Chapter 4
Charge at Interfaces

Contents

4.1 The Maxwell-Wagner-Sillars Effect

Charge accumulation can take place at any interface, following the Maxwell-Wagner-Sillars effect that is observed whenever current flows across the interface of two materials [1].

Two parameters, dielectric constant ε and conductivity σ, define the macroscopic electrical properties of materials and their ratio $\tau = \varepsilon/\sigma$ is the relaxation time for each equivalent electric circuit given by the parallel capacitance and resistance of each material. When an electric current j crosses the interface, the difference in the relaxation times produces charge accumulation at the interface. This is a macroscopic dielectric polarization process that is called interfacial polarization.

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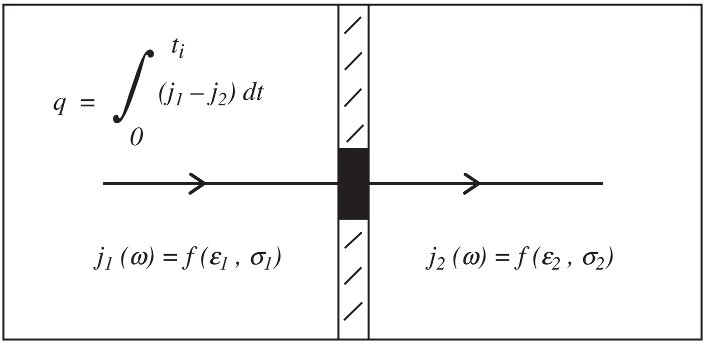

Fig. 4.1 Schematic description of the Maxwell-Wagner-Sillars effect

The time constant for charge accumulation is different from the time constants for each contacting material forming a series circuit, because it also depends on geometric factors. This is understood considering that the contribution of each material to the capacitance and impedance of the series circuit depends not only on the respective values for ε and σ but also on film thickness and interfacial area. This is represented in Fig. 4.1.

Given the non-specificity of the Maxwell-Wagner-Sillars effect, it should be expected to take place in every kind of interface, thus producing interfacial polarization in any interface.

4.2 Solid–Liquid Interfaces

Solid–liquid interfaces acquire charge for many additional reasons: ionization of solid surface groups, selective adsorption/desorption of ions from the solid surface, and differential solubility of ions from an ionic compound. Selective adsorption of H^+ or OH^- ions from water has paramount importance, because is found in most natural environments.

4.2.1 Mechanisms for S/L Interface Charging

Ionization of solid surface groups is expected in acidic metal oxides and in polymers containing carboxylic groups, like cross-linked poly(styrene sulfonate) resins. On the other hand, polyethylene surfaces are more or less oxidized [2] and they may contain pendant carboxylic groups that undergo ionization in the presence of water and other solvents. When these systems are considered, it is important to keep in mind that the pK_a for the -COOH dissociation reaction is not a constant, as in low-MW solutes. Instead, pK_a for ionizable groups bound to a polymer chain or a surface varies with the degree of ionization [3], due to the effect of the increased negative charge density on the retention of H^+ ions leaving the surface.

Differential solubility is observed in salts and it is often neglected because chemistry teachers normally introduce the topics of solubility and the solubility product K_{ps} using an oversimplified picture. A frequent example is silver iodide and its solubility equilibrium is represented by Eq. (4.1).

$$AgI = Ag^{+} + \mathrm{I}^{-} \ with \ K_{ps} = \left[Ag^{+}\right]\left[\mathrm{I}^{-}\right] = 8.52 \times 10^{-17} \tag{4.1}$$

This suggests that the remaining undissolved AgI particles are electroneutral and the saturated solution contains equal concentrations of Ag^+ and I^- ions, yielding $p_{Ag} \approx 8$. Indeed, AgI particles are only neutral when $p_{Ag} = 5.5$ and $p_{I} = 10.5$, this means, the two concentrations differ by five orders of magnitude and both concentrations depart from equilibrium by nearly three orders of magnitude.

This is easily understood, considering that unsolvated silver cations are significantly smaller (129 pm radius) [4] and thus more solvated [5] by water than iodide (206 pm). Consequently, silver ion activity is lower within water than the activity of iodide, at the same concentration and Ag^+ actually exhibits extreme solvation effects that are not observed for any other ions except Zn^{2+} and Au^+ [6].

