complementary atomic force microscopy measurements show that the transition to partial wetting is accompanied by cation adsorption to the mica–electrolyte interface, which leads to charge reversal in the case of divalent cations. In addition to electrostatics, hydration forces seem to play an important role, in particular for the monovalent cations.

INTRODUCTION

Competitive wetting of oil and water on solid surfaces plays an important role in many applications of colloid and interface science, including environmental two-phase flows, remediation of environmental contamination,1 Pickering emulsions, separation of emulsions,2 and the recovery of crude oil from geological reservoirs.3 Under wetting involves the interfacial tension.12,13 While surfactants are arguably the most important common additive to control interfacial tensions and wettability, almost any other solute does the same unless a fortuitous compensation of molecular interaction forces suppresses any interfacial activity. In the present work, we focus on the effect of dissolved salts on the wettability of oil–water–mineral systems, in particular, aqueous electrolytes on mica, an aluminosilicate mineral, in an ambient alkane. While the work is motivated by the possibility of enhancing the production of crude oil by reducing the salinity of the water that is injected into geological reservoirs in the course of the standard water flooding oil recovery process, our primary goal is to identify the microscopic mechanisms controlling wettability in this idealized model system.

For both oil–water and mica–water interfaces the adsorption of ions from the aqueous phase has been studied in great detail throughout several decades. Specific attention has been paid to air–water interfaces. They serve as a general representative of hydrophobic-water interfaces also including interfaces of water with inert oils such as alkanes. In the case of air–water interfaces, the interfacial tension increases with the increasing concentration for the majority of “inert” inorganic ions. The basic origin of this trend was explained by Onsager and Samaras,14 who realized that ions dissolved in a more polar medium, water, are repelled from an interface with a less polar medium, oil, by electrostatic image forces. Even for point charges, this leads to a depletion of ions from the interface and hence to an increase of the surface tension following Gibbs’ adsorption equation. Yet, dielectric polarization of the media involved is not the only force acting on the ions. The surface
tension is also affected by the polarizability of the ion itself and also by hydration effects, which are highly ion-specific. For many anions, their larger size leads to a stronger polarizability of the ion that overcompensates the effect of image charge forces, and thus leads to accumulation rather than depletion. In recent years, advanced experimental techniques such as X-ray spectroscopy have generated a wealth of detailed information about density profiles of various ions reflecting their specific affinity towards (or depletion from) the water surface.

Mineral-water interfaces have classically been studied using titration measurements, electrokinetic techniques such as streaming potential measurements, as well as various types of surface force measurements (surface forces apparatus (SFA), atomic force microscopy (AFM), colloidal probe-AFM),

Mica has been studied in particular detail because it can be prepared by cleaving to generate clean atomically smooth surfaces over macroscopic areas with well-defined tetrahedra of silicon oxide at the surface. Mica displays a rather strong intrinsic negative surface charge caused by isomorphic substitution of Si by Al atoms in the top layer of the crystal lattice. Cations are known to adsorb to these interfaces to compensate the negative charge density. Their affinity increases with the increasing ion size along the alkali series, as reported consistently in both electrokinetic and force measurements. Results for divalent cations are less consistent. Early SFA measurements came to the conclusion that the strong hydration of Ca$^{2+}$ and Mg$^{2+}$ suppress surface adsorption.

Later, however, charge reversal of mica–electrolyte interfaces was found for divalent cation concentrations of the order of 10$^{-2}$−20 mM implying rather strong adsorption. This is consistent with the stronger decreases of the ζ-potential as a function of divalent cations’ concentration compared to monovalent ones.

Many aspects of these measurements could be captured by surface speciation models that describe the adsorption of ions to specific sites on the surface in combination with a standard Poisson–Boltzmann description of the diffuse part of the electric double layer.

More recently, high-resolution AFM experiments as well as X-ray reflectivity measurements confirmed the overall increasing adhesion with the increasing alkali ion size as well as the stronger adhesion of divalent compared to monovalent cations. In addition, these experiments provided a lot more details regarding, e.g., competing inner shell and outer shell adsorption, the lateral position of adsorption sites, and in particular, the role of hydration water for the stabilization of adsorbed ions.

