



# Electrochemical Impedance Spectroscopy analysis of an adsorption process with a coupled preceding chemical step



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## ABSTRACT

The impedance equations for the case of an adsorption process including a preceding homogeneous chemical step have been derived and compared to the corresponding equations for the case of a pure adsorption process. They involve behaviours with the frequency that differ from those of the impedance equations for a pure adsorption process. However, two limiting cases have been deduced in which the frequency behaviour of the impedance cannot be distinguished from the case of an adsorption process without any chemical step: the *high frequency* and the *low frequency* limits that hold for low and high values of the rate constant of the chemical reaction, respectively.

The analysis as a function of the frequency is discussed on the basis of the complex frequency-normalized admittance plots and also based on the frequency dependence of the real and imaginary frequency-normalized admittance components. The influence of the values of the equilibrium and the rate constants of the chemical step is discussed for different adsorption kinetic regimes. In this way the conditions for detecting the chemical step are delimited and suitable analysis are proposed to obtain the adsorption parameters and the characteristic constants of the chemical step.

The analysis is applied as an example, to the impedance of adenine adsorption on Au(111) electrodes from acidic solutions at a representative electrode potential. It is proved that the low frequency limit applies and the equilibrium constant for the chemical step is obtained.

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## 1. INTRODUCTION

It has frequently been observed in the study of electrochemical process that the electroactive species that undergo an electron transfer are also involved in chemical reactions in solution that are named as “homogeneous reactions”. Therefore, the concentration profiles of electroactive species are altered and it is necessary to take into account the chemical reaction in the equations of the flux of the species towards or from the electrode. One of these cases takes place when the electroactive species is not initially present in solution but it is generated in the chemical reaction, which is so named as the “preceding chemical reaction” and the corresponding mechanism as the CE mechanism. A chemical adsorption process on an electrode is similar, in some ways, to an electron transfer process, as some charge is transferred to or from the electrode due to the chemical interaction between the metal and the adsorbate. Many electrode adsorption processes of organic compounds are known to be affected by chemical reactions,

specially by protonation/deprotonation equilibria [1–9]. That is the case, for instance, with adenine adsorption on gold electrodes from acidic solutions for which the IR-spectro-electrochemical studies has shown that the species that get adsorbed is the deprotonated form, even at pH values long below the  $pK_a$  of the adenine form that is present in solution [10].

The adsorption of biologically relevant molecules on metal electrodes is of great interest in relation to the understanding of the respective biological roles and also for technical applications such as biosensors and drug delivery platforms fabrication. Although significant advances concerning the molecular interpretation of the adsorption on solid metal electrodes have been reached nowadays by application of spectro-electrochemical and nanoscopic techniques, the kinetics of the adsorption has been scarcely addressed. The Electrochemical Impedance Spectroscopy (EIS) technique and the use of single crystal electrodes with well-defined surfaces, are suitable tools to study the kinetics of adsorption and so we have applied them to study the kinetics of adenine adsorption on Au(111) electrodes from solutions of several pH values, ranging from 1 to 12 [11,12].

The first adsorption kinetic models were reported by Dolin and Ershler for the limiting case of kinetic control only by the activation

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step, [13], and by Frumkin and Melik-Gaykazyan for the case of an adsorption process in which the kinetic control only takes place by diffusion, [14]. Both limiting cases were later combined, and the adsorption impedance equations for a general kinetic control were derived by Sluyters-Rehbach and Sluyters, [15,16]. The derivation developed later by Kerner and Pajkossy, based on the same principles [17], allows a more clear identification of the physical meaning of the impedance parameters involved in the model, and also the splitting of the net rate of absorption (or desorption) on a proper rate constant and on a surface excess depending function, related to the adsorption isotherm.

In this paper, the impedance equations for an electrochemical adsorption process that is preceded by a chemical homogeneous reaction are derived, following the development in reference [17]. To derive the impedance equations in this work, the chemical reaction has now been included in the flux equations of the species that can adsorb on the electrode. The frequency dependence of the impedance or admittance equations is analysed in comparison to the case of an adsorption process with only diffusional mass transport, without coupled homogeneous kinetics. As an example, the analysis is applied to adenine adsorption on Au(111) electrodes from 0.1M HClO<sub>4</sub> solutions at a representative adsorption potential, in order to detect electrochemical evidences of the chemical reaction that according to the previous IR spectroelectrochemical results is preceding the adsorption process.

## 2. THEORY

An adsorption process including a preceding first order chemical step can be represented as in Scheme 1:

The rate of the chemical step is formulated as:

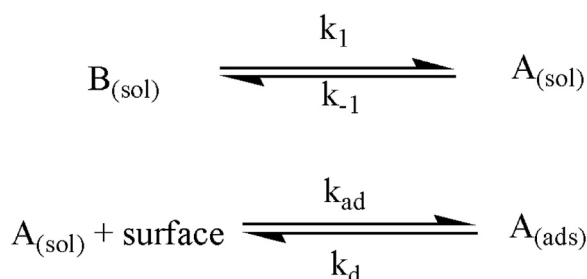
$$v_{chem} = \frac{dc_B}{dt} = k_1 c_B - k_{-1} c_A \quad (1)$$

where  $k_1$  and  $k_{-1}$  are the forward and backward rate constants of the preceding chemical step and  $c_B$  and  $c_A$  are the concentrations of species B and A, respectively.

