



What Role Does the Electric Double Layer Play in Redox Reactions at Planar Electrostatically Charged Insulating Surfaces?

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Abstract

Redox reactions have been observed when an electrostatically charged insulator is placed in contact with a solution, and this phenomenon is referred to as single-electrode electrochemistry. In this study we explore how important is the chemical reactivity of the charge carriers on the surface compared to the voltage caused by the density of charges on the surface which set up an electric double layer. We address complications arising from the surface potential's dependence upon the electrolyte concentration caused by the fixed surface charge density of the electrode. We present an analytical solution for the effective potential in single-electrode electrochemistry at a planar surface and show that it is not the same as the potential at the insulating surface. We reach two major conclusions: (1) the voltage applied to the reaction from discharging the electrode approaches a limiting value, and (2) the majority of single-electrode reactions are caused primarily by the chemical reactivity of the charge carrier on the electrode surface and not from discharging the static charge on the electrode.

Keywords Electric double layer · Single-electrode electrochemistry · Gouy-Chapman model · Electrostatic potential

1 Introduction

There have been several reports of static electrical charges on insulating surfaces being used for electrochemical reactions. Liu and Bard showed copper deposition onto statically charged Teflon as well as chemiluminescence from a redox reaction resulting from a statically charged surface [1, 2]. In this work we wish to understand the role of voltage as it applies to single-electrode reactions. In particular, we seek to decouple the chemical reactivity of the charge carrier of the statically charged surface from the voltage caused by the density of charges on the surface.

The exact nature of the charge carrier resulting from triboelectric charging of the insulating electrode is a subject of debate. Some investigators attribute the surface charge to transfer of electrons [3], whereas others to the transfer of ionic fragments [4, 5]. Regardless of its exact nature, it is important to distinguish between the chemical reactivity of the charge carrying species and the voltage imparted by discharging the electrostatically charged surface.

In this work we are primarily concerned with calculating the voltage imparted by discharging the electrostatically charged surface. We model the system using the Gouy-Chapman model for a diffuse electric double layer at an infinite planar surface [6], and we calculate the electric potential energy change caused by the reaction at both the surface and the electric double layer.

The differential change in Gibbs free energy, dG , at constant temperature and pressure can be expressed as:

$$dG = dU_{el} + \sum_i \mu_i dN_i \quad (1)$$

where dU_{el} is the differential change in the electrostatic potential energy, dN_i is the differential change of the i^{th} species, and μ_i is the chemical potential of the i^{th} species. In an electrostatically charged single-electrode reaction, the first term represents change in the electrostatic potential energy from discharging the electrostatically charged surface, and the second term represents the energy associated with the redox reaction between the surface charge carrier and the chemical species in the reaction.

In a standard electrochemical setup, the dU_{el} term is simply the product of the differential charge transferred by the reaction times the applied voltage difference between two electrodes between which the charge is transferred. For an

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electrostatically charged single electrode, this differential electrostatic potential energy term is more complicated. As the reaction proceeds, the static electrical charge on the surface decreases and the electrostatic energy of the electric double layer (EDL) of the electrode is altered. This fact makes the effective voltage acting on the reaction different from the potential at the insulating surface.

Adding an additional wrinkle to this whole problem is that the potential at the surface of an electrostatically charged insulator immersed in an electrolyte is dependent on the ionic strength of the electrolyte. Unlike a typical conducting electrode, where the potential of the electrode is held constant and the surface charge density then varies with the electrolyte concentration, an electrostatically charged insulator electrode is characterized by a fixed surface charge density. Thus, the potential of the surface must vary with the electrolyte ionic strength. This dependence on the ionic strength of the surface potential underlies some of the difficulties in determining the voltage of an insulating surface.

We take both of these effects into account in our analysis of the effective voltage of a single electrode system on chemical reactions.

2 Results and Discussion

To calculate the electrostatic energy of the electric double layer (EDL), we need the ion distributions and potential inside the EDL. Fortunately, the distribution of ions in an electric double layer has been well studied. We make use of the Gouy-Chapman model for the EDL [6]. In short, a balance of electromigration versus diffusion of ions can be used to solve for the ion distributions in the diffuse portion of an EDL. For the classic one-dimensional case, where the electrode is modeled as a flat infinite plane in the other two dimensions, an analytical solution is known for the potential of the EDL for symmetric electrolytes. We restrict ourselves to this system, although the same analysis can be done for systems of other geometries using numerical methods.