Selective adsorption of ions on the solid surface is easily observed with surfactant [7] and polyelectrolyte solutions. For instance, immersion of most solids on aqueous solutions of anionic surfactants like sodium lauryl sulfate leads to strong adsorption of the lauryl sulfate anions, much more intensely than Na^+. This imparts to the surface a large negative charge that is one of the main factors of the dispersant capabilities of this and other surfactants, including detergency. The hydrophobic interactions responsible for surfactant adsorption largely overcome the electrostatic repulsion among adjacent adsorbed ions allowing the formation of adsorbed multilayers, hemimicelles [8, 9], and solloids[1] [10]. For these reasons, surfactants and their mixtures can drastically change the interfacial properties and hence they are used in many industrial processes such as dispersion/flocculation, flotation, emulsification, corrosion inhibition, cosmetics, drug delivery, chemical mechanical polishing, enhanced oil recovery, and nanolithography. On the other hand, since surface-active substances are widespread in any terrestrial environment and most are ionic compounds, they certainly play an important role in imparting charge to S/L interfaces.

4.2.2 The Electric Double Layer

Thus, a charged solid surface immersed in a liquid usually acquires excess charge and this interferes with the distribution of ions in the liquid forming an *electrical double layer* [11, 12], a peculiar, complex environment (Fig. 4.2). The water molecule dipoles adjacent to the surface are oriented and ions with opposite charge may bind strongly to the surface forming the *Stern layer* while other ions located beyond the *Stern plane* form the diffuse part of the double layer (or *Gouy-Chapman layer*), that obeys the Poisson-Boltzmann distribution of charge density. Strongly bound solvent

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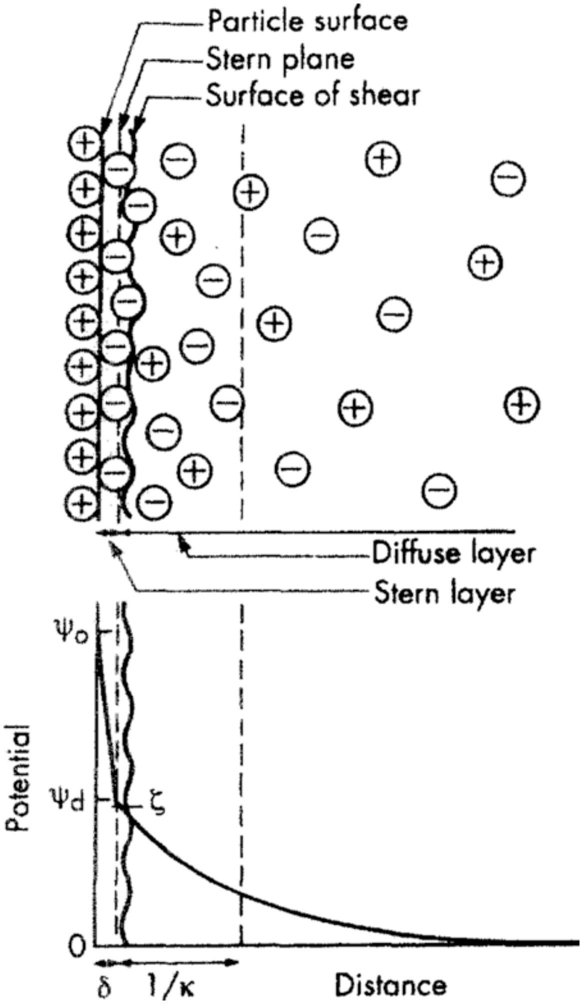
[1] Solloids are surface-mediated colloids or colloids made up of any chemical moieties on surfaces [10].

Fig. 4.2 Schematic representation of the structure of the electric double layer according to Stern's theory. Ψ_d = Stern potential, ζ = Zeta potential which corresponds to the shear plane close to Stern plane. Reprinted with permission from [11]



and ions move together with the surface and they are separated from the rest of liquid by a slipping plane. Electric potential at the slipping plane is named *zeta potential (*ζ).

This prevalent picture of the electrical double layer is often modified by specific adsorption effects. For instance, Ba^{2+} cations adsorb on hematite particles with excess charge and anionic surfactants adsorb on negative silicate and cellulose surfaces. pH plays a major role in determining surface charge, since most surfaces show specific binding of H^+ or OH^-, even inert surfaces like hydrocarbons and fluorocarbons. For instance, water flowing through polyethylene or polytetrafluoroethylene tubing acquires excess positive charge due to OH^- adsorption (Fig. 4.3) [13].

