

Moscow-Bavarian Joint Advanced Student School (MB JASS) 2006

Nanobiotechnology and Biosensors:

- The Solid-Liquid Interface -

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Within the following text there will be referred to equations, graphics and plots from the according presentation without directly including all of them into this essay - to more easily find the ones not included they will be quoted the following way: [name or position of equation/graphic/plot,...; number of ppt-page].

1. Motivation & Introduction

The solid-liquid interface (sli) is a quite complex topic with many different facets, which in most cases are not very well understood yet and therefore still need to be further examined. On the one hand the intention of this talk is to present some of the most important features, when dealing with slis. On the other hand also an impression of how this interesting field of study has evolved over the years is meant to be given. Therefore we start off with a theoretical approach by trying to find a mathematical way of describing important parameters related to a sli. After that we have a look at experiments done within the field of slis and find out how such an interface depends on certain parameters by measuring the reaction of the whole sli-system due to an applied change. In the chapter about simulation further mathematical models are developed allowing us to explain experimental data, which could not have been done with the so far existing theories. Including the chapter about applications we reach the state of the art of knowledge on solid-liquid interfaces.

Before starting we shortly want to answer the uprising question „Why should one examine solid-liquid interfaces in the context of nanobiotechnoloy and biosensors?“ Just being an interesting topic might not be convincing enough for everybody... The answer is short and clear: The understanding of the sli is a very important key to various applications in the field of nanobiotechnology and biosensors. A simple example for a biosensor could be an ISFET, where the sli is represented by the metal-electrolyte-contact being the important „sensing“

element. Another example could be a liquid within a nanotube [biosensors, nanotubes; 3]. In both cases we need to understand what happens at the sli on a molecular level, which leads us into nanometre-dimensions. Further more some basic ideas developed within the sli-theory are successfully used in fields of electrokinetics and microfluidics.

As we will see later some remarkable properties of slis like adsorption or spatial extension of charged layers can be correlated with the different conductance within a solid and a liquid respectively, which is electronic in the first and ionic in the second case.

2. Theoretical Approach - Concept of the „Electric Double Layer“

2.1 The Helmholtz Layer

Due to its high dielectric constant water is a good solvent for ions. Thus it is the most important liquid to be considered in our case as most surfaces get charged in water. The charging might either happen via adsorption of ions to a surface or via dissociation of ions from a surface. Another way to charge a surface is to apply an external electric potential to a conducting surface – this is e.g. done in electrochemical cells.

To theoretically describe the interface between a solid and a liquid the concept of the “electric double layer” has been developed. The first and most simple one is a model called Helmholtz Layer, which goes back to the end of the 19th century. Assuming a charged surface we know that there must be an electric field attracting counterions from the liquid. These are considered to cover the solid surface building a monolayer and neutralizing the surface charges [graphic; 5]. The arrangement we get in this simple model resembles the one of a plate capacitor with molecular size implying that the charge of the counterions is located within the central point of the ions. Using the corresponding equation known from electrostatics we can easily calculate the capacitance per unit area, which is one of the typical parameters for a sli and can be easily measured:

$$C_H^A = \frac{\varepsilon \cdot \varepsilon_0}{d}$$

There the dielectric constant ε is the one of water. The distance d between the two plates is half of the diameter of the solvated ions attached to the surface. Another typical parameter is the potential drop across the interface. Using the Poisson equation [potential; 5] and knowing

that between the plates of a capacitor the charge density is equal to zero, we can conclude that the potential drop must be linear.

2.2 Gouy-Chapman Theory

2.2.1 Poisson-Boltzmann Equation

A more advanced theory was proposed by Gouy and Chapman in the years 1910-1917 independently from each other being therefore called Gouy-Chapman Theory. Both took possible thermal fluctuations of the charge carriers into account, which leads to a “diffuse electric double layer” [both graphics; 6]. These thermal fluctuations are expressed with the help of the Boltzmann equation well known from thermodynamics [Boltzmann – first part; 6]. Within this equation the local ion concentration c_i is expressed via the total ion concentration c_i^0 times an exponential term. In our case this term includes the work W_i , which has to be done to bring an ion from infinite distance to a certain position closer to the surface in units of $k_B T$. To express the local charge density close to a surface depending on the absolute ion concentration at a certain distance away from it, we use the Boltzmann equation assuming first that there has only electric work to be done to move the ions and second that we are dealing with a monovalent salt (i.e. same overall amount of solvated anions and cations having both the charge $-e$ or $+e$ respectively) [Boltzmann – second part; 6]. Combining this equation with the Poisson equation we get the Poisson-Boltzmann equation:

