Solid electrolyte interfaces are central to reactivity, stability and self-organization in a large range of complementary fields and disciplines. It is widely appreciated, that solid\solution interfaces are central to processes involving cell-to-substrate interaction\cite{1-3}, self-assembly and self-organization in biological and biomaterials\cite{4}, stability of colloidal dispersions and electrochemical energy storage and electro-catalysis\cite{5-6} as well as corrosion\cite{7}. In all of these fields understanding, predicting and controlling solid\solution interfaces is of overarching importance to further advance technologic applications of even the most diametrically opposed materials used e.g. in biomedical or energy storage and energy harvesting applications. As such, the structure of solid\solution interfaces has always been appreciated as essential to interfacial interactions and reactions, yet a direct experimental probing of the atomistic structure of a solid\solution interface is still one of the most challenging fields in fundamental science.

In a very generalized view, the symmetry break from an extended solid surface into an electrolyte solution leads to a variety of phenomena that can be described in terms of a depletion or enrichment layer formation away from a surface into an electrolyte. As displayed in Figure 1, with enrichment or depletion layer formation we refer to the transition from any bulk solid (or thin film) through a solution-side layer with increased and/or decreased concentration of solution species (water, ions, solutes) that can be well-ordered or disordered. Depletion may occur due to strong solvent\solvent or solvent\solute interactions as well as due to repulsive interactions of solutes and/or solvent molecules with a surface. Enrichment may occur e.g. due to attractive solute\surface interactions or weak solute/solvent interactions. The detailed molecular arrangement of such a solution side structuring decisively determines e.g. reaction pathways of educts and products diffusing or migrating to/away from a reactive surfaces, and/or interaction forces felt by other ions.

**Fig. 1.** Electrolyte structuring at (A) hydrophobic and (B) hydrophilic surfaces and typical water/ion density $\rho$ versus distance profiles. (A) At a hydrophobic surface in aqueous solutions a small depletion layer (hydrophobic gap) of about 2-3 Å forms due to weak surface\water interactions and strong hydrogen bonding on the solution side. (B) At charged, hydrophilic and/or electrified surfaces ions of opposite charge are attracted, while ions of like charge are repelled, forming an enrichment/ depletion layer where charge neutrality is maintained. Also, at hydrophilic and/or charged surfaces water can strongly adsorb. Adsorption can be specific or non-specific, and ions may or may not strip their hydration shell depending on the overall energy balance.

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similarly structured interfaces approaching any solid|electrolyte interface e.g. during self-organisation of matter.

From a thermodynamic point of view, a subtle entropic (e.g. entropy of mixing) and enthalpic energy balance of possible chemical and physical interaction (specific and non-specific adsorption), hydrogen bonding and electrostatic attraction of solvent and solute molecules to surfaces and within the electrolyte side are directly leading to the formation of interfacial solutions-side layering up to tens of nanometers away from a solid surface. In this brief review, we will give an overview about the structuring of electrolyte solutions at (A) hydrophobic, (B) charged and (C) electrochemically polarized surfaces in aqueous solutions, as well as (D) ion layering in ionic liquids at charged and metallic surfaces. In particular, we will discuss recent advances in our understanding of interfacial water and ion structuring and it’s influence on interaction forces in electrolyte solutions.

Studying hydrophobic and charged solid|electrolyte interfaces has a long-standing tradition in colloid and interface science[18], with an ever increasing success to generate molecular and fundamental insight into structure and reactivity at solid|electrolyte interfaces. Currently, the surface science community is making a significant effort and transformation aiming towards realistic environments and in particular solid|electrolyte interfaces[19]. As such it is an exciting time in interface science; colloid and interface scientists as well as surface scientists are converging their efforts towards the same aim – an atomistic and molecular description of solid|electrolyte interfaces. We can expect vast advances in our molecular understanding of solid|electrolyte interfaces within the next decade.