Changing the solution pH is an important tool to change the interfacial charge. Adding acid usually increases solid surface charge while adding base makes the surfaces more negative [14], as seen in Fig. 4.4. On the other hand, measuring

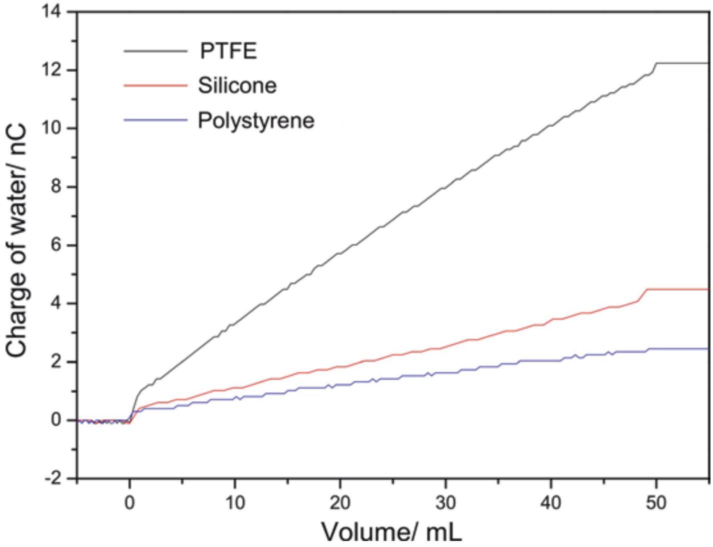


Fig. 4.3 Representative plots showing electrical charge acquired by 50 mL of deionized water after flowing through hydrophobic materials. Reprinted with permission from [13]

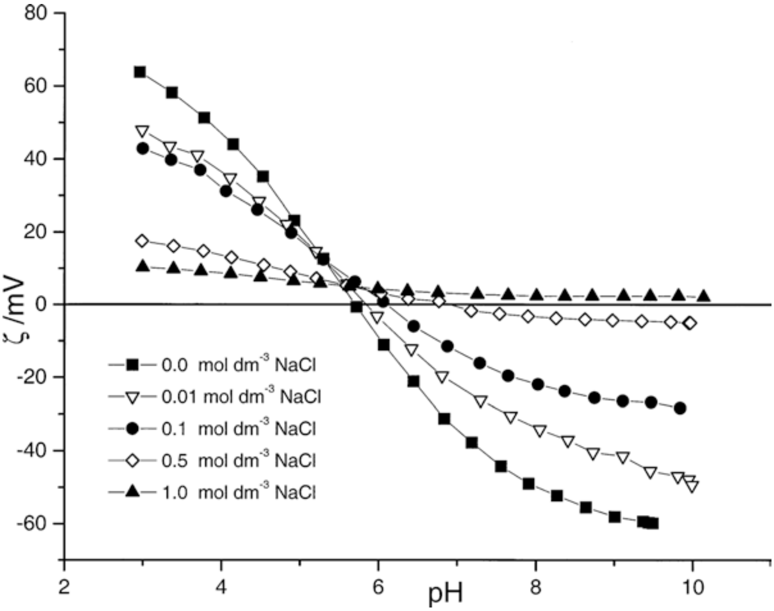


Fig. 4.4 Effect of pH for various NaCl concentrations on zeta potential of titanium dioxide (anatase). Reprinted with permission from [15]

the zeta potential of interfaces is an invaluable tool in the study of the chemical structure and properties of solid surfaces that is essential information, e.g. in mineral processing.

4.2.3 Experimental Methods

Potential measurements at the particle surface or at the limit of the Stern layer are not currently feasible. However, potential at the slipping plane is determined using electrokinetic data and it is called zeta potential. The main tools for assessing the electric properties of solid–liquid interfaces are thus potentiometric measurements using different types of electrodes and zeta potential measurements based on the various electrokinetic phenomena, especially electrophoresis, electrosmosis, and sedimentation potential. However, surface charge and electrokinetic charge are very different double layer characteristics and the significance of each should be clearly recognized, following a critical evaluation by Lyklema, who made outstanding contributions to this topic [16]. The availability of both types of data for well-defined systems makes accessible much relevant information on the electrical double layer, including counter-ion adsorption, stagnant layer conduction, and overcharging. Lyklema also discussed the interpretation in terms of specific adsorption and ion correlations.

Potentiometric techniques are apparently simple and easily implemented in a number of different systems. Unfortunately, this is often deceiving. Application of potentiometry to the determination of proton surface charge at mineral/water interfaces was recently reviewed [17], covering conventional experimental procedures and providing a critical discussion of problems with the techniques. Recommendations for obtaining reasonable and comparable results were made, discussing the most important experimental parameters. The authors proposed a reference titration procedure to allow comparisons of experimental data, providing a checklist for researchers and reviewers that could improve the usefulness of published data.

