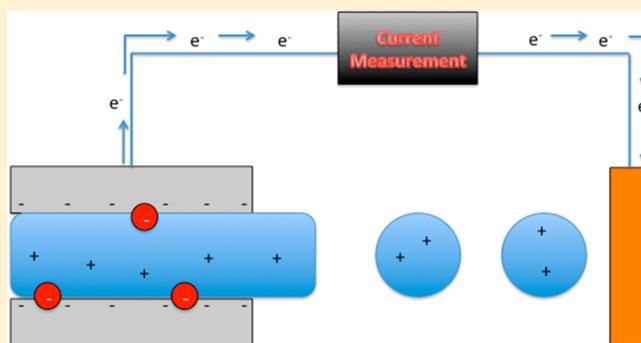


Exploring Solid/Aqueous Interfaces with Ultradilute Electrokinetic Analysis of Liquid Microjets

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ABSTRACT: We describe a novel method that exploits electrokinetic streaming current measurements for the study of ion–interface affinity. Through the use of liquid microjets and ultradilute solutions (<1 μM), we are able to overcome inherent difficulties in electrokinetic surface measurements engendered by changing double-layer thicknesses. Varying bulk KCl concentrations produce statistically significant changes in streaming current down at picomolar concentrations. Because the attending ion concentrations are below that from water autoionization, these data are compared with those from ultradilute HCl and KOH solutions assuming that the K⁺ and Cl[−] introduce no new counterions. This permits comparison of the individual effects of K⁺ and Cl[−] on the interface, evidencing a cooperative effect between these ions at silica surfaces. Altogether, these results establish the effectiveness of this experimental approach in revealing new ion–surface phenomena and indicate its promise for the general study of aqueous interfaces.



INTRODUCTION

The relative interfacial affinity of solvated ions is a phenomenon central to several unresolved issues in physics and chemistry. For example, controversy exists concerning the charge of the air–water^{1–3} and oil–water^{4–7} interfaces. In the former case, there are conflicting accounts as to whether the interface preferentially attracts hydronium or hydroxide ion, while disagreement exists as to the nature of charge at the oil–water interface. Additionally, the origin of the famous Hofmeister effects—encompassing some 40 different phenomena—remain unexplained, but are likely to be the result of ion/interface interactions.^{8–11}

Methods ranging in complexity from potentiometric titrations¹² to atomic force microscopy and nonlinear laser spectroscopy^{13,14} have been pursued with the goal of elucidating ion-specific interfacial phenomena. The experimental difficulty lies in both the low absolute number of surface sites available to probe as well as the very high bulk to surface background. Accordingly, the development of methods that entail both the high selectivity for signal arising from the interface and the high sensitivity required to detect small changes in these surface properties is at the forefront of interface science.

Electrokinetic (EK) current generation^{15–17} is one such method that fulfills these requirements. The basis of EK phenomena is the movement of diffuse charge in the electrical double layer formed by the presence of a charged surface in an electrolyte solution. The current results from the overlap between the spatial charge distribution and liquid flow profile,

shown schematically in Figure 1. This current is a direct function of the surface charge, flow profile, and the nature of the ions in solution (e.g., surface affinity, mobility); under laminar flow conditions through a long capillary, the current is described by eq 1¹⁸

$$I = -8\pi\epsilon_0 K\nu\zeta \quad (1)$$

Here, I represents the streaming current, ϵ_0 is the permittivity of free space, K is the dielectric constant, ν is the area-averaged flow velocity, and ζ the zeta-potential. The zeta potential is not exactly equal to the surface potential, because it includes contributions from ions that are not moved out of the diffuse double layer by the fluid flow. However, since the charge profile of the double-layer is dictated by the surface charge, this does imply that the ζ -potential is proportional to the surface charge, and can be directly compared between solutions possessing the same electric double layer thickness.

Despite providing an intrinsically interface-selective probe, previous EK experiments have features that complicate their use in studying the surface affinity of ions, the root of which is the dependence of the EK current on ionic strength.¹⁵ In a direct sense, the ionic strength dictates the thickness of the electrical double-layer, and thus the amount of charge that is moved via overlap with the fluid flow. To compare different EK potentials or currents, explicit consideration of the ionic