**EXPERIMENTAL TECHNIQUES FOR STUDYING SOLID|LIQUID INTERFACES**

In the following, we will first provide a very brief overview on techniques that allow for a direct probing of the solid|electrolyte interface. Both interfacial spectroscopies with non-linear optical techniques as well as spectroscopic ellipsometry provide a direct view into the molecular structure and optical properties of thin films at interfaces. For instance, R. Scheu et al. could recently show that no ions adsorb to hydrophobic surfaces from NaCl based solutions[10-11]. Complementary, synchrotron based X-ray diffraction experiments, surface sensitive X-ray absorption fine spectroscopy (XAFS)[12], and X-ray reflectivity experiments have been extensively used to unravel a detailed picture of the density profile and/or well-ordered (i.e. coherently diffracting) structures away from an isolated smooth and rough surfaces[13-16]. In particular, reflectivity experiments can also reveal dynamics at solid|electrolyte interfaces[17-18]. Direct imaging with scanning probe microscopies (SPM), and in particular with atomic force microscopy (AFM) and scanning tunnelling microscopy (STM)[19], provide an exciting potential for a real-space view into solvent structuring and ion adsorptions in electrolyte solutions. Here, the biggest challenge is to unambiguously determine, what exactly scanning probe microscope images detail on the molecular scale. It is extremely difficult to distinguish effects from structuring at the probe tip and the probe surface; both are integrated simultaneously into any taken image. Considerable simulation effort and comparison to experiments is necessary to further progress to a conclusive molecular picture based on SPM imaging[20].

**Force probe experiments** are an interesting and quite straightforward alternative for directly probing interfacial solvent and ion layering at any interfaces. Force probe experiments are typically performed using the two complementary techniques of force spectroscopy in an atomic force microscope[21] or surface forces apparatus measurements[22-23]. In a typical surface force experiment two surface are approaching to distance $D \to 0$, the force response due to overlapping of the hydration layers gives direct information about interactive forces, and at the same time discontinuities in the force versus distance characteristics indicate stable layer formations.

In a first approximation (neglecting discontinuities due to molecular details) force versus distance profiles can be very effectively described by a linear superposition of attractive Van der Waals forces ($F_{VDW}$), electric double layer forces ($F_{EDL}$) and hydration layer ($F_H$) dominated force contributions. Hydration effects are treated integral in terms of an exponential hydration force. Deviations form $F_H$ will be shown and discussed below. Additionally, even roughness effects can be extended into the linear superposition concept quite effectively[24-25], a subtlety we do not attempt to discuss in any detail here. The following equation has been used very successfully to model forces acting between a flat surfaces and a sphere of radius $R$ during approach:

$$
\frac{F}{R}(D) = F_{VDW} + F_{Hy} + F_{EDL}(+F_{roughness} + \ldots) = 4\pi\varepsilon_0 H \gamma_{eff} \frac{H}{D} + \frac{e_H}{\lambda_D} \left[2\Psi_1^2 \Psi_2 e^{-\frac{(D-D_0)/\lambda_D}{2}} - \left(\Psi_1^2 + \Psi_2^2\right) e^{-2\frac{(D-D_0)/\lambda_D}{2}}\right] + \ldots \text{[N m}^{-1}\text{]}(\text{Equation 1})$

with the Hamaker constant $A_H$, an effective hydration parameter Hydra, $H\gamma$, an effective interfacial tension $\gamma_{eff}$, the typical decay length of hydration interactions $\lambda_D \sim 0.1 \text{nm}$, the Debye screening length of the electrolyte $\lambda_D$, and the surface potentials of the two interacting surfaces $\Psi_1$ and $\Psi_2$. Here we use a constant potential solution for modelling $F_{EDL}$. Constant charge[26] and mixed analytical solutions (including charge regulations[27]) are available but beyond the scope of this article. $H\gamma = 1$ characterizes the interaction between two fully hydrophobic surfaces, while $H\gamma < 0$ characterizes repulsive hydration layering due to specific and non-specific adsorptions at the interface. $D$ is the separation distance, $D_0$ is the hydration force decay length, $D_0$ allows a shift of the plane of origin of the diffuse electric double layer interaction, that may be e.g. due to a strong inner layer structuring. $D_0$ is typically close to or equal to $D_0$, indicating that strong inner layer structuring switches to diffuse layering at $D \sim D_0$.

The first successful application of this linear superposition dates back to the well-known Derjaguin-Landau-Verwey-Overbeek theory (DLVO-theory) that considered VDW and EDL...
forces acting at the same time\cite{8}. Equation 1 extends this concept by additional linear contribution due to hydration of interface ($F_{in}$).

For instance, the stability of colloidal dispersions could be well predicted and rationalized in terms of the EDL based electrostatic repulsion between like particles that prevents colloids from approaching into an attractive VDW minimum\cite{8}. In the recent years we worked intensively on extending this concept to electrified interfaces with strongly adsorbed ions and with considerable surface roughness\cite{27-29}. Donaldson et al. unified hydration forces at hydrophobic and hydrophilic interfaces into the Hydra equation used in terms of $F_{Hy}$ in Equation 1\cite{23, 30].