$$\nabla^2 \psi = \frac{c_0 e}{\varepsilon \cdot \varepsilon_0} \cdot \left(e^{\frac{e\psi}{k_B T}} - e^{-\frac{e\psi}{k_B T}} \right)$$

This equation depends only on the position and can only be solved numerically in most cases.

2.2.2 Example: Planar Surface

One simple example where it is possible to find an analytical solution for the Poisson-Boltzmann equation is a planar, infinitely extended solid surface in contact with a solution. In this case symmetry allows a reduction from a three-dimensional to a one-dimensional problem. With the additional understanding that the electric work should be very small (i.e. smaller than 25mV) and thus the argument in the exponential-function is very close to zero, we can expand the function into a series and neglect all but the first (linear) term. This leads

to the linearized Poisson-Boltzmann equation also called Debye-Hückel approximation [Debye-Hückel approximation; 7]. Using common boundary conditions ($\psi(0) = \psi_0$ and $\psi(\infty) = 0$) we find a very easy solution for the partial differential equation of second order:

$$\psi = \psi_0 \cdot e^{-\kappa x}$$

Here κ is the reciprocal of the decay length λ_D also called Debye length [κ ; 7 and 8].

The results we get from our found solution can be well seen in the two plots [both plots; 8]. First of all the potential is decreasing exponentially with increasing distance to the surface. And second an increase of the salt concentration leads to a steeper drop and thus to a shorter Debye length. The reason for that can be explained with the better screening of the surface charge over a shorter distance as there are more ions available for charge compensation. In this model the longest possible Debye length in water is about 640nm. This is due to the auto dissociation of water leading to a fixed minimum of ions in the solution, which cannot be further reduced. What also can well be seen is that close to the surface the concentration of the counterions is dominant, but after a certain distance the concentration of co- and counterions is equal to each other, which indicates that this is the bulk solution without any net charge.

Now our next step to compare the linear and the full solution of the Poisson-Boltzmann equation [all three equations; 9] so that we can figure out whether the Debye-Hückel approximation is good. This is easily done by plotting the potential over the distance for both solutions at different potentials applied to the surface as it has been done in [plot; 9] for a 20mM monovalent salt. (Note that the y-axis has a logarithmic scale.) One thing we can conclude from the plot is that we achieve a good linear fit of the full solution using the Debye-Hückel approximation at small surface potentials. At higher applied potentials the curves of the full solution have a steeper decay for $x < \lambda_D/2$ and thus an overall lower potential within the solution.

As in the chapter about the Helmholtz Layer we also want to find an equation for the capacitance of the diffuse electric double layer described by the Gouy-Chapman Theory. Therefore we can use the Grahame equation in which Grahame derived a relation between surface charge σ and surface potential ψ_0 [Grahame equation; 10]. Plotting surface potential over surface charge [plot; 10] for different salt concentrations we can see that there is a linear behaviour for low potentials around 40...80mV and else we see that there is more surface charge required for reaching the same surface potential when rising the salt concentration.

Now building the differential fraction of surface charge and surface potential we get the capacitance we have been looking for [bottom equation; 10]. At low potentials we can use the series expansion for cosh getting the following term:

$$C_{GC}^A = \frac{\varepsilon \cdot \varepsilon_0}{\lambda_D}$$

In the Gouy-Chapman Theory the diffuse electric double layer resembles a plate capacitor of a thickness equal to the decay length λ_D .

2.2.3 Limitations of the Gouy-Chapman Theory

In this chapter we want to discuss the limitations of the Gouy-Chapman Theory as there were many assumptions made, which compulsorily lead to imperfections.