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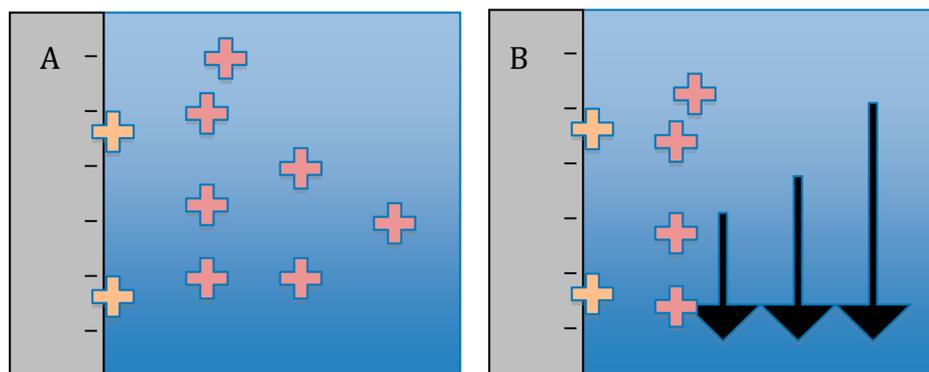


Figure 1. Origin of electrokinetic current. (A) Snapshot of the electrical double layer formed by a charged silica surface. The surface has a negative charge at neutral pH, which attracts the (orange) positive charges directly to the surface and (red) charges into a diffuse layer. (B) When hydrodynamic flow is added, some charges in the diffuse layer are moved, creating the electrokinetic current. See ref 20 for details.

strength is required. This is typically achieved by using a large concentration of spectator ions to maintain a constant ionic strength while varying a smaller concentration of the desired analyte. However, the large background of spectator ions poses competition for surface association with the analyte ions, and thus their presence alters the surface with which the analyte is interacting.

One way to address this issue is to use concentrations wherein the ionic strength of the solution, and thus the double layer thickness, is dictated by autoionization of water rather than by the concentration of analyte ions, which must then be less than 100 nM. Recent work shows that Hofmeister effects remain in force even at similarly low concentrations.¹⁰ However, this presents another difficulty, since measurement of the electrokinetic parameters with a traditional approach relies on having a solution resistivity low enough that back-conduction or surface conduction do not interfere with the measurement.^{19,20} A method developed by Duffin et al.^{21–23} is able to limit back-conduction through use of a liquid microjet, rather than the traditional reservoir system. In this microjet apparatus, the capillary does not electrically connect to a reservoir, but instead ejects the solution into air (or vacuum), severing the electrical connectivity between the separated charges when Rayleigh instabilities break up the microjet into a droplet beam. Without a back-conduction pathway, the current measured in this type of experiment comprises a faithful representation of the surface charge.

In the present study, we examine the capabilities of liquid microjets for measuring electrokinetic currents of ultradilute (<1 μM) solutions, and thus to probe relative surface affinities of ions. We test our apparatus with a series of three related analytes: HCl, KOH, and KCl in aqueous solutions. Because of the low concentrations used, the HCl and KOH solutions can be treated in terms of the individual Cl^- and K^+ ions, whereas the concentrations of $[\text{H}^+]$ and $[\text{OH}^-]$ will be dominated by the autoionization equilibrium. Hence, the only substantive change in the solutions relative to pure water will be addition of the individual alkali or halide ions. The specific effects of these ions are then contrasted with the behavior of solutions wherein both ions are present. This approach presents a unique opportunity to study the interfacial properties of individual ions with only the background ionic content of water to interfere with the dynamics, as well as to observe cooperative ionic effects that would elude detection without having the individual ion profiles.

■ EXPERIMENTAL METHODS

The electrokinetic microjet apparatus used here is that described in previous publications^{21,22} with some minor changes. A Knauer K-1001 HPLC pump drives the solution through PEEK tubing into a fused silica capillary with a 30 μM diameter. The flow rate of solution was controlled such that all experiments were performed under laminar flow conditions. Electrokinetic currents were measured from the electrically isolated metal fitting that holds the silica jet using a FEMTO DDPCA-300 variable gain subfemtoampere current amplifier. Measurements at a copper electrode in the downstream path of the microjet, where an equal but opposite current relative to the metal fitting is expected, were also monitored. The water used in all experiments is Millipore-filtered with a resistivity of 18.2 $\text{M}\Omega$ [TOC < 5 ppm]. Reagent grade KCl, KOH, and HCl (Sigma-Aldrich) with ion impurities of less than 0.5% were used in making solutions through serial dilution. Glassware was cleaned with Nochromix/sulfuric acid solution regularly and rinsed thoroughly with the purified water. All solutions were vacuum-degassed prior to experimentation.