Exemplarily, Figure 2 shows calculated forces (Equation 1) acting between a flat surfaces and a sphere of radius R during approach. Here, we directly compare to cases, a fully hydrophobic force versus distance characteristic with $Hy = 1$ and a hydrophilic case with $Hy = -0.15$. In addition, in Figure 2 (A) long range electric double layer forces are set repulsive with $\Psi_1 = 80$ mV and $\Psi_2 = 80$ mV. Two regimes are clearly visible: First, at long range electric double layer forces dominate the force profiles for both hydrophilic and hydrophobic interfaces. At short range below about $D \leq 5-6$ nm hydration forces lead to an attractive or repulsive regime at hydrophobic and hydrophilic surfaces, respectively. In Figure 2 (B) long range electric double layer forces are set attractive with $\Psi_1 = -80$ mV and $\Psi_2 = 80$ mV. Similarly, an electrostatic and an electrolyte-laying dominated regime are clearly visible as indicated. Interestingly, hydrophilic interfaces show an electric double layer mediated attractive minimum at separation distances of $D \sim 4$ nm, that is overpowered by a strong repulsion at $D \leq 4$ nm. In the following section we discuss selected examples, and discuss how this model can describe the behaviour of hydrated interfaces during approach and during interaction.

A - ELECTROLYTE STRUCTURING AND FORCES ACROSS HYDROPHOBIC INTERFACES

As indicated in Figure 1 (A), in aqueous solutions hydrophobicity leads to a depletion of water and ions away from any hydrophobic interface, giving rise to what is famously known as hydrophobic gap, where the distribution-density of water molecules and ions at the interface is minimized. For instance X-ray reflectivity measurements could show a clear decrease of the water density, $\rho_{H2O}$ within the first few Å (about 3-5 Å) away from hydrophobic interfaces in aqueous electrolytes\cite{17-18}. Similarly, non-linear optical spectroscopy revealed that NaCl-ions do not adsorb to hydrophobic interfaces from aqueous solutions\cite{10-11}.

Thermodynamically, this depletion of water at the interface is due to the strong water | water interaction compared to the relatively small interaction energy of water molecules with hydrophobic surfaces. Hydrophobic surfaces essentially only attract ions and water through Van der Waals interactions, while no specific or non-specific surfaces sites allow for hydrogen bonding between hydrophobes and water.

A direct result of this interfacial depletion layer is a strong attractive force between hydrophobic units in aqueous electrolytes, that is well-known as the so-called hydrophobic force\cite{8, 30}. Figure 3 shows a typical AFM force versus distance characteristic recorded during approach of two hydrophobic surfaces in aqueous solution. Figure 3 also indicates the calculated interaction force based on a linear superposition of VDW and exponential hydrophobic forces with typical decay length of about 1 nm, indicating a good description in terms of the assumptions of Equation 1 (e.g. linear superposition).

As can be seen directly, during approach, this hydrophobic force effectively leads to deviations from DLVO forces at $D \sim 5-6$ nm.
attractive force and strong adhesion upon separation. FEDL = 0 in this case.
hydration depletion at hydrophobic surfaces leads to an additional strong
As can be seen directly from the plot, compared to acting VDW force, the
centration with Reff ~ 10nm. A
hydrophobic surfaces in aqueous solution at pH = 5.5 and 5 mM NaCl con-
only a single layer of K+ ions separates the two mica surfaces. In
surfaces in dry argon under high load. Under these conditions,
as well as 100 mM LiCl and CsCl solutions at pH = 5. The zero
Fig. 3. Semi-logarithmic force versus distance profile recorded between two
hydrophobic surfaces in aqueous solution at pH = 5.5 and 5 mM NaCl con-
centration with R∞ ~ 30nm. A fit to equation 1 with Hy ~ 1 is shown as well. As
can be seen directly from the plot, compared to acting VDW force, the
hydration depletion at hydrophobic surfaces leads to an additional strong
strong adhesion upon separation. FEDL = 0 in this case because hydrophobic surfaces carry almost no charge.
Hence, the hydrophobic force is quite long ranged (10’s of molecular water diameters) and as such it plays an essential role in protein folding and aggregation of hydrophobic and amphiphilic molecules in water (lipid-bilayer formations). It may also be important in technological applications, where wetting/de-wetting and controlled aggregation of hydrophobes are critical.
In the future, force probe experiments will provide further detailed insight into hydrophobic interactions, and in particular high salt concentrations and specific influence of dissolved ions on hydrophobic forces. Of particular interest will also be the influence of the size of hydrophobic units on hydrophobic interactions. E.g. small hydrophobes such as methane can be effectively enclosed into water structures based on enthalpic energy gains [31-32], which prevents direct harvesting of methane-ice reservoirs. Salt and additives can directly affect hydrophobic forces and may provide interesting strategies for an economic harvesting of these abundant natural resources.

