



Investigation of the structure of interfaces and transport mechanisms for adsorbed alkylsulfates
by Penny Maureen Oconnor

A thesis submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy in
Chemistry of
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Abstract:

Investigation of the structure of surfactants at metallic surfaces immersed in aqueous solutions was pursued as a means to better understand electrode transport and kinetics. It is thought that modified electrode surfaces can be utilized to study transport phenomena through a biological membrane.

Cyclic voltammetry was used to probe the characteristics of the modified surface and provide experimental tests of model predictions. The surface was not formed spontaneously, but was induced by a large negative potential. Several alkylsulfates with different counterions were investigated. Quantitative determination of differential capacitance and thermodynamic values showed that all of them follow the same mechanism for the reorganization within the metastable surface. Use of reducible analytes when added to the surfactant solution, revealed that the ions were being reduced at the electrode surface. Oxygen was shown to be reduced at some distance from the electrode, possibly on the outside of the thin film. Several mechanisms were proposed for the reduction of oxygen in the surfactant solution.

Computer simulation aided in the visualization of surfactant reorganization after a potential was applied to the electrode. Certain simplifications were used, so the system could be studied through a reasonably long period of time. Information regarding the effect of the water molecules and counterions on the thickness of the surfactant layer was obtained.

A model is proposed involving the information collected. The interface consists of a double layer of solvated surfactant and counterions. The geometry of this layer is very much dependent on the charge on the electrode. Reorganization towards a metastable state occurs when this charge is dramatically changed.

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AND TRANSPORT MECHANISMS FOR
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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date 13 August 1991

To mom, dad and Pedro

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ABSTRACT

Investigation of the structure of surfactants at metallic surfaces immersed in aqueous solutions was pursued as a means to better understand electrode transport and kinetics. It is thought that modified electrode surfaces can be utilized to study transport phenomena through a biological membrane.

Cyclic voltammetry was used to probe the characteristics of the modified surface and provide experimental tests of model predictions. The surface was not formed spontaneously, but was induced by a large negative potential. Several alkylsulfates with different counterions were investigated. Quantitative determination of differential capacitance and thermodynamic values showed that all of them follow the same mechanism for the reorganization within the metastable surface. Use of reducible analytes when added to the surfactant solution, revealed that the ions were being reduced at the electrode surface. Oxygen was shown to be reduced at some distance from the electrode, possibly on the outside of the thin film. Several mechanisms were proposed for the reduction of oxygen in the surfactant solution.

Computer simulation aided in the visualization of surfactant reorganization after a potential was applied to the electrode. Certain simplifications were used, so the system could be studied through a reasonably long period of time. Information regarding the effect of the water molecules and counterions on the thickness of the surfactant layer was obtained.

A model is proposed involving the information collected. The interface consists of a double layer of solvated surfactant and counterions. The geometry of this layer is very much dependent on the charge on the electrode. Reorganization towards a metastable state occurs when this charge is dramatically changed.

INTRODUCTION

Major attention has been given in recent years to the study of the structure of oriented monolayers. This is related in part to the fact that such systems are convenient models of the lipid region in biological membranes. Electrochemistry has long been used for the investigation of interfacial phenomena in systems such as the solid-liquid interface. Several years ago, in a voltammetric study of micelle solutions, we discovered that solutions of sodium dodecylsulfate (SDS) could be forced to self-assemble as a highly organized metastable surface on mercury coated electrodes. This phenomena led us to believe that the surfactant/electrode interface could be used to model a biological membrane. Because the double layer charging current shows the SDS to have four different conformations, which can be related to thickness changes in the surface, it was thought that the use of electrochemical methods as well as surface science techniques could be used to measure these thicknesses. With the advancement of computer methods, a series of molecular dynamic simulations should provide a microscopic understanding of the interface. The following sections in the introduction are offered to the reader so that the nature of the problem will be better understood.

The Electric Double Layer

History

The problem of the electric double layer is of fundamental importance in electrochemistry, and is continually being studied. The original idea of the electric double layer was described by Gouy¹ and Chapman² in 1913. Their analysis of the problem was based on the same premises as the Debye-Hückel theory (Poisson-Boltzmann equation). They considered the laws of electrostatic adsorption of ions caused by the interactions of the ions with the outer charge of the electrode. This theory found wide application in the interpretation of electrochemical experiments dealing with surface forces and electrokinetic phenomena. The Gouy-Chapman theory is still one of the basic theories of the equilibrium double layer.