- One of these assumptions is considering the charge distribution as a continuum, which does not correlate with its discrete nature.
- Another imperfection is the negligence of the ion's finite size.
- Disregarding any possible non-Coulombic interaction like the overlapping of the ions' hydration shells can also lead to inaccuracies.
- Furthermore the solvent – water in our case – is treated like a continuous solvent with constant permittivity ε . This cannot be correct as polar molecules (water is a dipole!) are hindered from rotating freely due to the strong electric field near the charged surface and thus a drastic change of the permittivity can be caused (in fact ε is reduced from 81 down to 6 in the primary bound water layer!).
- Assuming flat surfaces on a molecular scale we exclude biological membranes from our considerations as there one can observe molecules of sizes bigger than the decay length. If such a molecule (e.g. a phospholipid) has charges distributed all over itself and is additionally realising thermal motion, mistakes will automatically been made.
- ...

Nevertheless the comparison of theory and experiment shows that good predictions can be made using the Gouy-Chapman Theory for symmetric electrolytes at salt concentrations below 0.2M and potentials below 50...80mV.

2.2.4 Stern's Modification

A further development has been made by Stern, who combined the ideas of the Helmholtz Layer and the Gouy-Chapman Theory. Basically he divided the “electric double layer” into two different ones – the inner layer also being called Stern Layer right on the solid and the diffuse outer layer called Gouy-Chapman Layer passing into the bulk water. Both layers are separated by the ζ -potential. The Stern layer is a bound layer of adsorbed and immobile ions whereas the Gouy-Chapman Layer is a diffuse layer with mobile charge carriers. The inner layer is again subdivided into two layers – the Inner and the Outer Helmholtz Plane (IHP or OHP) [scheme; 12]. Within the IHP specific adsorption can be observed i.e. the ions' hydration shell is prised open allowing the ions to covalently bond to the surface. The OHP contains only non-specifically adsorbed ions in their hydration shells [graphic; 12]. The potential drop in the IHP and the OHP respectively is linear, the drop in the diffuse layer is again exponential [potential characteristics; 12]. The capacitance of the double layer in Stern's modification is the one of two capacitors in series [capacitance; 12].

3. Experiment - Adsorption at the Interface

3.1 The Mercury Drop

As we have already seen above there is different ways of adsorption at the interface (IHP and OHP). What made Stern act on this assumption is discussed in this paragraph.

One aim when dealing with a sli is to know the charge density right at the interface, with the former somehow being linked to the adsorption at the interface. A very famous experiment dealing with that problem during the first half of the 20th century is the mercury experiment basically investigating a charged mercury drop within an electrolyte. Though mercury is not a solid, it has similar properties as a solid metal and such way it should be suitable for finding out more about charge density at a metal-electrolyte-contact. Furthermore being liquid, the mercury surface shows low chemical activity and can be easily cleaned and renewed. A special feature of mercury is that it has a measurable surface tension γ . For constant pressure and temperature the surface tension can be written as the fraction of change in Gibbs free energy over change in surface area [surface tension; 14]. As one can see the formation of a bigger surface is unfavourable. An equation describing the whole energy balance at a sli is

Gibbs' Adsorption Equation including thermodynamic changes as well as changes in surface tension, the overall potential and chemical potentials [Gibbs' Adsorption equation; 14]. To make this equation easier we assume pressure, temperature and overall potential not to change. This way we get the Gibbs' Adsorption Isotherm Equation. Considering the excess charge (or surface charge density) at the surface to be the number of charge carriers per unit area times the Faraday constant and entering this into the Gibbs' Adsorption Isotherm we reach the electrocapillary equation [excess charge, electrocapillary equation; 14]. So now for the excess charge we can write:

$$\sigma^M = -\left(\frac{d\gamma}{dE}\right)$$

And we see that the repelling excess charges (they are of same sign) lead to a lowering of the surface tension.

For our next step we define the so called point of zero charge (pzc) as the potential where there is now charge left within the metal (i.e. the mercury drop in our case), because all implied charges have recombined with charges from the liquid. When now plotting surface tension over potential the plot should have a maximum at the pzc, as there is no repelling charges reducing γ . In addition we would expect the plot to be symmetric as there is now difference in the repulsion i.e. the Coulombic interaction of positive or negative charges each among themselves. Looking at plots for different electrolytes we see that there is *no* symmetry [left plot; 15]! (Note that the x-axis is normalised to the pzc and averaged according to the different electrolytes.) An explanation found for the observed asymmetry is the phenomenon of specific adsorption – in the case of mercury anions do specifically adsorb and cations do not. If we integrate the asymmetric plot we get excess charge plotted over potential, what nicely depicts the meaning of the pzc [right plot; 15].