The increasing experimental insights have been complemented by theoretical developments attempting to account for the observations in terms of ion size, charge, and polarizability, invoking Coulombic and dispersion forces, and crucially, hydration. Yet, disentangling the various individual contributions often proved very challenging and perhaps even conceptually impossible. Molecular dynamics simulations seem to provide a way out of this stalemate. Rather than attempting to identify specific interaction mechanisms, simulation results can be used to extract interaction potentials of the mean force that include the full complexity of the ion-specific behavior at interfaces. Such calculations have confirmed many of the experimental trends. In particular, they consistently highlight the prominent role of hydration for ion-specific adsorption to hydrophilic solid substrates. In this context, classical concepts such as the like-likes-like principle have received renewed attention and support.

Given the importance of ion-specific effects for the adsorption of ions to the individual interfaces, it is plausible that they will also affect the wetting properties. Indeed, a number of studies analyzed the wettability of electrolytes on solid surfaces. Yet, these reports mainly focused on the pH dependence and evaluated the variation of the charge density and energy of the diffuse part of the electric double layer making use of Lippmann’s equation. Little attention was paid to specific ion effects. Recently, some of us reported very distinct variations of the wettability of aqueous solutions of CaCl$_2$ on mica in ambient decane as a function of concentration and pH.$^{24}$ While the solutions displayed immeasurably small contact angles at low salt concentrations and pH, finite contact angles were found for concentrations exceeding a few tens of millimolar, first at elevated pH and for higher concentrations beyond $\approx$100 mM across a wide pH range from 3 to 10. In contrast, NaCl and KCl solutions were found to display near-zero contact angles for all concentrations and pH values. Complementary streaming potential measurements showed that the transition from vanishing to finite contact angles for CaCl$_2$ coincided with the reversal of the charge of the mica–electrolyte interfaces. A numerical model based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and surface speciation provided an excellent description of the experimental observations for the limited set of salts investigated at that time. A subsequent more detailed modeling effort highlighted the role of charge regulation and short-range chemical forces for the exact value of the contact angles.

In the present article, we extend our previous work on salt and pH-dependent wettability measurements to a wider range of ions, namely for the chloride salts the alkali metals Li, Na, K, Rb, Cs, and for the earth alkaline metals Mg, Ca, and Ba. Except for Na$^+$ and K$^+$, all of these cations induce a transition to finite contact angles beyond the salt- and pH-dependent threshold concentrations. We identified an order of increasing capability of cations to induce partial wetting, which we will refer to as “Hofmeister series of wettability” for the present system. The macroscopic contact angle measurements are complemented by surface charge measurements using atomic force microscopy (AFM). While the AFM results confirm that the reduction of electrostatic repulsion due to cation adsorption indeed promotes partial wetting. Yet, in contrast to the suggestions of our previous experiments based on a limited set of cations, the present measurements also show that charge reversal is not a prerequisite for achieving finite contact angles.

The manuscript is organized as follows: in the subsequent section, we describe the experimental methods and procedures. In the Results and Discussion section, we report first the brine composition-dependent contact angle measurements followed by a description of a model of the wetting properties based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory including an unknown part due to short-range chemical (hydration) forces. Subsequently, we describe our atomic force microscopy (AFM) measurements and the resulting surface charge densities.

**EXPERIMENTAL SECTION**

**Materials.** Anhydrous alkanes (decane, heptane, hexadecane: >99%) were purchased from Sigma-Aldrich. Prior to the experiments, they were purified by passing them five times through a column of alumina powder (Al$_2$O$_3$, Sigma-Aldrich, Puriss grade >98%) to
Figure 1. Snapshots of sessile brine drops on mica in ambient decane (concentration: 1 M; pH 9). NaCl and KCl drops assume near-zero, yet finite contact angles (<1°), as confirmed by visualizing the contact line in top view (ellipsometric imaging). We observe the finite contact angle not only for the heavier Rb+ and Cs+ ions but also for Li+. Consistently higher contact angles are found for divalent cations. Blue lines: circle fitting. 

