

# Theory of square-wave stripping voltammetry with adsorptive accumulation

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## Theorie der Square-Wave Stripping Voltammetrie mit adsorptiver Anreicherung

**Summary.** A model of the anion-induced adsorptive accumulation combined with a square-wave voltammetric stripping is developed. The dependence of peak currents and peak potentials on the reversibility of redox reactions and on the reaction mechanism is demonstrated. The sensitivity of the method is estimated.

## Introduction

Organic compounds which are both surface active and electroactive, may be determined at the nanomolar concentration level by stripping voltammetry combined with adsorptive accumulation [1–13]. Also, the anion-induced adsorption of metal ions at a mercury electrode surface can be used as a preconcentration step of stripping analysis [1, 2, 14–23], what is especially valuable when the amalgam formation cannot be applied for this purpose [1, 2, 14, 18–22]. Adsorptive accumulation is analytically useful only if the portion of the electrode surface covered by the adsorbed analyte is very small, not more than 20% of the total area. Under this condition the relationship between the surface concentration of the adsorbed reactant and its bulk concentration may be considered as approximately linear. For the detection of the amount of initially adsorbed analyte, square-wave voltammetry can be applied [7, 9–11, 17]. This method is very sensitive, fast and highly discriminative against the capacitive current [24–26]. However, the characteristics of the response depend on the reversibility of redox reaction and on the surface activity of its products [27, 28]. In the present communication, a simple model of the anion-induced adsorptive accumulation of metal ions is developed in order to demonstrate that square-wave stripping voltammetry is not equally recommendable to all classes of redox reactions from the adsorbed state.

## The model

### 1 The equilibria

#### a) The bulk of the solution

The formation of a single and highly stable complex species in a bulk of the solution is assumed:



A large excess of a ligand is also assumed:  $c_{L,tot}^* \gg c_{M,tot}^*$  and  $K_1 c_{L,tot}^* \gg 1$  (where  $K_1$  is a stability constant  $K_1 = c_{ML}^*/(c_{M^+} \cdot c_L^*)$  and the meanings of other symbols are given in the Appendix). Under these conditions, the ionic species distribution is defined by:

$$c_L^* = c_{L,tot}^* \quad (1)$$

$$c_{M^+}^* = K_1^{-1} c_{M,tot}^*/c_{L,tot}^* \quad (2)$$

$$c_{ML}^* = c_{M,tot}^* \quad (3)$$

#### b) The surface complexation

The electrode surface is assumed to be totally covered by the adsorbed species. The surface complexation reaction [29]:



is defined by the equilibrium and the mass balance equations:

$$\lambda_1 = \Gamma_{ML}/(\Gamma_L \cdot c_{M^+,x=0}) \quad (4)$$

$$\Gamma_L + \Gamma_{ML} = \Gamma_{max} \quad (5)$$

The equilibrium is established when the diffusion equilibrates the concentrations of free metal ions near the electrode surface and in the bulk of the solution:  $c_{M^+,x=0} = c_{M^+}^*$ . The surface distribution is then defined by:

$$\Gamma_{ML} = \lambda_1 \Gamma_{max} c_{M,tot}^*/(K_1 c_{L,tot}^* + \lambda_1 c_{M,tot}^*) \quad (6)$$

$$\Gamma_L = K_1 \Gamma_{max} c_{L,tot}^*/(K_1 c_{L,tot}^* + \lambda_1 c_{M,tot}^*) \quad (7)$$

The assumption of a single complex species appearing in a solution implies that the highest coordination number of  $M^+$  for  $L^-$  is  $m = 1$  and that the adsorbed complex  $(ML_2)_{ads}$  cannot be formed.

### c) The competitive adsorption

The ligand and the complex are competing for the place on the surface [30]. It is assumed that the concentration of  $M^+$ ,  $ML$  and  $L^-$  are uniform throughout the space (Eqs. (1–3)) and that the electrode surface is totally covered [(Eq. (5))]. The adsorption rate of the complex is proportional to its bulk concentration and to the surface concentration of the ligand:

$$v_{\text{ads}} = k_{\text{ads}} c_{\text{ML}}^* \Gamma_L \quad (8)$$

The rate of its desorption is proportional to the surface concentration of the complex species and to the bulk concentration of the ligand:

$$v_{\text{des}} = k_{\text{des}} c_{\text{L,tot}}^* \Gamma_{\text{ML}} \quad (9)$$