3.2 Specific Adsorption and its Parameters

Based on the results of various experiments we want to find out what influences specific adsorption.

Concerning the charge density on the solid surface it has been observed that the specific adsorption of an ion rises with rising amount of opposite charge carriers within the solid due to Coulombic attraction. Plotting the charge of specifically adsorbed ions over the charge density [upper plot; 16] one can see that anions can be absorbed even when having a negative net charge within the solid. Thus it is not astonishing that anions seem to have a greater

tendency to specifically adsorb, which leads to the conclusion that the ion type always has to be taken into consideration. Looking at [lower plot; 16] we see that with rising ion size - i.e. rising radius - also the specific adsorption is rising. So e.g. F^- is a very small ion and as such is very unlikely to be specifically adsorbed. This has to do with its respectively strong primary hydration sheath, which first of all needs to be broken to achieve specific adsorption – also see [table; 17]. Another observation, which has been made, is that rising the salt concentration within the electrolyte leads to a higher specific adsorption. The influence of temperature can be seen in [plot; 17]. As thermal fluctuations hinder the covalent bonding an increase of temperature tends to result in a decrease of specific adsorption.

We can conclude that of general importance are:

- The type of the solid (metal, organic, hydrophobic or hydrophilic,...) with its surface texture.
- The solvent-solid interaction (mainly water-solid), which by solvation of the surface and desorption processes can in turn create vacancies for adsorption.
- The solvent-adsorbate interaction expressed e.g. via the hydration sheath.
- ...

4. Simulation

By now we have seen that many influences on adsorption at a sli can be directly measured. But there are also limits of observation. In fact many experimental results are striking the so far developed theory! Facing a rising complexity of parameters to be considered there has no “all-describing”-theory been found yet! One resort being practiced is to develop models for simulation and then to compare the results with the real experiment. Starting with the development of the computer technology in the early 1970ies this path has been chosen by many theoretical physicists.

4.1 The Four State Model

In 1975 Roger Parsons presented a “Primitive Four State Model For [a] Solvent At The Electrode-Solution Interface” based on an idea already proposed by Damaskin and Frumkin. The intention of this model is to explain the shape of experimental capacitance-surface charge

curves of the electric double layer, where two typical minima and one maximum were observed [plot; 20], which could not be explained so far. In the Four State Model special attention is turned to the dipole moment of water [upper graphic; 20] which is supposed to cause an extra potential drop and therefore having influence on the capacitance. The model is developed assuming that there are no ions specifically adsorbed to the surface of the solid and instead of that the first adsorbed layer is supposed to be a monolayer of water. Within this monolayer four states are differed. First of all single water molecules are distinguished from water molecules in clusters. And second two different possible dipole orientations towards or away from the surface are taken into account [graphic; 21]. To each state the number of its appearance is assigned in a way that the sum of all four numbers renders the total number of water molecules in the monolayer. Furthermore each water molecule is assigned its dipole moment - μ_c for a water molecule in a cluster and μ for a free water molecule. Every state is matching certain energy values [solvent molecule in cluster, free solvent molecule; 21]. Here one should especially pay attention to the additional energy term for free solvent molecules, which is provided for different bonding to the interface of either free molecules or molecules in clusters. The potential drop over the electric double layer $\Delta\phi$ is now imagined to be the sum of a potential ψ due to free charges and a potential χ due to the water dipoles [potential drop, 21]. With σ being the charge on the metal, the total capacitance for this model can be calculated as:

$$\frac{1}{C_i} = \frac{d\Delta\phi}{d\sigma} = \frac{1}{C_0} + \frac{d\chi}{d\sigma}$$

Now the basic idea is to vary all unknown parameters $\varepsilon, \mu_c, U_b^+, U_b^-, C_0$ of the model and to use Boltzmann statistics for the number of appearance of each state. Some plots which are achieved this way allow us to compare the simulation with the real experiment [all plots; 22] and indeed one can see that certain characteristics seem to be covered by the Four State Model.