■ RESULTS AND DISCUSSION

An issue of vital concern in these ultralow concentration studies is the presence of contaminant ion signals in either the prepared solutions or the purified water. Atomic absorption spectroscopy (AAS) was used to set a reasonable window of ion concentrations that we could employ without encountering such contamination issues, either from the reagents or our water purification process. Potassium AAS data were obtained using a PerkinElmer AAnalyst 200 (graphite furnace, potassium lamp: 766.5 nm) with an Autosampler AS-800. The absorbance peak area was plotted as a function of K^+ concentration, from 1 to 10 pM, as shown in Figure 2. The calibration data show an average baseline signal equivalent to 3.5 pM K^+ in purified water samples, setting the lower limit of concentration used in our study at that level. The calibration curve itself represents a good fit of the concentrations from 1 to 10 pM, indicating that the solution preparation is not introducing errors at these levels. Solutions above the 3.5 pM threshold set by the purified water will thus yield accurate measures of concentration. In light of these data, solutions with nominal concentrations from 10 pM to 100 nM were examined with our electrokinetic method. The lower bound is set by the previously described water purity, while the upper bound corresponds to the

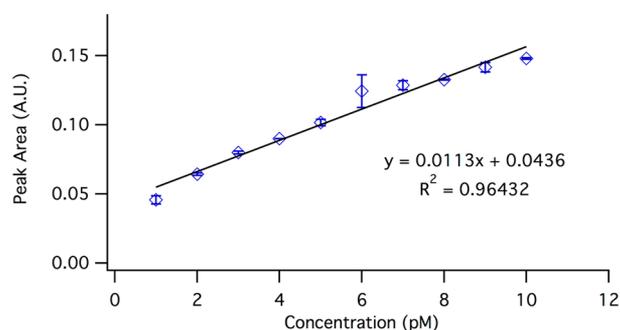


Figure 2. Potassium ion calibration curve from atomic absorption spectroscopy, establishing the baseline K^+ concentration in $18M\Omega$ Millipore purified water at 3.4 pM . Error bars represent the standard error of the measurements.

concentration at which added ions will appreciably influence the electrical double layer thickness.

In order to verify that changes observed in EK current are actually due to the solution ionic composition rather than to some permanent contamination of the jet surface, we report the current from dilute solutions as a ratio relative to the EK current obtained from a pure water blank. The protocol employed in a typical experiment (100 pM KCl), is shown in Figure 3, displaying the EK current as a function of time.

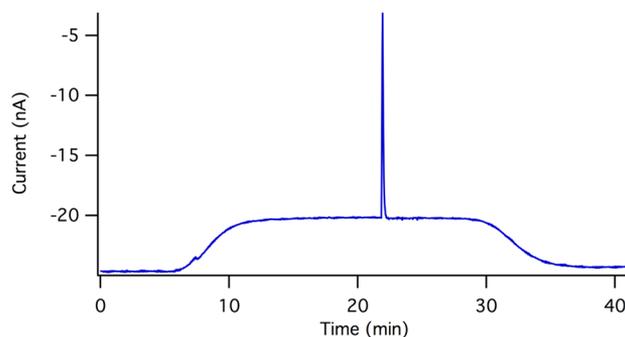


Figure 3. Typical data from the electrokinetic microjet experiment, showing the transition in current generated by flowing purified water, switched to a 100 pM KCl solution, and then back to purified water.

Initially, the pump is filled with the blank solution. Then, the dilute salt solution is introduced into the pump. The data in the early portion of the graph represent the blank solution that is being expelled from the pump. This current is negative because the current is being measured at the nozzle, which is negative due to the negative surface charge of the fused silica at $\text{pH } 7$.²⁴ Once the blank solution has been expelled from the pump, the current changes, as the salt solution (100 pM KCl) interacts with the silica surface, creating a new electrokinetic potential. After collecting data for long enough to ensure equilibration with the ionic solution (at least 5 min of steady current), we briefly shut off the pump and switched back to the blank solution, evidenced by the spike to zero current. While the blank solution travels to the pump, the dilute salt solution is still being expelled, yielding the same current as previously observed. Eventually, the blank solution reaches the jet, and the current returns to the blank output level. Data were collected in this fashion as a quality control measure, to ensure that microscopic variations or buildup on the silica microjet surface did not influence either the blank current or the salt current. Experiments with mismatched currents between blank samples

were deemed contaminated and disregarded. As evidenced in the figure, the signal-to-noise ratio is quite high, with a noise range of approximately 1 nA . Despite the very dilute concentrations employed, there are clear changes in the EK current among the different solutions, indicating that these changes do not represent minor fluctuations at the jet surface or the buildup of insoluble surface contaminants.

