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## The inevitable accumulation of large ions and neutral molecules near hydrophobic surfaces and small ions near hydrophilic ones



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#### 1. Introduction

The seminal 1934 article by Onsager and Samaras [1] accounted for the enhanced surface tension of electrolyte solutions compared with pure water. The enhanced surface tension was traced there to the electrostatic repulsion of ions by their image charge across the water-air interface, and the resulting ion depletion from the interfacial layer. The effect of ion size was small in that theory, leading to weak dependence upon it. Compilation of surface tension data in the presence of different salts [2] and their analysis [3] disclosed, however, marked dependence upon ion size, particularly with anions. While the small chlorine ion was found to be depleted from the interface, the bromine ion was found to be only weakly affected by it and the iodine was found to accumulate at the interface, opposite to the prediction of Ref. [1]. A similar trend, albeit weaker, was found with cations. This trend was also reproduced in molecular dynamics [4] and in a recent experiment that measured water dynamics at the air-electrolyte interface [5]. Since this ion-specificity, and particularly ion accumulation at the interface, cannot be explained in terms of electrostatic forces, a question is begged regarding the non-electrostatic driving force acting on these ions. Various theories [6,7] have been suggested to account for this effect but as we show below, it can briefly be summarized as hydrophobic expulsion of large ions from the hydrophilic water environment to the interface with air where the hydrogen bond network is minimally affected by their presence.

Similar accumulation, this time of neutral air molecules, takes place at the interface between water and hydrophobic surfaces as seen in neutron scattering [8–10], numerical simulations [11,12], and force

#### ABSTRACT

The present contribution offers a unified explanation to three central phenomena in physical chemistry of interfaces in contact with aqueous solution: (1) Accumulation of large anions at the air/water interface. (2) Accumulation of neutral gas molecules near hydrophobic surfaces and the resulting hydrophobic interaction between two such surfaces, and (3) The Hofmeister effect, namely, the enhanced propensity of small ions to hydrophilic surfaces and large ions to hydrophobic surfaces. The common thread linking these phenomena is the free energy balance between ion or molecule hydration in solution and the cost of localizing these objects at the watersurface interface. Comparing the results of an abstract lattice-gas model to force spectroscopy data collected by AFM we reveal the underlying principles and demonstrate their universality.

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spectroscopy by colloidal AFM [13–17]. Here, again, the free energy is minimized by expelling the hydrophobic air molecules from water, where they strain the hydrogen bond network, to the hydrophobic surface where hydrogen bonds are weaker or inexistent. As shown recently [18], the same hydrophobic expulsion of air molecules from water to the interface with hydrophobic surfaces is responsible for the mid-range hydrophobic attraction found in numerous experiments and the recently discovered short-range hydrophobic repulsion [18,19].

The third phenomenon concerns ion specific adsorption to inorganic oxide surfaces and the effect of this adsorption on the interaction between such surfaces. Similarly to the examples listed above, experiments [20–22] and molecular dynamics calculations [23,24] found excess adsorption of large ions to hydrophobic surfaces, namely surfaces whose interaction with water was weaker than the interaction between water molecules. On the same footing, we found [21], in agreement with molecular dynamics calculations [23], that small ions accumulate next to hydrophilic surfaces whose interaction with water is stronger than that between water molecules. The preferential binding of large ions to hydrophobic surfaces and small ions to hydrophilic surfaces, and the induced surface–surface interaction, offers complete explanation of the famous Hofmeister effect.

lons are conventionally classified according to their interaction with the surrounding water. The small ones typically attract adjacent water molecules more strongly than two neighboring water molecules do. Large ions, on the other hand, bind water weaker than water itself. The latter strain the hydrogen bond network and are generally characterized by a less negative solvation free energy compared with smaller ions of the same charge. The stronger interaction of small ions with water is manifested in a thicker hydration shell and a lower diffusion coefficient compared with large ions. Traditionally, the small and large

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ions were classified as kosmotropes and chaotropes, namely, waterstructure "makers" and "breakers", respectively. This view has been seriously challenged in recent years but the names prevail and will be used here as well.

To link ion specific adsorption with hydrophobic interactions note that the above classification of ions matches chaotropes with hydrophobes and kosmotropes with hydrophiles.

According to Gurney [25], the short-range hydration forces modify the interaction between oppositely charged ions. They enhance attraction between two kosmotropes or two chaotropes and induce shortrange repulsion between two ions of opposite nature. This principle was generalized by Gierst et al. [26] to surfaces and macromolecules. Similar ideas were later introduced by Collins [27,28] in his formulation of the "law of matching water affinity" to explain ion specific effects in the context of proteins.

A particularly insightful application of Gurney's [25] and Gierst's [26] ideas to explain the universal reversal of the Hofmeister series on going from pzc < 4 to pzc > 4 oxides [29] is found in Bérubé and de Bruyn [30] and Dumont and collaborators [31,32]. Finally, Lyklema adopted a similar point of view, arguing that the propensity of ions to various surfaces reflects the similarity of solution ions to the surface charged groups [33].