Several years later a modification of the Gouy-Chapman theory was made by Wagner, Onsager, and Samaras.^{3,4} The correction was to account for the effect of image forces caused by differences in the dielectric permittivities of the solvent and electrode. The distortion of the Debye atmosphere near the interface was also considered. The alteration assumed that the electrode was uncharged, so the theory only found use in calculating surface tension of electrolyte solutions at the solution/air interface.

The Stern modification⁵ in 1924, suggested that there should be a thin region adjacent to the charged surface, a *compact double layer*, possibly with different dielectric properties from the bulk solution. The early Gouy-Chapman theory made no mention of non-electrostatic adsorption of ions at the electrode surface. Although Gouy first recognized this problem it was Stern who introduced the idea of specific adsorption and treated it quantitatively. Much later the Stern isotherm was declared "obsolete",⁶ but because there has been no reasonable substitute it is still discussed in most all text books. By the late forties Grahame⁷⁻⁹ was working toward a theory that would assume that the compact double layer capacity was dependent only on the charge of the electrode and not on the electrolyte concentration.

The current and possibly most exciting model of the electric double layer at the metal/electrolyte interface is called the *jellium-dipole-ion model*.¹⁰⁻¹⁵ Numerous experiments have shown that the capacity of the double layer at the metal/electrolyte interface is dependent on both the nature of the metal and of the solution. Recent theoretical studies of the electric double layer regard the electrolyte as a mixture of charged and dipolar hard spheres.^{16,17} By using statistical mechanics¹⁰ it has been shown that at small potential differences between the electrode and solution, the Gouy-Chapman theory is valid, but that the microscopic picture underlying this early theory is incorrect. It has been established by differential capacity-potential data that the double layer theory must involve both metal and electrolyte. However, no theory yet

predicts the unusual shape of differential capacity-potential curves. The continued interest in developing a better understanding of the electric double layer is both intrinsic and due to the important role the double layer plays in processes of adsorption and charge transfer at electrodes, and in general, at surfaces.

Theory

The electric double layer is often described as having the solution side of the double layer consisting of several *layers*. The closest layer to the electrode contains solvent molecules and, in some cases, other species (ions or molecules) that are said to be *specifically adsorbed*. The first layer is often referred to as the *Helmholtz layer*, or the *compact*, or *Stern layer*. The locus of the electrical centers of the specifically adsorbed ions is called the *inner Helmholtz plane* (IHP). The IHP is at a distance x_1 from the electrode, figure 1. The total charge density ($\mu\text{C}/\text{cm}^2$) from the specifically adsorbed ions in the IHP is represented by σ^i . When solvated ions approach the surface, they can only approach to a distance x_2 . The *outer Helmholtz plane* (OHP) is used to describe the plane created by the nearest solvated ions. The interaction of the solvated ions with the charged metal involves only long-range electrostatic forces. Thus, their interaction is essentially independent of the chemical properties of the ions. These ions are referred to as *nonspecifically adsorbed*. Ions such as these are distributed in a three-dimensional region called the

diffuse layer; which extends from the OHP to the bulk of the solution. The thickness of the diffuse layer depends on the total ionic concentration in the solution.

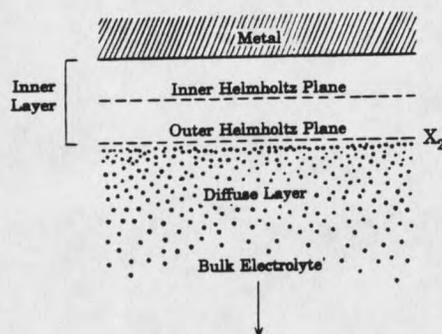


Figure 1. Double layer.

The name double layer originated from the writings of Helmholtz^{18,19} in which he proposed the idea of charge separation at the electrode surface. It was proposed that the countercharge in solution also would reside at the surface. This would be similar to having two sheets of charge, having opposite polarity and being separated by a distance of molecular order.

It is easiest to think of this structure as a parallel-plate capacitor, which has the following relationship between stored charge density, σ ($\mu\text{C}/\text{cm}^2$), and the voltage drop V between the plates²⁰:

$$\sigma = \frac{\epsilon \epsilon_0}{d} V \quad (1)$$

where ϵ is the dielectric constant of the media, ϵ_0 is the permittivity of free space, and d is the interplate distance. The differential capacitance can then be written as

$$\frac{\partial \sigma}{\partial V} = C_d = \frac{\epsilon \epsilon_0}{d} \quad (2)$$

This equation suggests that C_d should remain constant, but as Grahame has shown⁸ this is not the case in real electrolyte solutions, figure 2.