In Figure 4, we plot the observed current ratio (electrolyte solution/pure water) of HCl solutions as a function of

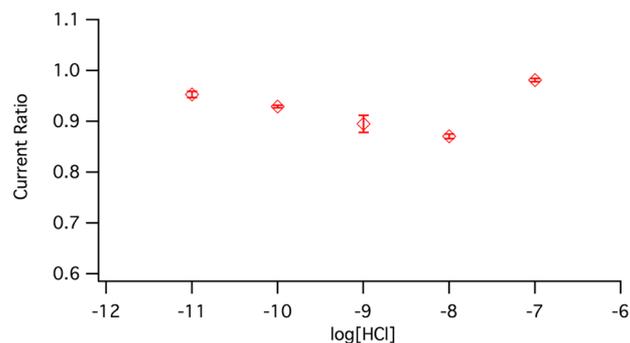


Figure 4. Electrokinetic current ratio (solution/blank) plotted as a function of the log of HCl concentration. Error bars represent the standard error of the measurements.

concentration. Because of the low ionic strength of these solutions, the (negative) current should be dominated by the surface charge of the silica under the given conditions. The initial (negative) current ratio drops as the concentration increases, indicating that the surface is becoming less negative. The added positive ion in this solution, H^+ , should not be strongly influencing the surface due to the higher concentration of H^+ already present in water from autoionization (nM – pM HCl compared to 100 nM H^+ in pure water at equilibrium). This leaves the Cl^- as the likely source of the current change with electrolyte concentration. As a negative ion, one way that chloride could make the surface charge less negative is if adsorption of a chloride at the surface replaces or repels a larger number of hydroxide ions and water molecules. In particular, chloride ion is a poor hydrogen bond acceptor, and its adsorption could influence the stability of other species at the surface. For example, hydroxide ions could be destabilized by having a hydrogen bond acceptor replaced by a chloride ion. Alternatively, Vácha et al.⁴ discuss how asymmetrically distributed oriented water molecules at an interface can impart surface charge through a charge transfer process among hydrogen bonds; the adsorption of chloride at the surface could disrupt this orientation in a manner that reduces the apparent surface charge. A net loss of charge at the surface would lower the EK current, and the trend with increasing HCl concentration is observed because of the corresponding increasing availability of chloride for associating with the surface. In any case, the mechanism for this observed current decrease would be interesting to examine with detailed simulations, but this is beyond the scope of the present paper.

Interestingly, the current ratio exhibits a minimum near 50 nM HCl , when the added electrolyte concentration is nearly equivalent to that of the background hydronium and hydroxide ions, and increases rapidly thereafter. The increase of the current ratio suggests an interaction that does not compete with hydroxide, since the change results in a more negatively charged surface. The abrupt nature of the change could be

explained by a specific interaction between chloride and the surface, rather than a general preference for chloride at the surface versus in solution. In this case, the data would suggest that the association has an equilibrium constant of approximately $1/[\text{Cl}^-]$, or $\sim 1 \times 10^8$. These interesting questions would seem to merit examination with detailed calculations.

Complementing the HCl data, the effect of varying KOH concentration is shown in Figure 5. Here, there is only a small

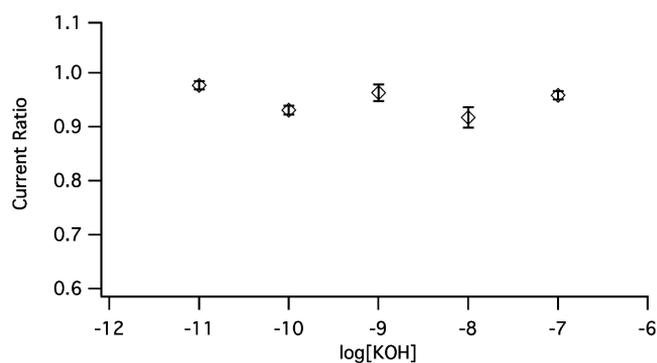


Figure 5. Electrokinetic current ratio (solution/blank) plotted as a function of the log of KOH concentration. Error bars represent the standard error of the measurements.

deviation of the EK current over the entire concentration range studied, in contrast to the HCl dependence described above. This is in agreement with other findings concerning the behavior of cations at surfaces, wherein the observed effects are usually smaller than those induced by anions.²⁵ The uncertainty in the present data limits the interpretation possible in this particular case.