The surface charge density (σ_o) for the one-dimensional system with a symmetric electrolyte of charge z is given by Hunter [6] as:

$$\sigma_o = A^{-1} \sinh\left(\frac{z\psi_o}{2V_t}\right), \quad (2)$$

where

$$A = \frac{\kappa}{4n_i^0 z e}, \quad (3)$$

ψ_o (V) is the potential at the wall, V_t (V) is the thermal voltage, z (unitless) is the absolute value of the valence charge on an ion of the symmetric electrolyte, κ (m^{-1}) is the Debye-Hückel parameter, n_i^0 (ions m^{-3}) is the number of

i^{th} electrolyte species per unit volume in the bulk with $n_i^0 = n^0$ for our symmetric electrolyte, and e (C) is the charge on an electron. A has units of $m^2 C^{-1}$.

The inverse of Eq. (3) gives us the surface voltage as a function of surface concentration and ionic strength of the liquid, bearing in mind that the Debye-Hückel parameter also depends on the ionic strength. The relationship between surface potential to surface charge density at different ionic strengths is shown in Fig. 1. Thus, the potential at the wall is

$$\psi_o = \frac{2V_t}{z} \operatorname{arsinh}(\sigma_o A). \quad (4)$$

The implication of this equation is that two identical electrostatically charged insulating electrodes that have the same surface charge density will end up with different surface potentials if placed into electrolyte solutions with different electrolyte concentrations. This fact greatly complicates experimental attempts to study the electrochemical reactions taking place.

It is worth noting that the Gouy-Chapman model for the EDL assumes a dilute electrolyte. As the solution becomes more concentrated, the Gouy-Chapman model becomes less accurate.

We are ultimately interested in how the electrostatic energy of the system changes as the surface charge density reduces during the reaction. The electrostatic potential energy of the system can be found by multiplying half the net charge density by the potential at each location and integrating over the whole system [7].

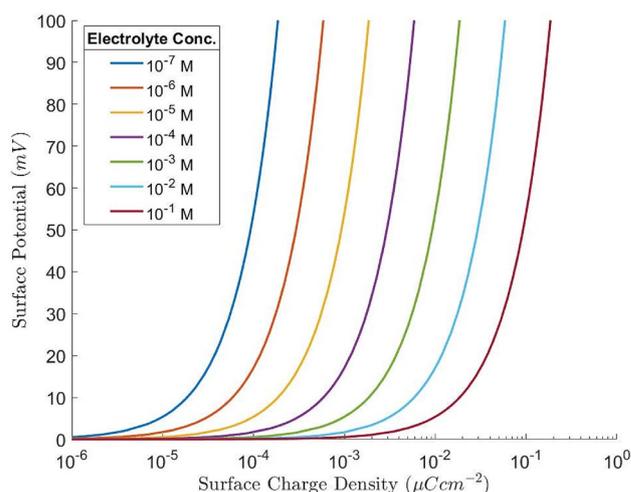


Fig. 1 Surface potential as a function of surface charge density for a uni-univalent electrolyte resulting from a Gouy-Chapman treatment of a charged parallel plate at different electrolyte concentrations. Solution shown for a temperature of 25 °C ($V_T = 25.7$ mV)

$$U_{el} = \frac{1}{2} \sigma_o \psi_o + \frac{1}{2} \int_0^{\infty} \psi(x) \rho(x) dx. \quad (5)$$

Note that this definition of U_{el} has units of joules per unit area. Both $\psi(x)$ and $\rho(x)$ have known analytical solutions for our system [6]

$$\psi(x) = \frac{4V_T}{z} \operatorname{artanh} \left[\tanh \left(\frac{z\psi_o}{4V_T} \right) \exp(-\kappa x) \right] \quad (6)$$

and $\rho(x)$ can be found from Gauss' law

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \quad (7)$$

where ϵ is the permittivity of the material. As is shown in the calculations section, substitution of Eqs. (6) and (7) into Eq. (5) followed by integration yields the result

$$U_{el} = \frac{V_T}{Az} \left(\cosh \left(\frac{z\psi_o}{2V_T} \right) - 1 \right). \quad (8)$$