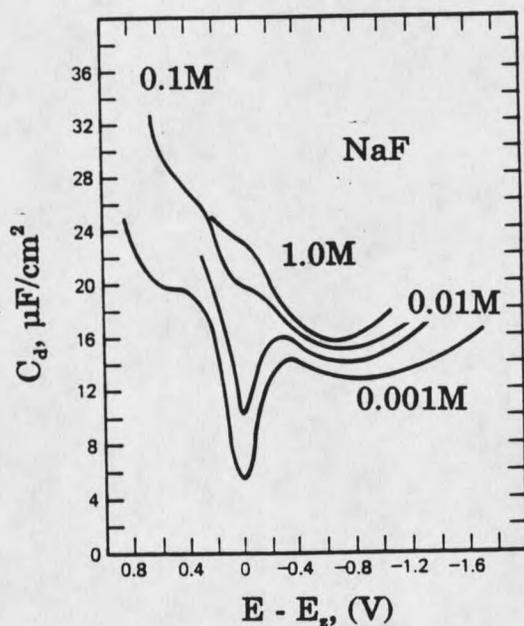


Figure 2. Differential capacity vs. potential for NaF.⁸

Helmholtz's theory provides an unsatisfactory explanation of the double layer. He fails to account for thermal agitation that causes some counterions to diffuse throughout the solution. Gouy and Chapman were the first to provide a detailed explanation of the effects of the diffuse layer on the double

layer. They independently proposed a model of the double layer based on a statistical mechanics approach. The basis of their model was the one dimensional Poisson-Boltzmann equation:

$$\frac{d^2\phi}{dx^2} = \frac{4\pi e}{\epsilon} \sum_m^i z_i \rho_i \exp(\beta z_i e \phi(x)) \quad (3)$$

where $\phi(x)$ is the mean electrostatic potential at a distance x from the electrode, e is the magnitude of the electronic charge, z_i and ρ_i are the valence (including the sign) and number density of ions of species i , $\beta = 1/kT$, k is the Boltzmann constant and T is the temperature. The parameter m is the number of species of ion in the region of space in which this equation is being applied.²¹ This assumption concerning distribution of charge density and potential is the same as that used by Debye and Hückel for stating the same quantities in their theory of strong electrolytes.

In the Gouy-Chapman model, adsorption occurs as a result of the electrostatic interaction between point-charge ions and the charge on the electrode. A finite thickness would arise essentially because there is an interplay between the tendency of the charge on the metallic phase to attract or repel the carriers. This results in an ionic atmosphere or *diffuse layer* that decays into the bulk, the net charge on the diffuse layer being equal and opposite to that on the metal surface.^{6,22}

Capacity predictions calculated from the Gouy-Chapman theory tend to be much higher than measured values for ions of finite size, thus, it is necessary to modify the model. Stern introduced the idea of ions that are *specifically adsorbed* by postulating that ions cannot approach the electrode nearer than the "plane of closest approach" (x_2). Hence the name double layer was applied for the Gouy-Chapman-Stern theory; the compact or inner layer and the diffuse layer. The difference of potential ϕ_m between the metal and solution ($\phi_s=0$ by convention) is now divided into two parts.^{8,23}

$$\phi_m = (\phi_m - \phi_2) + \phi_2 \quad (4)$$

According to this view the double layer can be regarded as two capacitors in series.

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D} \quad (5)$$

A single capacitor can be broken into several capacitors, thus the differential capacitance, C_d (which is the change in the excess charge on the electrode with respect to the change in the electrode potential), can be split into a Helmholtz capacitance, C_H , and a diffuse capacitance, C_D . The term C_H contains important structural information that has been found to depend characteristically on the nature of the metal, the solvent, and for a given interface, also on the electrode charge and on the temperature.