For the adsorption step the Frumkin and Melik-Gaykazyan adsorption kinetics model [14] was adopted, following further modifications that do not require any “a priori” assumption concerning the type of isotherm or the potential dependence of the adsorption and desorption rate constants [16,17]. According to them, the rate of the adsorption can be formulated as:

$$v_{ad} = \frac{d\Gamma_A}{dt} = k_{ad} f_{ad}(\Gamma_A) c_{A,x=0} - k_d f_d(\Gamma_A) \quad (2)$$

where  $k_{ad}$  and  $k_d$  are the potential dependent adsorption and desorption rate constants;  $\Gamma_A$  is the surface excess of species A; and  $f_{ad}(\Gamma_A)$  and  $f_d(\Gamma_A)$  are monotonic functions of the surface excess with values between 0 and 1.  $f_{ad}(\Gamma_A)$  tends to 0 and  $f_d(\Gamma_A)$  tends to 1 as the surface excess tends to its maximum value. The



**Scheme 1.** Schematic representation of an adsorption process with a preceding homogeneous chemical reaction.

explicit expressions of  $f_{ad}(\Gamma_A)$  and  $f_d(\Gamma_A)$  depend on the specific isotherm that applies to the adsorption process.

The adsorption rate,  $v_{ad} = v_{ad}(\Gamma_A, c_A, E)$  is a function of three interdependent variables: the surface excess and the concentration of A at the electrode surface ( $x=0$ ), and the applied potential, E. On the other hand, for a small amplitude ac potential perturbation a linear approximation can be considered applicable [16] so, the total change in the adsorption rate that results,  $\Delta v_{ad}$ , can be expressed as a function of the changes in the three variables,  $\Delta E$ ,  $\Delta\Gamma$  and  $\Delta c_A$ ,  $x=0$ , which in the Laplace's transformation domain can be expressed as:

$$\begin{aligned} \mathfrak{L}(\Delta v_{ad}) = \overline{\Delta v_{ad}} = & \left( \frac{\partial v_{ad}}{\partial E} \right)_{\Gamma_A, c_A} \overline{\Delta E} + \left( \frac{\partial v_{ad}}{\partial \Gamma_A} \right)_{E, c_A} \overline{\Delta \Gamma_A} \\ & + \left( \frac{\partial v_{ad}}{\partial c_{A,x=0}} \right)_{E, \Gamma_A} \overline{\Delta c_{A,x=0}} \end{aligned} \quad (3)$$

Evidently,  $\Delta c_{A,x=0}$  must be related to the changes in the concentration of  $c_B$ ,  $\Delta c_B$ , and both changes in the Laplace's domain can be expressed as functions of the changes in the adsorption rate,  $\overline{\Delta v_{ad}}$ , as deduced in the Appendix A for  $\overline{\Delta c_{A,x=0}}$ , Eq. (A7). On the other hand, Laplace transformation of Eq. (2) provides the relation between  $\overline{\Delta \Gamma_A}$  and  $\overline{\Delta v_{ad}}$ :

$$\overline{\Delta \Gamma_A} = s^{-1} \overline{\Delta v_{ad}} \quad (4)$$

where  $s$  is defined as  $s = \omega i$  with  $i = \sqrt{-1}$ .

The adsorption impedance,  $Z_{ad}$ , is defined as the ratio of the changes in the Laplace domain of the potential and of the current density due to the adsorption:

$$Z_{ad} = \frac{\overline{\Delta E}}{\overline{\Delta I_{ad}}} \quad (5)$$

where the current density of adsorption is defined as:

$$I_{ad} = \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)_E \frac{d\Gamma_A}{dt} = \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)_E v_{ad} \quad (6)$$

with  $\sigma^M$  being the charge density on the metal.

Substitution of Eqs. (A7) and (4) into Eq. (3) allows the derivation of the expression for the adsorption impedance defined in Eq. (5), as:

$$Z_{ad} = R_{ad} + \sigma_{ad} G(s) + (C_{ad} s)^{-1} \quad (7)$$

where  $G(s)$  is given by the same expression deduced for an electron transfer process coupled to a preceding homogeneous chemical step, named Gerischer impedance [16,18–20]:

$$G(s) = \left[ \frac{K_c}{K_c + 1} s^{-\frac{1}{2}} + \frac{1}{K_c + 1} (s + k_c)^{-\frac{1}{2}} \right] \quad (8)$$

with  $K_c = k_1/k_{-1}$  being the equilibrium constant of the chemical step and  $k_c = k_1 + k_{-1}$  is the global rate constant (addition of the forward and backward rate constants) for the chemical step.

The frequency independent parameters  $R_{ad}$ ,  $\sigma_{ad}$  and  $C_{ad}$  are the adsorption resistance, the adsorption Warburg coefficient and the adsorption capacitance, respectively. Their definitions are the same that in the impedance model for the adsorption kinetics in the absence of coupled chemistry [16,17]:

$$R_{ad}^{-1} = \left( \frac{\partial v_{ads}}{\partial E} \right)_{\Gamma_A, c_A} \left( \frac{\partial \sigma^M}{\partial \Gamma_A} \right)_E \quad (9a)$$

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