From adapting the parameters following qualitative results can be made: There must be about three water molecules in each cluster. The total dipole moment of one cluster is approximately the same as the one of a single water molecule due to possible ring groupings within the cluster [graphic; 23]. The asymmetry in the shape of the capacitance-surface charge curves can be explained with the different stability of the two possible orientations of the molecules. The shape itself with its maximum and the two minima can be well understood when plotting the number of appearance of each state over the charge density [plot; 23] (the overall number is normalized). The maximum is reached when the charge density on the metal is zero. In this

case as many clusters are oriented towards the surface as away from it and thus switching the orientation of clusters is very easy, which can be interpreted as a high ability to store charges what again is equal to a high capacitance. The single water dipoles do not show any orientation at zero charge and thus must not be considered yet. Applying a potential and this way putting charge on the metal one orientation of the clusters is being preferred, which reduces the “switching possibilities” and thus the capacitance. Increasing the potential more and more starts including oriented single water molecules into the monolayer and at high charge densities we reach a saturation region for each sign of charge. In between the maximum and each saturation region the minima are located.

4.2 Diffuse Layer Capacitance

When looking at more experimental data on the double layer capacitance like in [left plot; 24] one can observe a huge capacitance minimum around the pzc for very low salt concentrations. The influence of the diffuse layer capacitance [equation; 24] being in series with the capacitance of the Helmholtz Layer capacitance can be viewed in [right plot; 24]. And being in fact a very low capacitance, the diffuse double layer (Gouy-Chapman Layer) dominates the total capacitance as accordingly applies:

$$\frac{1}{C_{tot}} = \frac{1}{C_H^A} + \frac{1}{C_{GC}^A}$$

4.3 Adsorption Capacitance

To round off the picture of parameters influencing the capacitance of the electric double layer a third one has to be mentioned at this place – adsorption. Assuming adsorbed charged molecules we can make use of the adsorption isotherm in this case being the so called Langmuir isotherm [Langmuir isotherm; 25]. On the left side of this equation θ is the surface coverage allowing us to calculate the surface charge as indicated in [surface charge; 25]. On the right side a is the activity and the two exponential functions being combined to one have ΔG equal to the energy needed for adsorbing a molecule in units of RT as their argument. How to calculate the capacitance caused by adsorption can be seen in [lowest equation; 25]. Now plotting the surface coverage over ΔG we get a plot like in [left plot; 25]. If there is no free energy available i.e. $\Delta G = 0$ than half of the surface is covered with adsorbed molecules and half is not. Reducing the energy leads to a “cleaning of the surface”, rising the energy lets

the surface be completely covered with adsorbed molecules. The differentiation of [left plot; 25] gives us [right plot; 25], which is nothing else but the capacitance over ΔG . For energies around zero ΔG we see a maximum of the capacitance and thus the evidence that adsorption does have an influence on it is given.

4.4 Molecular Dynamics Simulations

Nowadays the most advanced level of computer simulations in context with the sli are the so called Molecular Dynamics Simulations taking into account the molecular structure and interactions of thousands of molecules.

Recently in 2004 a group of scientists dedicated their attention to water at hydrophobic (i.e. nonpolar) substrates having in mind to learn more about the driving force behind the self-assembly of organic substrates in water, such as protein folding or enzymatic reactions. The aim of the group was to measure the water density at the interface depending on the curvature of the substrate (i.e. the solid), the temperature and the pressure using Molecular Dynamics Simulations. Therefore a simulation cell being a cubic box filled with $\sim 1000 - 3000$ water molecules has been modelled. Periodic boundary conditions simulate an “endless” amount of the molecules. For modelling the water an already developed model has been used – the SPC/E water model. For the water-water interactions the standard Lennard-Jones potential has been applied. The solvent-water interactions were described with the repulsive (solvent = hydrophobic substrate) part of the so called Buckingham potential.

Putting a spherical solute into the simulation cell leads to the following results: For a solute with a small radius (here 0.4nm) the water density close to the surface is increased, whereas for a solute with a big radius (here 1nm) a depletion of water can be observed right at the surface [plots; 26]. A temperature increase always causes a density decrease, which for large spherical solutes results in a rising depletion layer thickness. The plots with different applied pressure show that by increasing the pressure for small solutes the water density at the surface can be increased even more and that the depletion layer of bigger solutes is being reduced – both only for remarkably high pressure increase.