Contact Angle Measurements. Figure 1 shows side view images of a series of drops for all types of salts investigated. For each of these drops, the concentration of the respective salt was set to 1 M and the pH was adjusted to 9. These images summarize the essence of our observation. There is a clear trend of the contact angle increasing systematically from (in side view images) immeasurably small values for NaCl and KCl solutions to values of ≈15° in the case of BaCl₂. In the absence of any added salt, the contact angle is equally immeasurably small as in the case of NaCl and KCl. Figure 1, thus, provides an order of increasing capability of the cations to increase the water contact angle. We denote this order as the cationic Hofmeister series of wettability.

\[
\text{Na}^+ < K^+ < Li^+ < Rb^+ < Cs^+ < Ca^{2+} < Mg^{2+} < Ba^{2+} \\
\]
To provide a more complete and quantitative account of our basic observation, we conducted the same type of contact angle measurements for the full concentration range from 1 mM to 1 M for pH 3 to 9. The results of these experiments are summarized in Figure 2a–c for the alkali series of monovalent cations and in Figure 2d–f for the divalent earth alkaline cations. For Na\(^+\) and K\(^+\) ions, the contact angle is immeasurably small for all concentrations and pH values, as reported previously.\(^{54}\) For all other salts, a clear trend towards increasing the contact angle with increasing salt concentration and pH is observed. For all these salts, there is a threshold concentration beyond which the water contact angle is finite. The threshold concentration decreases with the increasing pH. The relative order of the different cations that is shown in Figure 1 was found to persist for all other concentrations and pH values, supporting the robustness of this Hofmeister series of wettability. In summary, there are three key observations:

1. for all salts except for NaCl and KCl, a finite macroscopic contact angle is observed beyond some threshold concentration.
2. whenever a finite contact angle can be detected, it increases upon increasing pH and/or the salt concentration.
3. there are strong ion-specific effects as summarized by the Hofmeister series of wettability.

A few additional remarks are in order: first of all, the divalent cations systematically display a stronger dewetting capability than the monovalent ones, i.e., the threshold concentrations for observing finite contact angles are lower and the contact angles at identical concentrations and pHs are higher. Secondly, within the series of alkali ions, the order of cations in eq 2 essentially corresponds to the classical “direct” Hofmeister series of protein precipitation,\(^{39}\) with the exception of Li\(^+\) compared to the position of Na\(^+\) and K\(^+\). The relative order of the divalent cations with respect to the monovalents, however, does not follow the expectations of the classical Hofmeister series, yet consistent with their stronger adsorption to the mica surface (see below). The reversal of the order of Mg\(^2+\) with respect to Ca\(^2+\) may have similar reasons as in the positioning of Li\(^+\) wrt Na\(^+\) and K\(^+\). (Figure SI6 in the Supporting Information shows the detailed comparison between Mg\(^2+\) and Ca\(^2+\) for a series of additional intermediate...
Macropscopic Force Balance and Disjoining Pressure.

To understand our key observations, we need to relate the macroscopic contact angle to the microscopic physico-chemical properties of the various interfaces involved in the wetting process. To this end, we will regard the observed contact angles as equilibrium values. Doing so, we know from Young’s equation, eq 1, that the contact angle is determined by the balance of the three interfacial tension forces at the contact line. It is obvious that tensions of the oil–water and the solid–water interface can (and indeed do) change upon changing the composition of the brine, whereas, at first glance, one might think that the solid–oil interfacial tension might not depend on the brine composition. Yet, it does: Young’s force balance applies on the macroscopic scale, i.e., outside the range of molecular interaction forces at the interface, as indicated by the dotted control volume in Figure 3. Systems with rather small contact angles such as the present one usually fall into the regime of “pseudopartial wetting”. In this regime, the macroscopic drop is accompanied by a microscopic equilibrium film of the droplet phase that is interspersed between the solid and the ambient medium next to the drop, as sketched in Figure 3a. The thickness $h_0$ of this equilibrium film typically falls in the range between zero and at most a few nanometers. It is governed by the balance of molecular interaction forces, as given by the minimum of the effective interface potential $\Phi(h)$ (blue curves in Figure 3b, which describes the excess tension of the thin film caused by the proximity of the two interfaces). In our earlier work, we showed using imaging ellipsometry that such an equilibrium film is indeed present next to droplets of NaCl and CaCl₂ solutions. It was found to extend for at least 1 mm next to the macroscopic drop and—as qualitatively expected—it displayed a thickness ranging from $\approx 0.5$ to 10 nm, depending on the type of cation and the salt concentration. From a macroscopic perspective, the existence of this film implies that the value of $\gamma_{sw}$ is in fact the equilibrium tension of the composite solid–oil interface including the microscopic water film. In the language of the effective interface potential, this means that $\gamma_{sw}$ is given by the sum of $\gamma$, $\gamma_{sw}$ and the excess tension of the equilibrium film, i.e., $\Phi(h_0)$, as illustrated in Figure 3a

$$\gamma_{sw} = \gamma + \gamma_{sw} + \Phi(h_0)$$

(3)

