



Investigation of Hofmeister effects in ultra-dilute solutions at the water/silica interface using electrokinetic current generation



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ABSTRACT

Microjet-based electrokinetic streaming current experiments were used to track changes at the surface of fused silica in the presence of ultra-dilute (≤ 100 nM) acid and base solutions. These concentrations allow isolated study of the individual ions with minimal counter-ion interference. The observed changes in the streaming current upon exposure to these solutions demonstrate the first observed Hofmeister relationships at sub-micromolar concentrations, with a direct series observed relating to the absorption of cations and anions. Behavior of the divalent cations and chloride differ from the rest of the ions studied, which is attributed to multiple mechanisms of chemical interaction with the surface beyond adsorption. The presence of these Hofmeister trends at such dilute concentrations supports other work indicating changes in interfacial properties for mobile vs. stagnant liquid/solid interfaces.

1. Introduction

The nature of interaction of ions at interfaces has been a long-standing and difficult problem to fully unravel. There has been much work done to understand ion adsorption at both a fundamental level [1–6] and towards specific applications or situations [7–9]. Underlying many of these specific ion interactions is an ordering first discovered in 1886 by Franz Hofmeister [10], and has since been named the Hofmeister series. Hofmeister determined that the identity of ions in solution affected the ability of proteins to precipitate. Over the years, many other phenomena have been linked to similar patterns in ion activities. A phenomenon with a direct ordering demonstrates an increasing effect as ions are changed from traditional chaotropes to cosmotropes, while an indirect or reverse ordering displays the opposite trend. For example, specific adsorption that follows a Direct Series would have stronger adsorption of lithium than potassium. Select ions have been highlighted in Fig. 1 to showcase these orderings [11].

Within the last decade, there have been numerous articles that examine the connection between the Hofmeister series and the interfacial activity of ions [4,12–20]. The growing consensus is that these effects arise from surface interactions [12], however the complete mechanisms are not fully understood [20]. To this end, computer modeling and calculations have provided useful tools in trying to uncover the full details of these surface interactions [4,17–23]. Experimental efforts to study the interfacial nature of the Hofmeister ordering have included atomic force microscopy [17–18], SFG spectroscopy [13,23–24],

surface tension [15], electrochemical methods [25–26], and many others. Of particular interest are low-concentration examples of Hofmeister effects; while most Hofmeister effects are observed at millimolar and greater concentrations, there are multiple reports of the effects being observed at micromolar concentrations [16,27–30]. These effects at such low concentrations are not predicted by current Hofmeister theory, and thus need further data to elucidate the full range of Hofmeister effects.

Part of the difficulty when studying the connection between the Hofmeister series and chemical interfaces is the inherent difficulty in studying interfaces because the method of investigation must be sensitive and selective to the small number of interfacial particles. Electrokinetic streaming current is one such phenomenon [31,32], arising from the physical movement of diffuse ionic charges away from a charged surface. In an ionic solution, ions can become adsorbed to the surface in the Stern layer, altering the profile of the diffuse charge and changing the amount of streaming current generated. When confined to a narrow, cylindrical orifice such as a fused silica capillary, the electrokinetic current is a function of the all of the charges at the surface (native and adsorbed), the nature of the liquid flow (laminar versus turbulent flow), and the ionic strength of the solution; under laminar flow conditions through a long capillary, the current is described by Eq. (1) [31]. The I represents the streaming current, ϵ the permittivity of water, v the area-averaged velocity, and ζ the zeta-potential.

$$I = -8\pi\epsilon v\zeta \quad (1)$$

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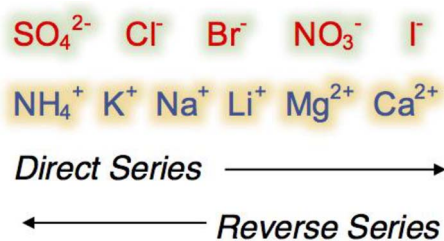


Fig. 1. Hofmeister ordering for select ions in this work, indicating the direction of the direct and reverse series.

Under equivalent ionic strength conditions, the contributions of the screening to the observed electrokinetic current are equivalent. Because this study spans several different ionic strengths, Guoy's Eq. (2) can be used to translate an observed zeta potential into a surface charge density. Here ρ^s represents the total charge of the surface, C_i the concentration of the i th ion in number/m³, and e_i the unit charge of the ion. This sum is taken over all of the ions present in solution, including H₃O⁺, OH⁻, and other salt ions present in the solution. The calculation of C_i values can be achieved by determining the concentration of salt-related ions in the solution and then calculating the appropriate hydronium and hydroxide concentrations from the autoionization constant of water.

$$(\rho^s)^2 = 2k_b T \epsilon \sum C_i \left[\exp\left(-\frac{e_i \xi}{k_b T}\right) - 1 \right] \quad (2)$$