Notwithstanding the significant predictive power of these principles, recent studies, including the experiment presented below, point to additional key elements, most notably surface polarity and hydrophobicity [21-24,34], which are naturally missing in these theories that originated from ion-ion interactions. The understanding of ion specific adsorption requires, hence, notions beyond hydration modification of Coulomb attraction between oppositely charged groups. Indeed, we show below that the Hofmeister adsorption order is dictated by the strength of surface hydration rather than by electrostatics [21] where large cations adsorb to positively charged hydrophobic surfaces, despite their Coulomb repulsion from the surface. The secondary role of Coulomb interaction is also evident from the accumulation of neutral air molecules near hydrophobic surfaces and the excess accumulation of large anions at the air-electrolyte interface, against Coulomb repulsion of these ions by their image charges. The main message of this short review is hence that ion and neutral molecule adsorption to surfaces is dominated by hydration physics rather than by electrostatics.

#### 2. Experiment

Due to space limitations we focus here on the third phenomenon, ion specific adsorption to inorganic oxides immersed in water with silica serving as an architype example. Fig. 1 depicts the normalized force measured between a silica surface and an R = 2.5  $\mu$ m radius silica sphere glued to the AFM cantilever [21] as a function of sphere-surface distance, h, for three concentrations of LiCl, NaCl and CsCl solutions and two pH values. At large separations, the Debye–Hückel approximation holds and the force on the colloid decays exponentially with h according to a characteristic screening length  $\lambda$ , which shortens with concentration. At these low concentrations, the screening length is practically independent of salt type.

Potential and total charge near the surface are estimated by fitting force curves to the Poisson–Boltzmann equation at separations greater than several  $\lambda$ . In the limit that the bound layer is much thinner than  $\lambda$ , these quantities approximate the potential and the total surface charge up to the outer Helmholtz plane [35] (OHP).

As a reference, we added to Fig. 1(a) best fit of the 1 mM LiCl curve to DLVO theory, assuming  $\varepsilon = 78$  for the water dielectric constant and a Hamaker constant of  $H = 6.6 \times 10^{-21}$  J. The experimental curve clearly rests between the constant charge (CC) and constant potential (CP) limiting cases, except at small separations, where short-range repulsion, attributed to hydration forces, replaces the expected vdW attraction.

The force magnitude at all concentrations near pH 5.5 (Fig. 1(a)) decreases with increasing bare ionic radius, in accordance with the direct



**Fig. 1.** AFM force curves in the presence of LiCl, NaCl and CsCl salts at 1 mM, 3 mM and 30 mM concentrations, presented near pH 5.5 (a) and pH 9.8 (b). All curves were measured with the same colloid-substrate pair. The direct Hofmeister series observed at low pH is reversed at high pH. For reference, the LiCl pH 5.5 curves are fitted with the DLVO model at constant surface charge (CC) and constant potential (CP), respectively. Figure insets show the force at small separations in the presence of Li<sup>+</sup> (a) and Cs<sup>+</sup> (b) measured near pH 5.5, 8.8 and 9.8. Force in the insets increases with pH in both cases but short-range repulsion due to surface hydration is seen only in the presence of a kosmotrope.

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Hofmeister series; the larger  $Cs^+$  adsorbs more readily than  $Na^+$  and the latter adsorbs better than  $Li^+$ . A dramatic change takes place at high pH (Fig. 1(b)). The force in the presence of  $Cs^+$  is now greater than in  $Li^+$ , with  $Na^+$  fitting in between. The Hofmeister series is clearly reversed, indicating a corresponding reversal of cationic propensity to the silica surface.

The insets to Fig. 1 highlight the short-range interaction at different pH. In inset 1(a), the force is measured at 3 mM LiCl near pH 5.5, 9.3 and 10. With increasing pH, the force increases slightly but more importantly, a clear short-range repulsion evolves. This repulsion is missing with  $Cs^+$  (Inset to Fig. 1(b)).

Fig. 2 depicts OHP potential and total charge as a function of pH at 10 mM salt concentrations. The total negative charge includes deprotonated silanol groups as well as adsorbed cations. Each plot point indicates an average of roughly ten consecutive measurements on the same sample.

From pH 3.0 to 4.7 the negative OHP charge and potential increase monotonically for all salts, retaining the direct Hofmeister order. The steep increase of charge is attributed to full depletion of the doubly protonated silanols and deprotonation of 1-2% of the neutral silanols. As pH is further increased, the OHP charge grows monotonically in the presence of Cs<sup>+</sup>, reaching a limiting value at pH 7.5. In contrast to Cs<sup>+</sup>, and despite the increasing deprotonation of surface groups, the OHP Download English Version:

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