To simulate a planar hydrophobic surface within water 64 alkane molecules and 2781 water molecules were modelled [graphic; 27]. As a planar surface can be considered a sphere with endless radius it is plausible that the results achieved are qualitatively the same ones as for the big spheres [left and right plot; 27]. Here a layer thickness of 0.25nm has been observed.

Besides a potential drop at the interface caused by dipoles and giving reason to assume the top water layer at the interface to be oriented has been noticed [central plot; 27].

Experimental data also gives reason to the existence of a depletion layer of water on hydrophobic substrates. In 2003 heavy water (D_2O) on a hydrophobic plane has been studied using Neutron Reflectivity Measurements (NRM) and Atomic Force Microscopy (AFM). In the former a depletion layer thickness of 2-5nm has been observed and in the latter a thickness of 20nm. In NRM observed Kiessing oscillations gave reason to a gas layer at the interface [plot; 28]. The local maxima and minima in the plot of reflectivity over $Q \propto \sin \theta$ of neutron beam were deduced from possibly occurring interference at the supposed gas layer similar to Bragg reflexions. The pictures obtained with AFM [right plot; 28] show the tapping mode topology image of “nanobubbles” interpreted as gas bubbles on top of the solid surface. Here also a memory-effect has been observed: After taking the solid out of the heavy water and later on putting it back into it, bigger “nanobubbles” were asserted, what is supposed to be caused by gas bubbles remaining on the solid and later on fusing with others.

5. Application

5.1 Electrokinetics

The research done on the sli allowed a lot of useful applications to emerge. One of these applications is the field of electrokinetics. This field is for example important for developing lab on chip components aiming at reducing scales and costs, the power needed and thereby having the advantage of being portable and multifunctional devices.

5.1.1 Zeta-Potential, Stream Current and Stream Potential

The key to electrokinetics is the so called zeta-Potential. As discussed in 2.2.4 it separates the immobile inner layer from the mobile diffusive layer [upper graphic; 30]. The exact position of the ζ -potential in fact is not the exact border between the inner layer and the diffuse layer as can be seen in [lower graphic; 30]. Under a pressure driven flow ions of the diffusive layer are able to move and such way a shear plane is formed. In this context a qualitative expression for the ζ -potential would be:

$$\zeta = \psi(x_{shear}) - \psi(x_{bulk})$$

(Until now the potential of the bulk solution has been regarded to be zero, which is just a simplification, of course.)

Now we want to investigate a fluid in a microtube [graphic; 31]. A ζ -potential unequal zero grants us movable net charges within the diffuse layer. Thus an applied gradient in pressure at the ends of the tube induces a stream of charges with a stream current in this case equal to:

$$I_{stream} = 2\pi r \sigma_D v_D$$

The parameter r is the radius of the tube, σ_D the charge density and v_D the drift velocity in the diffuse layer. The stream of charges due to the pressure driven flow leads to a depletion and an accumulation of charges respectively at the ends of the tube and therefore a streaming potential can be measured:

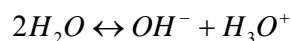
$$U_{stream} = \frac{2\sigma_D v_D l}{r \cdot k}$$

Here l is the length of the tube and k the specific conductivity of the solution.

5.1.2 Electrokinetic Measurements on Adsorption

In the year 2001 a group of scientists analysed the charge density of the inner layer at the sli using electrokinetic measurements and thereafter making conclusions on preferential adsorption. Their utilised experimental setup is called Microslit Electrokinetic Setup basically consisting of two parallel plates of variable very small distance to each other and a liquid in between them [graphic; 32]. This setup allows one to measure the stream current and the stream potential within the slit. Now the basic idea of this experiment is that the sign of the ζ -potential reveals the sign of the total charge within the immobile inner layer. To determine the ζ -potential two equations indicating its correlation to the stream current and the stream potential respectively can be used [equations; 32].