Other techniques for ion adsorption measurements are also used to determine surface charge. However, simple comparison of adsorption and potentiometry results may lead to apparent disagreement that may indeed reveal previously unsuspected complexity of the surface. For instance, in a study on charge in soil particles the authors observed that "...estimates of net surface charge by potentiometric titration and ion adsorption did not agree, especially as the soil pH was adjusted away from the point of zero charge. This lack of agreement is attributed to dissolution reactions of minerals and organic matter at high and low pH, which consume acid or base and overestimate surface charge [18]."

Electrophoresis is by far the richest source of zeta potential data but it is unsuitable to the study of macroscopic S/L interfaces, like glass or textiles. These can be comminuted into small particles for electrophoresis experiments but comminution is often accompanied by mechano-chemical reactions that produce new surfaces, different from those existing in the original solid. In this case, zeta potentials are calculated from electro-osmosis or streaming potential experimental results [19].

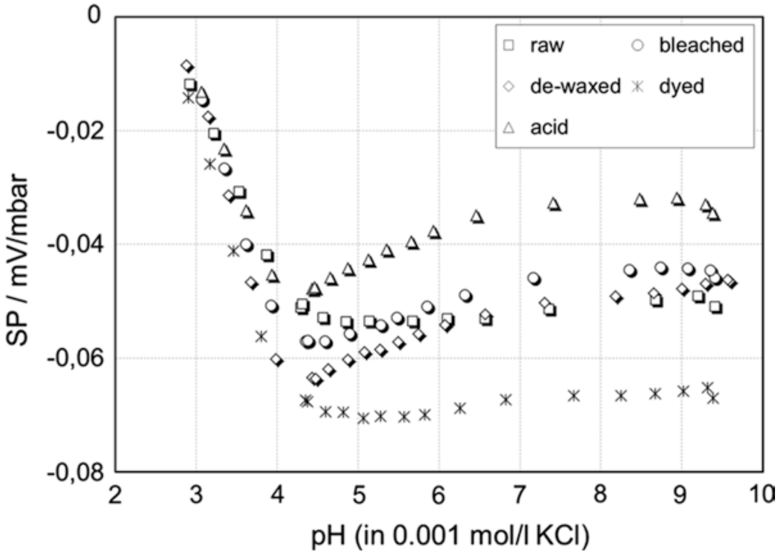


Fig. 4.5 Streaming potential of raw cotton fiber and the same but following various treatments. Reprinted with permission from [22]

Cellulose is a rather intractable polymer due to the scarcity of solvents and to the fact that it decomposes thermally prior to melting. For this reason, cellulose and cellulosic materials are interesting examples of the use of streaming potentials (Fig. 4.5) to characterize charged groups in a complex, fibrous, and hardly soluble solid, including film membranes [20–22].

4.3 Liquid–Liquid Interfaces

Potential difference is observed across liquid–liquid interfaces following different mechanisms. An important case is differential ion diffusion across the interface that produces junction potentials (see Chap. 2). Another type of frequently observed phenomena is selective ion adsorption, as in the so-called membrane electrodes and in negative charge formation at water–oil interfaces.

The latter is the important case of OH^- ion accumulation at the interfaces between water and non-polar media like oils [23] and polyolefins. It is also related to the complex behavior or ions at water–air interfaces that will be discussed in the forthcoming section.

4.4 Solid– and Liquid–Gas Interfaces

This is a broad topic covering many different situations, depending on the nature of the solid or liquid. The possibility of charge transfer to and from the atmosphere, mediated by water droplets and vapor, was recognized by Faraday in the "vapor electricity" discovered by Lord Armstrong and by Kelvin in his "water drop equalizer". This instrument was used to measure atmospheric electricity and his functioning was based on charge transfer between a water tank and the atmosphere, at a fast rate. According to Kelvin, ". . . any difference of potentials between the insulated conductor and the air at the place where the stream from the nozzle breaks into drops is done away with at the rate of five per cent, per half second, or even faster" [24].

However, this information was later neglected, e.g. in E. Schrödinger's doctoral thesis [25], and other work [26, 27] that assigned the effect of air humidity on electrostatic charge dissipation to the increased surface conductance of the electrified solids. The dominating role of water vapor as a charge carrier to and from S/L interfaces and the role of the atmosphere as a charge reservoir received additional support, recently [28].