When considering the differential change in electrostatic potential energy during the course of a reaction, we note that the surface charge density decreases proportional to the reaction progress such that dU_{el} can be expressed as the negative of a partial derivative of U_{el} with respect to the surface charge density σ_o

$$dU_{el} = -\frac{\partial U_{el}}{\partial \sigma_o} dn, \quad (9)$$

where dn is the differential charge transferred by the reaction. Note that dn needs to be in units of coulombs. As shown in the calculations section, the derivative of U_{el} with respect to σ_o yields the following voltage

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \tanh \left(\frac{z\psi_o}{2V_T} \right). \quad (10)$$

The same equation can be expressed in terms of surface charge density

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \frac{\sigma_o A}{[(\sigma_o A)^2 + 1]^{1/2}}. \quad (11)$$

Figure 2 presents graphs of both Eqs. 10 and 11. As can be seen, there is a cap on the maximum effective voltage that the statically charged electrode can provide. In Fig. 2A, an onset surface charge density is observed which varies with the electrolyte concentration. Oddly, this onset surface charge density takes place earlier for solutions of lower concentrations. This rather counterintuitive observation implies that in some cases reactivity with an electrostatically charged electrode may be seen at lower electrolyte concentrations but not at higher electrolyte concentrations.

Work from Lui and Bard [2] on reduction of Cu^{2+} by an electrostatically charged PTFE electrode estimated the surface charge density at $1.3 \times 10^{-3} \mu\text{C cm}^{-2}$ (8×10^{14} charges cm^{-2}) for their experimental setup. This estimate of surface charge density is in the middle of this window where the electrolyte concentration matters.

The electrolyte concentration dependence of the electrode potential is purely a result of the surface charge density dependence on the electrolyte concentration and cancels out when the electrode potential is compared to the surface potential, as in Fig. 2b.

Due to the hyperbolic tangent function in Eq. (10), the electrostatic contribution to the Gibbs free energy of the system is capped at the thermal voltage divided by the charge

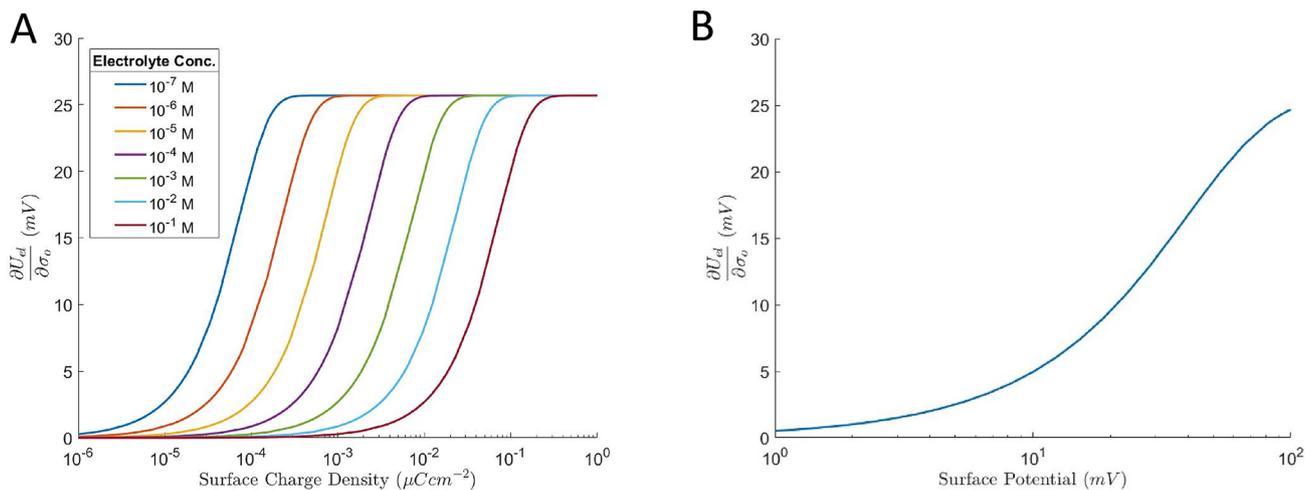


Fig. 2 a Electrostatic contribution to the potential $\left(\frac{\partial U_{el}}{\partial \sigma_o}\right)$ as a function of surface charge density for a uni-univalent electrolyte resulting from a Gouy-Chapman treatment of a charged parallel plate at different

electrolyte concentrations. **b** Electrostatic contribution to the potential $\left(\frac{\partial U_{el}}{\partial \sigma_o}\right)$ as a function of surface potential resulting from a Gouy-Chapman treatment of a charged parallel plate. Solutions shown for a temperature of 25 °C ($V_T = 25.7$ mV)

of the symmetric electrolyte. For a system of water at 25° C with only monovalent electrolytes, the value of this cap is at 25.7 mV. Thus, while the driving force from the discharging the electrostatic charge on the electrode is not negligible, the major contribution to the Gibbs free energy is the reactivity of the surface charge carrier.