This thin water film is in diffusive equilibrium with the bulk aqueous drop. As a consequence, $\gamma_{sw}$ is also expected to depend on the composition of the brine. To understand the observed increase of the contact angle increasing salt concentrations and pH, we therefore need to consider the variations of all three interfacial tensions.

According to the Gibbs law, the variation of the tension $\gamma_i$ of an arbitrary interface $i$ as a function of the fluid composition is determined by the surface excess $\Gamma$ with respect to some reference state following $d\gamma_i = -\Gamma d\mu_i$, where $\mu = kT \ln(c/c_0)$ is the chemical potential of the dissolved species with bulk concentration $c$. ($c_0$ is the bulk reference concentration.) Spontaneous adsorption of solute to an interface, i.e., a positive surface excess $\Gamma$, thus implies a reduction of $\gamma_i$. Vice versa, a negative surface excess implies a spontaneous increase of $\gamma_i$. As mentioned in the introduction, hydrophobic-water interfaces including oil—water and air—water interfaces display a negative surface excess for the majority of “simple” inorganic ions such as the ones studied here because image charge forces repel electrostatic charges in the highly polarizable aqueous phase from the interface with the less polarizable ambient oil. As explained above, for hydrophobic-water interfaces the effect is dominated by anions. For air—water interfaces $d\gamma_i/dc \approx 1.5$ mJ/m² for all chloride salts of alkali metals, with a slightly
lower coefficient for Cs+ because of the higher polarizability of this large ion. MgCl2 and CaCl2 dependence is approximately twice as strong.  

We performed a few test experiments with selected salts to reproduce these trends (see Supporting Information Figure S15). Indeed, we find positive values of dy/dc with absolute values approximately half the ones mentioned above for water–air interfaces. This is consistent with the higher dielectric constant of decane compared to air. Qualitatively, an increase of γ with the increasing salt concentration translates into an increasing contact angle. Yet, while the variation of γ certainly contributes to the absolute values of the contact angles observed, it is unlikely that the oil–water interface is the primary driver for the observed phenomena for the following reasons. First of all, if we insert eq 3 into Young’s equation, we can rewrite the force balance as

\[ \gamma(\cos \theta - 1) = \Phi(h_0) \]  

(4)

In this equation, all quantities depend on the salt concentration and pH. The variation of the left-hand side with fluid composition is given by Δ(γ(\cos \theta - 1)) = Δγ × (\cos \theta - 1) + γ × Δcos θ. Since θ varies approximately between 0 and 10° in our experiments and γ between 50 and 52 mJ/m², it is clear that the variation of γ is less important than the variation of cos θ. Moreover, as mentioned above, ion specificity at hydrophobic-water interfaces is generally dominated by anions and not by cations. The strong cation effect in our experiments can certainly not be caused by the oil–water interface. This statement is also supported by the comparison of the contact angle data for CaCl2 and Ca(NO3)2 solutions: dy/dc for CaCl2 is 60% higher than for Ca(NO3)2 because of the larger surface affinity of the nitrate anion compared to chloride.  

Nevertheless, the contact angle data for the two different salts agree with each other within error (see Figure S17).

Similarly, the solid–water interface cannot be at the origin of the phenomenon. As discussed in the introduction, it is well-established that cations spontaneously adsorb to mica–water interfaces in an ion-specific manner with adsorption energies ranging between a few and several tens of kJ/mol. Hence, γ_w in Young’s equation is expected to decrease with increasing salt concentration. This would lead to a decrease in θ with the increasing salt concentration, in contrast to the experimental findings. If we phrase the force balance equation in the form of eq 4, γ_w formally even completely drops out of the equation. Hence, we conclude that the observed increase in θ with the increasing salt concentration and pH must be driven primarily by the variation of the tension γ_w of the composite solid–oil interface, or, according to eq 4, by Φ(h_0). (Note that the density of adsorbed ions at the mica surface will be different in the thin equilbrium film compared to the macroscopic drop.) This difference, however, is included in Φ(h_0), and thus does not change the cancellation of γ_w in the derivation of eq 4.