B - STRUCTURING AND ELECTRIC DOUBLE LAYER FORCES AT CHARGED INTERFACES

Conversely to hydrophobic interfaces, and as shown in Figure 1(B), charging of surfaces in electrolyte solutions leads to the formation of the so-called electric double layer, where oppositely charged ions and dipolar water molecules are attracted/adsorbed to any charged surface. Frequently observed charging mechanisms in electrolytes include protonation/depolarization of surface species, electrochemical polarization [28-29] or selective dissolution of charged surface species.

Figure 4 shows a semi-logarithmic plot of the interaction forces between two mica surfaces in hydrochloric acid at pH 4 and 1, as well as 100 mM LiCl and CsCl solutions at pH = 5. The zero distance (D = 0) is defined as the distance between two dry mica surfaces in dry argon under high load. Under these conditions, only a single layer of K+ ions separates the two mica surfaces. In solution the K+ ions dissolve and a mica surface obtain a maximum negative charge density of half a monolayer. This amounts to a charge density of about 0.2 C/cm², or a surface potential of 471 mV obtained from Grahame’s equation in pure water. This surface charge is balanced at the interface by the formation of an equally but oppositely charged EDL, which gives rise to the measured interaction forces. Figure 4(A/B) reveals several subtle information such as shifts of the force distance characteristics, strong variation of the diffuse double layer, oscillatory behavior within the hydration layer (discrete inner layer hydration layer effects), and significant differences in the adhesion forces measured during separation (not discussed here).

In Figure 4(A) long range EDL forces are visible only in hydrochloric acid at pH = 3. At this pH the mica surfaces are charged negative. This negative surface charge is compensated by the formation of an EDL consisting entirely of protons. Forces can be modelled well in this case using only VDW and EDL forces with the experimental Debye length of 9.6 nm. Interestingly, no hydration forces are detectable in proton based solutions, surfaces directly approach to D = 0. This indicates, that protons do not form any significant hydration layering. This is consistent with the fact that protons do not carry any hydration shell with them.

In contrast, in hydrochloric solution at pH = 1, the force distance profile is considerably shifted out and also shifted to higher forces. This pH is well below the point of zero charge (PZC) at pH = 2.5, and the used mica surfaces are protonated and charged positively. Hence, anions are attracted towards the interface. The Debye length at pH = 1 is a much less than one nm, and hence EDL forces can not explain the observed almost exponential long range repulsive regime with λD ~ 2.5 nm. Clearly, hydrated anions adsorb to the positively charged mica interface and give rise to hydration forces between the two approaching surfaces. Additionally, the approach curve significantly deviates from a pure exponential force increase, indicating a layering of the anion species.

If LiCl or CsCl salts (same chloride anions) are added to the solutions at pH values above the point of zero charge of 2.5, force versus distance characteristics change dramatically (see Figure 4(B)). First, the long-range component is suppressed due to the decreased Debye length. Second, in confinement the weakly hydrated Cs+ ions condensate into the mica-lattice screening the entire surface charge within the Stern layer. No EDL force is detectable in 100 mM CsCl solutions [33]. In contrast, strongly hydrated Li+ ions only partially compensate the surface charge within the Stern layer, leading to the formation of a diffuse outer double layer with DLVO behavior as indicated in Figure 4(B). This is consistent with a strong binding of water to the Li+ ions that cannot specifically adsorb to mica. Cs+ on the other hand bind water weakly, and hence may exothermically condensate into the lattice of mica. This is also the reason why mica-like materials are well known and technically used as Cs-absorbers (feeding additives) in milk-production since the radioactive fall out from Chernobyl in the 1980’s. This is a clear example, where a subtle balance between hydration energies and adsorption energies dominate the resulting surface layering. As such, both LiCl and CsCl solutions exhibit oscillatory ion-hydration forces at surface separations from 2.2 nm to 4-8 Å marked with arrows in Figure 4(A) and (B) [33].
Applying a potential at a metallic or semi-conducting interface leads to a considerable change of the surface charge, and as such directly effects the layering of electrolytes at electrified interfaces. In the last few years we have developed electrochemical cells and attachments for both Surface Forces Apparatus (SFA) and Atomic Force Microscopy (AFM), and measured the influence of surface hydration on interactions forces and ion-layering in-situ.\(^{28-29}\)