We note that the reactivity of the surface carrier being the primary driving force of the reaction is in good agreement with experimental work by Zhang et al. [8]. They showed that the metal deposited on a surface has a nearly linear dependence on the surface charge density with a constant of proportionality related to the stability of anionic charge carriers on the surface. This suggests that the energy from discharging the surface charge is dwarfed by the chemical reactivity term.

In the case of metal plating onto the electrostatically charged surface, the ion moves from a nonzero potential in the electric double layer, to the wall surface. Thus, the required voltage is the difference of the wall potential to the potential some distance into the electric double layer. At larger surface potentials, the ion starts also at a higher potential. Thus, the cap in the voltage applies to this reaction.

For the opposite case where the reactive species generates a new ion in the electric double layer, a simplified picture is that the ion generated by the redox reaction at the surface also removes its counter ion from the EDL as both move out to zero potential. The voltage on the redox reaction then becomes the voltage difference between the surface and the potential at the counter ion's original location in the EDL. At large surface potentials, the potential of the counter ion also increases as it is drawn more closely to the surface. Therefore, the voltage drop from the surface to the location of the counter ion in the EDL converges to a single voltage as the surface voltage increases. Both these pictures are oversimplifications as they neglect the small energy changes from rearrangements of other ions than the counter ion in the EDL (which is captured in the calculation).

These results also suggest an interesting experiment. Starting from a reaction with a Gibbs free energy of reaction is less than 25.7 mV short of that needed to be spontaneous, one could then demonstrate that the reaction takes place at lower electrolyte concentrations but not higher concentrations for otherwise identically charged electrodes.

2.1 Limitations of the Model

The calculations in this work apply only to the diffuse layer of an electric double layer. For systems with large surface charge densities such that a Stern layer forms in addition to the diffuse layer, a different potential as a function of distance will need to be used. As a rough approximation, we propose adding the potential drop across the Stern layer to the value of the potential from the diffuse layer as shown in

this work with the caveat that the potential after the Stern layer should be used for the calculation of the diffuse layer.

We have assumed a homogeneous distribution of surface charge along the insulating surface. It is worth noting that the static charge on insulating surfaces can be inhomogeneous wherein it consists of mosaic of highly but opposite signed charges across the material with a small net charge for the surface. Such a patchwork system of charges on the surface would not yield the same result as a homogeneous distribution of the net charge across the surface. The scale of the inhomogeneities is an important factor. Work by Baytekin et al. revealed a mosaic with scales of hundreds of nanometers [4]. This does not satisfy the initial homogeneous plate condition of the 1D electric double layer model we used. However, the same principles could be applied to calculate an effective voltage, albeit with a numerical solution required for the distribution of ions in the electric double layer. Work by Burgo et al. showed mm to cm scale negative and positive domains forming on the surface [5]. Such domains are large enough that each domain could be treated separately using the model presented here.

3 Conclusion

Great care should be taken when referring to the potential involving redox reactions using electrostatically charged single electrodes. The surface potential varies greatly with the electrolyte concentration; furthermore, the surface potential is not the same as the applied voltage to the redox reaction. A major result is that the voltage applied to the reaction from discharging the electrode reaches a small limiting value, and thus, the majority of static electricity driven electrode reactions are driven primarily by the chemical reactivity of the charge carrier on the electrode surface and not from discharging the static charge on the electrode.

4 Calculations

In order to calculate the electrostatic energy of the EDL, we need the ion distributions and potential inside the EDL. Fortunately, the distribution of ions in an EDL has been well studied. In short, a balance of electromigration versus diffusion of ions is used to solve for the ion distributions in the diffuse portion of an EDL. For the classic one-dimensional case, where the electrode is modeled as a flat infinite plane in the other two dimensions, an analytical solution is known for cases with symmetric electrolytes. In what follows, we build heavily on Hunter's textbook [6].