Studies of the surface of glass under aqueous conditions go back to the 1940s with the streaming potential measurements of Rutgers and de Smet [33,34] as well as Overbeek's summary in Kruyt's *Colloid Science* [35]. The original work of Rutgers in particular examined many different ion combinations down to concentrations of 1 μ M, with surface conduction becoming a larger issue at the lower concentrations. These showed notable changes around those concentrations for divalent cations but only acid/base-related changes for monovalent cations or anions. Flores et al. [13,36] used Vibrational Sum-Frequency Spectroscopy, or VSFS, to study silica and titania surfaces in contact with salt solutions of 100 μ M and greater, where they found a direct Hofmeister ordering in the exclusion of anions from the silica surface. They observed a direct ordering for cations under basic conditions with a notable exception of lithium, which they attribute to the strong hydration sphere making the lithium act as a smaller charge density ion than the bare lithium alone. When tested at near-neutral pH, the effects go below their capabilities of detection with the VSFS method, indicating the important role of the negatively charged surface. Further work from the same research group by Azam and coworkers [37,38] using SHG at 0.1 + M concentration found cooperative differentiation of specific adsorption for alkali chloride salt solutions, but not the corresponding iodide solutions, which they interpreted as strong influence of specific anion effects. They found a direct Hofmeister relationship for the specific adsorption of anions, with more iodide present at the silica surface than chloride. Further work headed by DeWalt-Kerian [39] with 0.5 M alkali chlorides saw a pH-dependence to the adsorption of monovalent cations to the silica surface, switching from direct to reverse as pH decreased below pH 10. The work of Salis [30] details the effects upon glass in the form of a pH electrode at concentrations as low as 100 μ M, with an anionic Hofmeister ordering that changes when sodium and potassium cations are present in solution. Studies continue to suggest interaction and cooperativity between cation and anion at the surface, which underscores the value of studying these ions under as much isolation as possible.

Previous electrokinetic work [9] has established the use of streaming current as a measure of ionic interactions with fused silica surfaces at sub-micromolar concentrations. The use of solutions with solute ion concentrations of 100 nM or less help minimize the effect of

diffuse charge on the zeta potential and allow more direct study of the charge at the aqueous/silica interface. At these concentrations, a large percentage of the ionic strength arises from the background auto-dissociation of water present in any aqueous solution. Changes in streaming current have a relationship with the charges at the capillary surface under these conditions, illustrating the changes as a result of the different concentrations of solute ions present. The use of a microjet apparatus in streaming current experiments also limits the effect of back-conduction. Once the water carrying the diffuse charge has left the capillary, the water breaks into a stream of individual, unconnected droplets, trapping the diffuse charge until it can be measured at the target electrode.

The aim of the present study is to examine the effects of specific cations and anions upon the charge of the silica capillaries. The cations and anions can be studied individually by the use of simple acids and bases at the ultra-dilute concentrations (nM). Cooperative effects between cations and anions such as potassium and chloride have been observed [9,30,37–39], complicating the interpretation and understanding of the underlying Hofmeister relationships. This ultra-dilute acid/base method allows the study of the ions without a corresponding counter-ion that is not naturally present in water (hydronium or hydroxide). With an ultra-dilute acid or base solution, the concentrations of H⁺ and OH⁻ ions added via the ionic salt are similar or smaller than when compared to the H⁺ and OH⁻ ions provided from the auto-dissociation of water. The effects observed are thus more easily attributed to individual ions without possible cooperative effects from other added ions.

2. Materials and methods

2.1. Materials

The water in all experiments is obtained from a Rios5/Millipore water filtration system, with water resistivity > 18 M Ω \times cm and TOC content < 5 ppb. Stock solutions of 0.1 M were made from potassium hydroxide (Sigma, \geq 99.97% trace metals base), sodium hydroxide (Sigma, ACS reagent, \geq 97%), ammonium hydroxide (Sigma, 28% NH₃ in water), lithium hydroxide (Sigma, \geq 98%), hydrochloric acid (Alfa-Aesar, 0.5 N standardized), hydrobromic acid (Sigma, 48 wt% in water), hydroiodic acid (Sigma, 57 wt% in water, no stabilizer), nitric acid (Sigma, 70% redistilled), and sulfuric acid (Sigma, 95–98%). Saturated solutions of calcium hydroxide (Sigma, > 95%) and magnesium hydroxide (Sigma, 95%) were used instead of normal stock solutions due to limited solubility. Recrystallization of the calcium hydroxide showed no statistical difference in the electrokinetic data collected. Serial dilutions were used to create solutions with final concentrations ranging from 10 pM to 100 nM, in accordance with the previous determination of lower-limit ionic concentrations from Millipore-filtered water [9]. Carbonate ions derived from atmospheric carbon dioxide would interfere with these studies; all solutions were vacuum degassed after preparation and used immediately to prevent interference from carbonate. Glassware was regularly cleaned with Nochromix/Sulfuric acid and thoroughly rinsed with the purified water described above.

2.2. Streaming current measurements

The electrokinetic apparatus used is similar to those described in earlier publications [9,40], and is diagrammed in Fig. 2. The solution flows through a Systec Multichannel Vacuum Degasser into a Knauer Smartline 100 Pump, which pushes the solution through PEEK tubing into a fused silica capillary with a 30 μ m inner diameter. The flow rate used in all experiments is 1.000 mL/min, maintaining conditions of laminar flow. The water is ejected through the silica capillary and impacts a copper electrode. Commercial fused silica capillaries (Poly-micro Technologies) are used as the jet orifice due to well-studied and consistent surface properties [41–42]. The current is measured through

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