The effective interface potential is determined by the molecular interaction forces acting across the thin water film next to the drop. In classical continuum wetting theory, Φ is decomposed into different contributions arising from van der Waals interaction Φ_{vdW}, electrostatic interactions Φ_el and short-range chemical forces Φ_{chem}, such as hydration forces

\[ \Phi(h) = \Phi_{vdW}(h) + \Phi_{el}(h) + \Phi_{chem}(h) \]  

(5)

The functional form of the last term is generally not very well-known because it depends on atomic scale details of the system. Frequently, it is modeled by an empirical exponentially decaying function with a decay length of the order of 1 nm.  

This functional form can be derived from a Landau-type free energy functional involving an order parameter of the water phase, as first proposed by Marčelja and Radic. DLVO theory provides expressions for the first two terms. Namely, the van der Waals contribution is given by

\[ \Phi_{vdW} = A/12\pi h^2 \]  

(6)

where A = −0.4 × 10⁻²¹ J is the Hamaker constant of the decane–water–mica system. (The exact value varies by 10–20% depending on the salt species and concentration.) The negative sign of the Hamaker constant indicates that the interfaces attract each other and that van der Waals interaction favors partial wetting.

The most interesting term for our present discussion is the electrostatic interaction Φ_{el}(h). It requires a solution of the Poisson–Boltzmann equation for the distribution of ions and electrostatic potential within the thin film. Frequently, this is done using either constant (i.e., h-independent) charge or constant potential boundary conditions. For the present situation, however, where h₀ becomes comparable to or smaller than the Debye screening length, this is not justified and the regulation of the interfacial charge due to adsorption (or desorption) of ions needs to be taken into account. The resulting nonlinear charge regulation boundary conditions leads to a self-consistent mathematical problem that is most easily addressed numerically. To understand the physical principle leading to the observed wetting transition, it is sufficient to consider the simplified linearized version of Φ_{el}(h). Here, we linearize both the Poisson–Boltzmann equation, which then reduces to the Debye–Hückel equation and the charge regulation boundary conditions. The latter leads to the linearized “constant regulation” approximation.  

\[ \Phi_{el}(h) = k_B T \Psi_i \Psi_{w,i} e^{-k_h - |\Delta \Psi_i \Psi_{w,i} + \Delta \Psi_w \Psi_{w,i}| e^{-2k_h}} \]  

(7)

Here, Ψ_i, with i = sw, ow are the (diffuse layer) potentials of the mica–water and the oil–water interface for h → ∞ and Δ is the corresponding regulation parameters of each interface. These parameters interpolate between a constant charge (Δ = −1) and constant potential (Δ = 1) behavior. Analysis of eq 7 shows that there are four generic wetting scenarios, namely complete wetting, pseudopartial wetting, true partial wetting (h₀ = 0), and a metastable wetting configuration in which a thin film can be metastable despite the existence of a true partial wetting state of lower energy depending on the values of the Δ_i’s and Ψ_i’s. For the present system, both regulation parameters are negative and the diffuse layer potentials in the absence of adsorbing ions are negative, too. In this case, Φ_{el} is positive and monotonically increasing with decreasing h, as illustrated by the red curve in Figure 3b. This corresponds to a situation of complete wetting. For NaCl and KCl solutions, this situation prevails for all salt concentrations and pH values. In contrast, for CaCl₂, the sign of the charge (and hence the potential) of the mica–water interface reverses beyond a certain pH-dependent threshold concentration, as described in ref 20. Under these conditions, the interface potential develops a local minimum with a finite equilibrium thickness h₀, as illustrated by the blue curves in Figure 2b. Consequently, the system undergoes a transition to partial
wetting with a contact angle determined by the value of $\Phi(h_0)$. On the basis of this scenario of ion adsorption-induced charge reversal, we could explain the transition from complete to partial wetting in our previous study that was limited to Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) ions.\(^{54}\)