The dependence of EK current upon KCl concentration is shown in Figure 6. For comparison, the KCl data are plotted

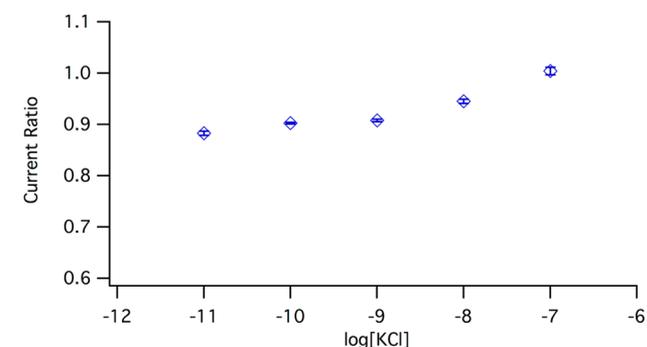


Figure 6. Electrokinetic current ratio (solution/blank) plotted as a function of the log of KCl concentration. Error bars represent the standard error of the measurements.

alongside the HCl and KOH data in Figure 7. If the ions did not have a significant cooperative or interfering effect with one another, we would expect the KCl data to resemble the combination of HCl and KOH data sets, but the current ratio at low KCl concentrations differs significantly. Most notably, the marked shift in current between 10 nM and 100 nM concentrations found for HCl is not evident in the KCl data. Instead, there is a slower climb in current with concentration.

The differences between the data sets strongly suggest the competitive nature of ion association with the silica surface. From the HCl data, it was proposed that increasing the bulk

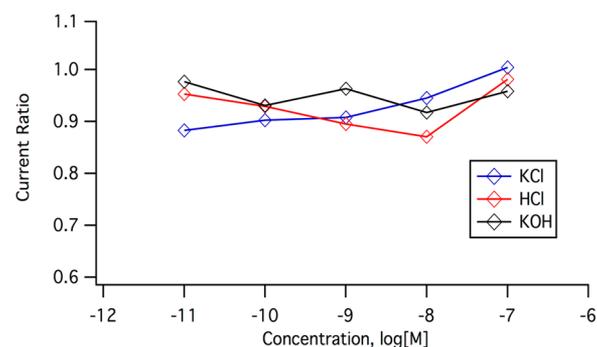


Figure 7. Overlay of data from Figures 4–6 for comparison.

chloride concentration increased its adsorption at the silica surface, displacing a larger number of hydroxide ions and decreasing the surface charge. The inclusion of chloride ions or loss of hydroxide ions could create a more favorable environment for association of K^+ ions from the bulk solution to the interface. In KOH solution, the potassium ion may have a lower affinity for the hydroxide anion and thus not adhere to the surface. The current ratio would be higher for the HCl solution at low concentrations because only part of the lower surface charge is driven by the loss of hydroxide from the surface. When the potassium ion is present and chloride rather than hydroxide is adsorbed at the surface, the potassium can approach the interface and reduce the negative surface charge, thus explaining the results with KCl solutions. The difference between HCl and KCl at higher bulk salt concentrations can then arise from the lower negative charge at the surface with KCl, wherein chloride is less repelled than it was in the absence of the potassium ions.

CONCLUSIONS

The data presented in this work demonstrates that the electrokinetic study of ultradilute solutions with liquid microjet technology presents a novel means for investigating ion–surface interactions. Through the use of this method, we conclude that the interaction of KCl with silica exhibits a degree of complexity that has not been previously revealed. This interaction is not fully described by the independent effects of potassium and chloride, suggesting a cooperative underlying mechanism. Further characterization of the KCl system could entail expanding the study to other alkali halides using the ultradilute electrokinetic current method. The currents obtained from these experiments are large enough to be measured with modern instrumentation, and there are statistically significant differences in this current at the lowest ion concentrations that can be reliably achieved. Additionally, the ultradilute conditions allow for the study of individual ions without interference from counterions not intrinsically present in water.

In addition to the above considerations, this new technique could be used in studies with important practical applications. The general phenomenon of ion–interface interaction is a major component of chemical separations, water purification, and desalination. A wide range of polymeric materials are used in these applications, wherein the choice of material has considerable impact on the effectiveness and efficiency of the process. Although not explicitly studied here, the chemical transformation of fused silica surfaces through sol–gel chemistry and evaporative deposition would permit the study

of different surface characteristics, such as magnitude of surface charge, sign of surface charge, and hydrophobicity. Such studies could help establish the general principles underlying ion-interface affinity. The combination of systematic surface modification with microjet-based dilute ion electrokinetic analysis could expand the application of experiments described here to areas difficult to address with other methods.

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Notes

The authors declare no competing financial interest.

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