4.4.1 Liquid–Gas Interfaces

Spontaneous establishment of electric potential difference at the water–air interface is historically very important since it was already used by Kelvin.

There are at least three other areas of investigation revealing important information on the electrical properties of liquid–gas interfaces: Langmuir-Blodgett monolayers, interfaces of aqueous electrolyte solutions, and the study of water carrying excess charge. The two first topics are discussed in this chapter while the latter is further discussed in Chaps. 6 and 7, in this book.

4.4.1.1 LB Monolayers

Langmuir-Blodgett monolayers [29, 30] have been widely used to study structure and properties of many systems, ranging from surfactants to viruses and quantum dots. They are also used to manufacture self-assembled films and multilayers. For these reasons, they are by themselves a huge topic where the importance of interfacial electric fields in phenomena like molecular interactions, reorientation, and induced conformational changes was clearly demonstrated [31] and this is often easier than is a 3D system. On the other hand, interfacial charge in monolayers is largely dependent on the complex monolayer-forming species rather than on more strictly interfacial phenomena. For this reason, this topic will not be treated in detail here and the interested reader is directed to the excellent books and reviews on this topic.

4.4.1.2 Interfaces of Water and Aqueous Electrolyte Solutions

Experiments [32–36], theoretical calculations [37, 38], modeling, and simulation [39, 40] done on these interfaces have produced an impressive amount of work [41], benefiting from new, sophisticated techniques [42] together with classical methods.

This section does not give a full account of all the work done in this area but it presents some examples of the experimental results addressing the main points of divergence among the various authors.

For instance, vibrational sum frequency spectroscopy has been a rich source of information on ion accumulation at L/G interfaces [43, 44], showing also their effect on the surface water structure. HCl, HBr, and HI cause a significant disruption in the hydrogen-bonding network at the air–liquid interface, similar to that which is observed for sodium halides. One of the observed effects is a decrease in the number of dangling OH bonds relative to the neat water surface. These authors also found evidence for the presence of hydronium and Zundel ions and for increased concentration of bromide and iodide ions at the interface, in agreement with the electron spectroscopy results.

One open question is especially relevant: is the surface of pure water acidic or basic [45, 46], this means, which ions are preferentially adsorbed at the water–air interface, H^+ or OH^-?

Garett [47] reviewed this topic emphasizing the accumulation of some anions at the air/water interface and not in the bulk, as usually happens to the cations. He also presented simulations explaining those positive surface adsorption excesses.

Jungwirth [33] used results from surface-selective spectroscopies and molecular simulations. Both approaches indicate that the heavier and thus softer halide ions can be present and even enhanced at the water surface. This author finds that hydronium but not hydroxide accumulate at the air/water and alkane/water interfaces. These findings were extended to water–protein interfaces and they supported a local model of interactions of ions with proteins aiming to the rationalization of ion-specific Hofmeister effects in the salting out of proteins.

An interesting analysis of the situation was made by Manciu and Ruckenstein [48], who applied a Poisson-Boltzmann model compatible with zeta potential experiments [49–52] to calculate the concentrations of ions at the interfaces. Their conclusions are as follows. For most pH values, the concentrations of both H^+ and OH^- are much larger in the interfacial region than in bulk. However, at very low pH values, the interfacial concentration of H^+ is lower than in bulk. At large pH values, the interfacial concentrations of both H^+ and OH^- are lower than in bulk for three independent sets of ion adsorption parameters, obtained from three different sets of experimental zeta potential results. These lower interfacial concentrations of H^+ and OH^-, at extreme pH values, arise from adsorption saturation due to the finite number of adsorption sites. The ratio between H^+ and OH^- concentrations is lower at the interface than in the bulk in most but not all cases. The interfacial ratio of H^+ and OH^-, divided by the same ratio in the bulk, depends on both the pH and salt concentration.

The thermodynamic model presented by Kallay and co-workers leads to some conclusions convergent with those in the previous paragraph, supporting experimental results on the dependency of the surface potential at the gas–water interface with the pH and showing that the interface is negative above pH 3.8 [53].

Further progress in this area is needed, not only to settle the current divergences but mainly because understanding these interfaces is needed to understand other important phenomena, like proton transfer at interfaces that is quite different from conventional proton transfer in bulk water [54]. The discrepancies between experimental results probably arise from the difficulty to avoid changing the excess charge in liquids and solids, inadvertently. This is probably due to handling or induction by neighboring solids, liquids, and the surrounding atmosphere that is often unduly neglected. The discrepancies among theoretical and computational results may arise from intrinsic limitations of the methods used or from computational difficulties to handle sufficiently large sets of molecules and ions.