**AFM Investigation of Ion Adsorption.** To test whether the mechanism described above also explains the alteration of the contact angles for all the salts in our present Hofmeister series of wettability, we determined the surface charge of mica–electrolyte interfaces for several types of salts using AFM. Solutions of LiCl, NaCl, CsCl, Mg\(^{2+}\), and Ca\(^{2+}\) were analyzed at a fixed pH of 6 for salt concentrations from 1 to 100 mM. (For higher concentrations, efficient screening leads to very small forces and unreliable measurements, similar to streaming potential measurements.) Figure 4 shows the typical force curves for NaCl, CsCl, and MgCl\(_2\). While the total forces (left column) remain repulsive for NaCl for all salt concentrations, a transition to attractive forces was observed for both CsCl and MgCl\(_2\) for elevated concentrations at short distances. To reveal the contribution of the electrostatic forces, we first subtract the van der Waals contribution to the force following the procedures described in ref 56. Subsequently, we focus on the range of tip–sample separations of $\approx$2 nm and larger, for which short-range hydration forces are negligible. Doing so, we found that the electrostatic force is obviously repulsive for all concentrations of NaCl. Yet, also for CsCl a small repulsive force prevails all the way up to the highest concentration investigated (Figure 4, right column). Only in the case of MgCl\(_2\), a clear reversal towards attractive electrostatic forces is observed at short distances beyond a threshold concentration of $\approx$10–30 mM. The latter implies a reversal of the surface charge consistent with our earlier streaming potential measurements.\(^{54}\) A similar behavior was found for CaCl\(_2\) solutions. In contrast, LiCl solutions were found to display very similar behavior as NaCl, despite the fact that they do induce partial wetting at higher concentrations.

Using the procedures described in refs 56, 57, we converted these forces into surface charge densities, Figure 5. As explained in the Experimental section, the charge density probed by such a colloidal scale AFM spectroscopy measurement is the negative of the charge density of the diffuse part of the electric double layer, i.e., the sum of the intrinsic charge density of the mica surface and any counter ion (including protons) adsorbed in the Stern layer, extrapolated to infinite tip–sample separation. For the monovalent ions Li\(^+\), Na\(^+\), and Cs\(^+\), this surface charge is negative for all concentrations investigated. (Note, that the diffuse layer charge probed by the AFM is only a fraction of this intrinsic charge density of mica ($\approx$2 e/nm\(^2\)).) As anticipated based on the force curves, the magnitude of the surface charge decreases with increasing salt concentration for all monovalent cations. While it remains clearly negative for Na\(^+\) and Li\(^+\), it approaches 0 within the error for Cs\(^+\) for concentrations approaching 100 mM. In contrast, for the divalent cations, a clear reversal of the surface
charge is observed for concentrations of 10−20 mM, consistent with various reports in the literature.20,63 The larger error bars at high salt concentrations arise from the very small forces under these conditions due to efficient screening within the fitting range of 1.5−15 nm.