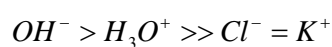
In pure water always a negative ζ -potential is observed. This happens due to the auto dissociation of water:



Obviously the negatively charged OH^- ion is preferentially adsorbed when competing with the H_3O^+ ion. Adding KOH into the water and rising its concentration step by step meanwhile measuring the ζ -potential results in a characteristic plot [KOH; 33]. One can see that at low concentrations the OH^- ions of KOH are preferentially adsorbed as the ζ -potential is getting even more negative as if there was only water. After reaching a concentration of $10^{-5} mol/l$

we observe the compression of the double layer, i.e. increasing surface charge compensation already within the inner layer (screening...) and thus the absolute value of the ζ -potential is reduced again. A totally different behaviour can be seen in [HCl; 33]. Due to the protons of hydrochloride a sign reversal can be found so that in this case the H^+ ions are the ones which are preferentially adsorbed. Once again one can observe the compression of the double layer as at high concentrations the value of the ζ -potential tends towards zero – this time coming from positive values though. Adding potassium chloride into the water besides the compression of the double layer nothing special seems to happen [KCl; 33].

At this point one can conclude that the so far obtained data reveals the existence of preferential adsorption ordered the following way:



The disequilibrium between OH^- and H_3O^+ implies a pH-dependence. Plotting the ζ -potential over the pH for different salt concentrations [plot; 34] shows us that the isoelectric point (IEP) can be found around pH 4, which is low indeed. By definition the IEP is the point where the ζ -potential is equal to zero. A pH equal to 4 indicates that there are much more H_3O^+ ions than OH^- ions in the solution and the IEP indicates that there is no net charge within the diffuse layer. Out of this we get another evidence for the order of preferential adsorption given above being correct.

Two important factors for adsorption have been worked out: The structure of the hydration shell and the capability to bind interfacial water via hydrogen bonds. The OH^- ion e.g. is known to have less stable hydration structures than the H_3O^+ ion and therefore might more easily escape out of its hydration sheath building up hydrogen bonds with the interfacial water.

Another experiment using ph-Dependant Force Spectroscopy has been conducted in 2002 leading to the conclusion that immobilized interfacial water is acting as a template for hydroxyl adsorption and thus favouring it. For this process the density of molecular units of water networks on the surface each building a template is a crucial parameter.

At this point it should be mentioned that the ideas and interpretations listed above are not based on any theory yet so they are nothing but suggestions how one could understand the experimental results.

5.2 Electroosmosis

The diffusive process of reaching equilibrium after an applied gradient in e.g. pressure, temperature or concentration is called osmosis. When applying a potential gradient in form of an electric field along a charged capillary filled with a liquid we deal with electroosmosis and observe a movement of the liquid relative to the stationary charged surface [upper graphic; 35]. The electric field induces a force on mobile net charges in the diffuse layer displacing the former. Due to the viscosity of the liquid the displacement in the diffuse layer drags the bulk fluid along. Such way a drift velocity of the fluid described with the Helmholtz-Smoluchowski equation can be measured:

$$v_{\zeta} = \frac{\varepsilon \zeta}{\eta} E_x$$

The fraction is describing the osmotic mobility with ε being the permittivity and η the viscosity of the fluid. The value of the zeta-potential is represented by ζ . One advantage of electroosmosis can be recognized when comparing it to a pressure driven flow [right graphic; 36]. Looking at the time development of the flow after switching on the electric field, at first one can see the dragging-effect and right afterwards the establishment of a laminar flow [left graphic; 36]. This way electroosmosis is a very useful technique of creating laminar flow at low Reynolds' numbers in microfluidics.

6. Review

Starting to describe the solid-liquid interface with the theoretical concept of the electric double layer the Helmholtz Layer, the Gouy-Chapman Theory as well as Stern's modification were presented. Continuing with experiments we studied adsorption and its parameters. Later on we even saw results of modern experimental techniques like AFM and NRM. Due to contradictions between theory and experiment a further step to understanding has been made: models for computer simulations were developed. The Four State Model for example could explain certain capacitance curves and Molecular Dynamics Simulations gave more insight to water density profiles at hydrophobic substrates. Until today a full describing theory has still not been found though. So at the moment the phenomena of slis are observed and lots of data is being collected aiming at a better understanding of what actually does happen and why. Nevertheless already a lot of useful applications have emerged from the field of slis.

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