4.4.2 Metal or Semiconductor/Liquid Interfaces

Metal or semiconductor–liquid interfaces are an essential topic of electrochemistry and electroanalytical chemistry, treated extensively in the excellent books authored by Bard [55] and Bockris [56]. A unique feature of electrodes is that the potential on the metal can be measured precisely with high time resolution. Moreover, it can also be changed by the researcher within a broad range, limited only by the onset of reduction and oxidation reactions at the two electrodes and the kinetics of the electrode reactions. The electrical double layer is a matter of great interest to electrochemists, who may count on a number of precise, time-resolved techniques whose power is not matched by the techniques available to colloid and surface chemists. For this reason, knowledge on the dynamic characteristics, structure and reactivity at electrode interfaces usually exceeds that available for many other kinds of interfaces [57].

A huge number of interesting and often unpredictable facts has been disclosed by electrochemical research, evidencing fascinating features of the electrode interfaces and of the power of electrochemical methods.

For instance, electrode interfaces can be used to generate unstable species, like radical ions in solution, by oxidizing or reducing stable precursors like polycyclic hydrocarbons and various nitrogenated compounds: aromatic amines, nitrocompounds, and nitrites. These free-radicals in solution engage in electron-transfer reactions that produce electrogenerated chemiluminescence (ECL), a powerful tool for ultrasensitive biomolecule detection and quantification using miniaturized biosensors capable of multiplexing detection with high sensitivity, low detection limit, and good selectivity and stability [58]. When ECL is produced within thermoresponsive redox microgels, its intensity is correlated with the collapse of microgel particles [59]. This is a good example of the flexibility in the access to complex, unstable species and fine control that are achieved by triggering chemical reactions at the metal–liquid interfaces.

4.5 Solid–Solid Interfaces

Potential differences develop across solid–solid interfaces, due to different mechanisms: (1) electron transfer, in metals and semiconductors; (2) transfer of tribo-ions formed mechanochemically; (3) selective partition of adsorbed ions, especially OH^-.

The first case is relevant in many areas, as in electrochemistry, corrosion, and microelectronics, and it is a well-developed topic that will not be further discussed here. The transfer of tribo-ions formed mechanochemically that was discovered recently is the topic of Chap. 9 in this book.

4.5.1 Selective Partition of Adsorbed Ions

Selective ion adsorption plays an important role that was first raised by the Whitesides group [60, 61], who described the fabrication and characterization of ionic electrets. These materials contain a long-lived electrostatic charge due to an imbalance between the number of cationic and anionic charges in the material. For instance, crosslinked polystyrene microspheres that contain covalently bound ions and mobile counterions transfer some of their mobile ions in air, in the absence of bulk liquid, to another contacting material. This selective transfer of mobile ions yields microspheres with a net electrostatic charge. A typical charge density is 1 elementary charge per 2000 nm^2, close to the theoretical limit imposed by the dielectric breakdown of air. It increases in an atmosphere of SF_6, compared to N_2. Other ionic electret materials are functionalized glass or silicon with covalently bound ions and mobile counterions. Charge patterns are built in these materials, using soft lithography [62].

These ideas have been extended to many other situations, because most solid surfaces contain some adsorbed water, even under low relative humidity, and water produces H^+ and OH^-. Moreover, the equilibrium concentrations of these two ions in pure water depend on the local electrostatic potential, under a non-zero electric potential. Following the presentation in Chap. 5, $[H^+]$ under a potential ϕ_1 is given by

$$-2.30RT\left(\log\left[H^+\right]-7\right)=F\left(\phi_1\right)$$

Thus, water in a region in space where $\phi_1 = 0.2\ V$ should have pH = 10.4. This is not macroscopically observed because the electric double layer formed at the aqueous interface shields the potential. Nevertheless, pure water contains excess concentration of H^+ or OH^- ions, depending on the adjacent electrostatic patterns so that it can supply ions for adsorption, depending not only on chemical affinity but also on the local potential.

4.6 Water Structures at Interfaces

The behavior of water at interfaces has been receiving great attention for many decades [63] with plenty of diverging results and conclusions drawn by distinguished authors. This is probably one of the topics where greatest disagreement is found, in current science. New proposals further contribute to the complexity of the situation and the level of conflict seems to increase continuously, adding to the many disputes that were already mentioned in this chapter. This is not surprising, considering that water itself is “The Most Anomalous Liquid” [64].

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