The solution for the potential of this system is

$$\tanh \frac{z\psi(x)}{4V_T} = \tanh \frac{z\psi_o}{4V_T} \exp(-\kappa x), \quad (12)$$

where all the symbols are as defined earlier in the text. Gauss's Law then gives ρ in terms of $\psi(x)$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon}. \quad (13)$$

We also need the derivative of the potential

$$\frac{d\psi}{dx} = -\frac{4n^0 z e}{\kappa \epsilon} \sinh\left(\frac{z\psi}{2V_T}\right). \quad (14)$$

The surface charge density is balanced by the charge in the electric double layer

$$\sigma_o = -\int_o^\infty \rho(x) dx = \int_o^\infty \epsilon \frac{d^2\psi}{dx^2} dx. \quad (15)$$

Note that integrating Eq. (15) using Eq. (14) gives Eq. (2).

Next, we start with the definition of the electrostatic potential energy of the system [7]

$$U_{el} = \frac{1}{2} \psi_o \sigma_o + \frac{1}{2} \int_o^\infty \psi(x) \rho(x) dx. \quad (16)$$

Substituting Eq. (13) into Eq. (16) yields:

$$U_{el} = \frac{1}{2} \psi_o \sigma_o - \frac{1}{2} \int_o^\infty \psi \epsilon \frac{d^2\psi}{dx^2} dx. \quad (17)$$

We integrate Eq. (17) by parts:

$$U_{el} = \frac{1}{2} \psi_o \sigma_o - \frac{1}{2} \left[\left(\psi \int_o^\infty \epsilon \frac{d^2\psi}{dx^2} dx \right) \Big|_o^\infty - \int_o^\infty \left(\epsilon \frac{d\psi}{dx} \right) \frac{d\psi}{dx} dx \right] \quad (18)$$

We define $\psi(0) = \psi_o$ and $\psi(\infty) = 0$. Substituting in σ_o from Eq. (15) gives

$$U_{el} = \frac{1}{2} \psi_o \sigma_o - \frac{1}{2} \left(\psi_o \sigma_o - \int_o^\infty \left(\epsilon \frac{d\psi}{dx} \right) \frac{d\psi}{dx} dx \right), \quad (19)$$

which may be simplified to yield

$$U_{el} = \frac{1}{2} \int_o^\infty \left(\epsilon \frac{d\psi}{dx} \right) \frac{d\psi}{dx} dx. \quad (20)$$

Substituting Eq. (14) into Eq. (20) gives

$$U_{el} = \frac{1}{2} \int_o^\infty -A^{-1} \sinh\left(\frac{z\psi}{2V_T}\right) \frac{d\psi}{dx} dx \quad (21)$$

with A as previously defined in Eq. (3). Evaluating the integral, we obtain

$$U_{el} = \left(\frac{V_T}{Az} \right) \left(\cosh\left(\frac{z\psi_o}{2V_T}\right) - 1 \right). \quad (22)$$

Taking the partial derivative with respect to σ_o and recalling that ψ_o is a function of σ_o yields

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{1}{2A} \sinh\left(\frac{z\psi_o}{2V_T}\right) \frac{\partial \psi_o}{\partial \sigma_o}. \quad (23)$$

Taking the same partial derivative of Eq. (4)

$$\frac{\partial \psi_o}{\partial \sigma_o} = \left(\frac{2V_T A}{z} \right) \left[(\sigma_o A)^2 + 1 \right]^{-\frac{1}{2}}. \quad (24)$$

Substitution of Eq. (24) into Eq. (23) allows simplification to

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \sinh\left(\frac{z\psi_o}{2V_T}\right) \left[(\sigma_o A)^2 + 1 \right]^{-\frac{1}{2}} \quad (25)$$

Substituting Eq. (2) into Eq. (25) gives

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \frac{\sigma_o A}{\left[(\sigma_o A)^2 + 1 \right]^{1/2}} \quad (26)$$

which is Eq. (11). Using the identity $\tanh(\operatorname{arsinh}(x)) = \frac{x}{(x^2+1)^{1/2}}$, we get:

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \tanh(\operatorname{arsinh}(\sigma_o A)) \quad (27)$$

Substituting Eq. (4) into Eq. (27), we obtain

$$\frac{\partial U_{el}}{\partial \sigma_o} = \frac{V_T}{z} \tanh\left(\frac{z\psi_o}{2V_T}\right), \quad (28)$$

which is Eq. (10). The implications of Eq. (28) and Eq. (26) are discussed in the results and discussion section.

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Declarations

Conflict of interest The authors declare no competing or conflicts of interest.

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