Figure 5 shows a set of characteristic force versus distance profiles measured between electrochemically polarized (from \(-150\) mV to \(800\) mV vs the potential of zero charge) gold surfaces and amine terminated self-assembled monolayers on gold in \(1\) mM \(\text{HNO}_3\) at \(\text{pH} = 3\), using the SFA. The plotted approach curves show two distinctly different force regimes: At separation distance, \(D\), ranging from \(40\) nm to about \(4\) nm, the data shows the long-ranged electric double layer force which is attractive for electrochemical potentials below the PZC and repulsive above the PZC. This interfacial force profile is consistent with the surface chemistry at the apposing interfaces. The surface terminating amine head group of the \(3\)-aminoproyl-triethylsilane monolayer (APTES) coated mica surface is charged positively at the experimental pH value of \(\text{pH} = 3\), while the surface potential of the gold electrode was modulated in situ using the electrochemical setup. At separation distance, \(D\), below \(4\) nm, the force runs indicate an additional exponential repulsive force contribution due to hydration forces arising from the confinement of hydrated ions and water between the two apposing surfaces. The shift of the hard wall above the potential of zero charge is indicated.

At electrified and charged interfaces ILs show a very interesting surface layering that is directly accessible to force probe experiments. Figure 6 shows force versus distance characteristic at a ceramic (Mica) and a metal (Pt) surface measured with AFM. The same AFM tip was used to probe both surfaces in order to minimize tip radii effects. It is apparent, that the two surfaces form completely different layering at distances...
D ≤ 10-15 Å. The final layer on Platinum surfaces shown in Figure 6(A) has a thickness of about 5.3 Å, while the final layer on mica surfaces probed in Figure 6(B) has a thickness of about 8.1 Å.

Comparing the forces during the typically observed instabilities with Figures 4 and 5, the actual interaction energy of ILs at charged interfaces seems to be weaker compared to ion adsorption in aqueous electrolytes. This constitutes another advantage of ILs over traditional electrolytes, as the ions will not interfere strongly with interfacial reactions by blocking active sites by strong adsorption – they can readily be replaced. An exact structure can unfortunately not be ascertained at this point in time, as the actual molecular structure is not probed here. In this direction molecular modelling may help to further understand the detailed molecular arrangements.

In typical battery fluids the interfacial solvent layering of ILs and/or organic electrolytes controls e.g. transition state barrier during charging and discharging of a battery, including in particular the formation of the solid-electrolyte interface that controls performance and lifetime of a rechargeable battery. In general, and as can be seen in Figure 6 layering of ILs at electrified interfaces is observed up to 4.5 nm distance. Considering the typical size of IL constituents (about 5Å – 1nm) this amounts to about 4-5 molecular layers. As such, the inner layer ordering effect in ILs is a bit less far reaching compared to layering observed in aqueous solutions that typically extends to 2-3nm in the structured inner hydration layer.

In addition, our recent force-probe experiments with the SFA revealed that ionic liquids might not be viewed as an infinitively concentrated solution of cations and anions[27]. Quite in contrast, ionic liquids behave as effectively neutral dielectric network of cations and anions containing a concentration of about ~0.1 mM of dissociated cations and anions, similar to a dilute electrolyte. As such, forces in ionic liquids show a strong inner surface layering, with a weak additional long-ranged force from overlapping diffuse double layers, which is conceptually similar to a space charge region in a semi-conductor.

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As such, force probe experiments provide a unique and complementary view into both the structuring of electrolyte and interaction forces during approach and separation of surfaces in aqueous and non-aqueous liquids. This is an aspect that other interface sensitive techniques can not probe directly – interactive forces and dynamic structure/property responses are accessible directly and uniquely in force probe experiments[34].

As a conclusive remark we want to emphasise that all of the techniques we mentioned in our experimental section above, as well as force probe experiments, provide unique pieces of the puzzle that will allow us to advance our molecular understanding of interfaces at steady-state and during active (interacting) conditions. However, high level theory such as molecular dynamics[35] or neural networks[36], and ab initio calibrated molecular dynamics[37] will play an important role as an integrative tool in linking results and data of interfacial experimental techniques to an actual and conclusive molecular and dynamic picture of an interface.

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SUMMARY

We showed and discussed the large variety of interfacial ion and solvent structuring at solid|electrolyte interfaces. In summary, protons do not form hydration layers, but protonation can lead to strong anions layering. Cation layering strongly depends on the hydration energies of the involved ions. Binding energies in ILs seem much weaker compared to ion binding in aqueous solutions. From the selected examples it is apparent, how a subtle balance between adsorption, solvent-solvent, ion-solvent and ion-surface energies directly steer and control interfacial structuring and resulting interactive forces at solid|liquid interfaces.


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