The AFM measurements confirm the reversal of the surface charge for Ca2+ and Mg2+ that was reported earlier. For these systems, charge reversal indeed occurs in the same concentration range as the finite contact angles. This is consistent with our earlier claim that the wetting transition in these systems is caused by ion adsorption-induced charge reversal. For Li+ and Cs+, however, we do not find charge reversal, despite the occurrence of finite contact angles. Unfortunately, the evidence is not completely conclusive given the increasing uncertainties of the AFM method for increasing concentrations. For CsCl, the measurement suggests that the surface charge vanishes at the highest concentrations. Yet, the error bar includes the possibility of a small positive surface charge. For LiCl, the surface charge remains almost constant at a negative value around -0.1 e/nm² up to c = 100 mM. Yet, the error bars at the highest concentration become very large—and the finite contact angles are only observed for even higher concentrations. Nevertheless, considering the AFM results as well as other classical reports in the literature, it seems highly unlikely that Li+ ions and (to a somewhat lesser extent) Cs+ ions induce charge reversal at mica−water interfaces at pH 6. Hence, it is also unlikely that our previous assignment of charge reversal as a driving force for the transition towards finite contact angles in the presence of divalent cations also holds for the monovalent ones. Instead, we would like to argue that the last term in eq 5, the contribution of hydration and short-range chemical effects, might play a decisive role. As already pointed out in refs 54, 55, this term plays an important role in the calculation of the exact location of the minimum of $\Phi(h)$ including the equilibrium contact angle. From our earlier ellipsometry measurements, we know that the equilibrium thickness $h_0$ of the wetting film frequently falls in the range below 2 nm for conditions of partial wetting. This is precisely the range for which hydration effects are important.7,15,46,63 Hydration effects arise from the complex interaction of water molecules with the mica surface and the ambient oil that are both modified by the presence of potentially adsorbed ions. In the first place, the presence of the interfaces gives rise to positional ordering of the water molecules. For atomically flat hydrophilic surfaces such as mica, this gives rise to a few discrete layers of water.64 For hydrophobic interfaces such as the water−oil interface, the water density is believed to decrease gradually within a few angstroms of the surface. In addition to the positional ordering, the hydrogen bonding network of water is affected by the (in)ability of forming H-bonds with the surface. This effect in combination with local electric fields at the interface gives rise to an additional orientational ordering in the interfacial water. Both types of order typically have a range of not more than a few molecular diameters, i.e., typically 1−2 nm, precisely the expected thickness of the wetting film next to the macroscopic drops. The contribution of hydration forces to the interface potential can be qualitatively understood in terms of the mean field model by Marcelja and Radic.64 According to this model, the mica−water and the water−oil interface interact via the order that they induce in the thin water film. This order is described by an order parameter $\eta$, $\eta$ vanishes in the bulk, but assumes finite values at the interfaces in response to local surface fields that—say—orient the water molecules. For the present system, the hydrophilic mica surface and the hydrophobic oil−water interface will impose rather different boundary conditions and order in the thin film. Microscopically, these boundary conditions arise for instance from the local electric fields at the interface that tend to orient the water molecules. The adsorption of cations to hydrophilic surfaces such as mica has a strong effect on the structure of the interfacial water, as shown in various recent X-ray reflectivity experiments27 and numerical simulations.59,67 Our proposed scenario to explain the observed wetting transition implies that such ion adsorption-induced variations of the water structure give rise to an increased attractive interaction between the mica surface and the oil−water interface. In the case of Rb+ and Ca2+ ions, which are known to be poorly hydrated,68 interfacial adsorption would effectively “hydrophobize” the mica surface and thereby destabilize the thin water layer. For the case of Li+, however, this explanation would not apply. A detailed and complete understanding of all observations can therefore not be provided. Possibly, the difficulties to explain the phenomenon also illustrate the intrinsic deficiencies of extending continuum physics models all the way down to molecular scales where very specific chemical interactions are at play.

## CONCLUSIONS

We investigated the dependence of the wettability of water on mica in ambient alkanes on the presence of dissolved chloride salts of a variety of alkali and earth alkaline cations. We observed a transition from near-zero to finite values of the contact angle (up to $\sim 15^\circ$). The ability of cations to induce partial wetting increases from Na+, K+ to Li+, Rb+, Cs+ and then to divalent cations (Ca2+, Mg2+, Ba2+). We denote this ranking as cationic Hofmeister series of wettability alteration—notwithstanding the fact that the order of the ions differs from the conventional Hofmeister series related to the precipitation of cations. While the strong effect of the divalent cations stems from their strong adsorption to the mica surface and the resulting charge reversal of the interface, the occurrence of partial wetting in the case of the monovalent cations is tentatively attributed to the alteration of the hydration structure of the mica−electrolyte interface. We emphasize that the present cationic series applies to the specific mica/
water/alkane system. Nevertheless, given the fact that the negative surface charge of oil–water interfaces is rather common and robust, we expect that the mechanism of an ion adsorption-induced charge reversal should apply to a wider class of mineral surfaces. Elucidating that the role of hydration forces is a more complex challenge that will require more targeted experimental and numerical approaches than the measurements presented here.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b03297.

Precision in contact angle goniometry measurements; interfacial tension of representative monovalent and divalent salts at various concentrations; CaCl₂ and MgCl₂ contact angles on mica at all pH values and various concentrations; comparison of anions (Cl⁻ and NO₃⁻) as the contributing factor in contact angles; hydrated ion radii of the cations used in our experiments (PDF)

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Notes
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