Experimentally it has been shown that the double layer capacity is dependent on the chemical nature of both the metal and the solution. The most recent theory to address this is referred to as the *jellium-dipole-ion model*. A simple quantum mechanical model of the metal surface -- the jellium model, is combined with a new dipole model of the solvent. This is thought to be the first microscopic theory that can explain qualitatively how the interaction of the metal with the solvent molecules determines the double layer capacity.^{10,14}

In the last decade two new ideas have arisen to describe the electric double layer. The first of these notions is based on the reality that electric fields can penetrate a short distance into a metal surface. Therefore the metal should make an important contribution to the interfacial capacitance. Although this was first suggested in 1928 by O. K. Rice,²⁴ his model was never successful. The second new idea originates from the statistical mechanics of liquids and solutions. The distribution functions for an ensemble of hard sphere ions and dipoles in the presence of a hard charged wall have been solved for small charges in the mean spherical approximation (MSA).^{16,17} This should provide a reasonable method to model an electrolyte. A combination of these two proposals should provide a new model for the electric double layer.

If the metal electrons and the electrolyte were strongly coupled, the jellium-dipole-ion model would be very complex. Fortunately, the coupling is

weak. The metal electrons penetrate into the electrolyte only enough to contribute to the Helmholtz capacitance C_H but not enough to disturb the electrolyte structure. Furthermore, the electrons do not penetrate far enough to sense the electrolyte structure and thus respond only to the magnitude of the double layer charge.¹⁴

Jellium.

Polycrystalline sp-metals can be modeled as a jellium. Jellium is described as having the charge of the metal ions smeared out onto a constant background charge density. This charge density then abruptly drops to zero at the metal surface. The electrons are treated as a quantum mechanical plasma interacting with a positive background and with any other external field that may be present.

An important feature of the jellium model is that electrons are able to penetrate the metal surface, because of their small size, and spill over into the adjacent region, vacuum or solution. The penetration length is typically of the order of 0.5 \AA only.¹⁴ Due to the high concentration of electrons this leads to sizable negative excess charge density outside the metal, which, at an uncharged surface, must be balanced by a corresponding excess charge on the metal side of the surface. What results is a dipole moment that leads to a surface dipole potential, V_{dip} . This potential is typically of the order of a few volts, which makes an important contribution to the electronic

work function.¹⁴ It also should be noted that within the jellium model all metal properties are a function of the bulk electronic density, n_+ , only.

Hard sphere electrolyte.

Charged hard spheres and hard spheres with embedded dipoles are used to describe the ions and the solvent molecules respectively in the hard sphere electrolyte model. The statistical mechanics of such an assembly of hard spheres in contact with a charged hard wall is computationally complex, but good approximate solutions have been obtained for small charges.^{16,17}

Combining the jellium model with the ensemble of hard sphere ions and dipoles, figure 3, gives the following equation for the Helmholtz capacity at the potential of zero charge.^{12,15}

$$\frac{1}{4\pi C_H} = \frac{\epsilon - 1}{2\lambda\epsilon} \sigma_s + \frac{1}{2\epsilon} \sigma_i + \frac{d}{d\phi} V_{dip} \quad (6)$$

The first two terms are the contribution of the electrolyte solution. The diameter of the solvent molecules and the ions are represented by σ_s and σ_i respectively. For simplicity the diameters of the cations and anions are considered to be equal. ϵ is the bulk dielectric constant for the solvent. λ is determined from ϵ via the following relationship,

$$\lambda^2(1 + \lambda)^4 = 16\epsilon \quad (7)$$

Typical values for λ are of the order of 2-3, thus, the second term in eq. 6 will be much smaller than the first because $\epsilon \gg \lambda$.¹⁴ Therefore the contribution of the solvent to the Helmholtz capacity, C_H , will be determined mainly by the properties of the solvent. This is in good agreement with the experimental findings, in which C_H is practically independent of the nature of the ions.¹⁴ The last term in the Helmholtz equation, (eq. 6), is the contribution of the jellium model. This is given by the variation of the surface dipole potential, V_{dip} , with the surface charge, q . V_{dip} is generally negative, as will be discussed later. The metal contribution is determined by the bulk electronic density. In calculations for specific systems, it is assumed that all the valence electrons of sp-metals are free.¹⁴

The variation of the surface dipole potential, V_{dip} , is the major concern for the double layer capacity. The effect of an applied electric field on the normalization electronic density profile, $n(x)/n_+$, has been investigated.¹⁴ The results show that a positive field leads to an accumulation of positive charge on the surface. Thus, the electrons are pushed back into the metal by a positive field, and the surface dipole potential, V_{dip} , decreases. Similarly, a negative applied field tends to pull electrons out of the metal, and the surface dipole potential increases. Simply stated, the variation of the surface dipole potential is opposite to the applied external potential. Hence this effect decreases the potential difference between the bulk of the metal and the solution for a given charge density, and thus increases the capacity. What