In the equilibrium these rates are equal:

$$\beta_{\text{ex,l}} c_{\text{ML}}^* / c_{\text{L,tot}}^* = \Gamma_{\text{ML}} / \Gamma_L \quad (10)$$

where  $\beta_{\text{ex,l}}$  is the exchange constant:  $\beta_{\text{ex,l}} = k_{\text{ads}} / k_{\text{des}}$ . Using Eqs. (3) and (5), the surface distribution can be obtained:

$$\Gamma_{\text{ML}} = \beta_{\text{ex,l}} \Gamma_{\text{max}} c_{\text{M,tot}}^* / (c_{\text{L,tot}}^* + \beta_{\text{ex,l}} c_{\text{M,tot}}^*) \quad (11)$$

$$\Gamma_L = \Gamma_{\text{max}} c_{\text{L,tot}}^* / (c_{\text{L,tot}}^* + \beta_{\text{ex,l}} c_{\text{M,tot}}^*) \quad (12)$$

The comparison of Eqs. (6) and (7) with (11) and (12) reveals the equality between the exchange constant and the ratio of the surface and the bulk stability constants:

$$\beta_{\text{ex,l}} = \lambda_1 / K_1 \quad (13)$$

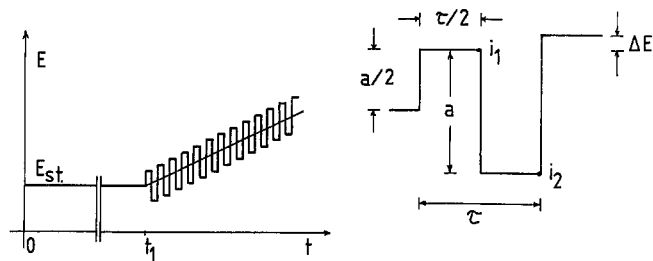
The ratio of Eqs. (6) and (7) is equal to the ratio of Eqs. (11) and (12) if the Eq. (13) is true.

The equilibrium surface distributions described above can be established only through the mass transfer. This process requires a certain time to be completed. The time depends on the nature of the mass transfer: whether it is obtained solely by the diffusion, or by the convection and the diffusion. At real electrodes the voltammetric measurements are frequently performed before the equilibrium is established.

### 2 The accumulation and the square-wave stripping scan

The square-wave signal is shown in Fig. 1. It is characterized by the frequency  $f = \tau^{-1}$  (or its half-period  $\tau/2$ ), the amplitude  $a$  and the scan increment  $\Delta E$ . It is preceded by an arbitrarily long delay period  $t_1$  during which the working electrode is charged to the potential  $E_{\text{st}}$  at which no redox reaction occurs. This period is used for the initial adsorptive accumulation of the analyte. When the sw signal is applied, the current is sampled near the end of each sw half-period ( $i_1$  and  $i_2$ ) and the difference between two successive readings ( $i = i_1 - i_2$ ) is recorded as a function of a mean potential of each sw period.

In the present model, the mass transfer is assumed to occur through the planar, stationary, semi-infinite diffusion. Furthermore, the linear relationship between the surface concentration of the adsorbed complex  $(ML)_{\text{ads}}$  and the total metal concentration near the electrode surface is assumed. This is justified if  $c_{\text{L,tot}}^* \gg \beta_{\text{ex,l}} c_{\text{M,tot},x=0}$  (see Eq. 11). These simplifications correspond to the short adsorptive accumulation of traces of metal ions from unstirred solution.



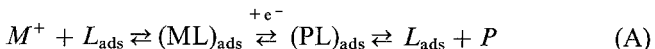
**Fig. 1.** Scheme of the square-wave voltammetric excitation signal.  $t_1$  the delay time;  $E_{\text{st}}$  starting potential,  $a$  sw amplitude;  $\Delta E$  sw scan increment,  $\tau$  sw period;  $i_1$  and  $i_2$  cathodic and the anodic currents and  $\bullet$  the points of their sampling

The mass transfer is mathematically represented by the system of differential equations:

$$\partial c_{\text{M,tot}} / \partial t = D(\partial^2 c_{\text{M,tot}} / \partial x^2) \quad (14)$$

$$\partial c_{\text{P,tot}} / \partial t = D(\partial^2 c_{\text{P,tot}} / \partial x^2) \quad (15)$$

Two reaction schemes are analyzed. In the first one it is assumed that the reduction of the adsorbed complex results in the formation of equally strong complex between the product  $P$  and the ligand  $L$ . Besides, the anion-induced adsorption of the product is assumed:



(Here  $M^+$  is only a symbol for any  $M^{n+}$ , so the charge of the product  $P$  is omitted). In the solution, the relationship between  $P$  and  $L$  is defined by the equilibrium equations:

$$c_{\text{P}} = K_{\text{P}}^{-1} c_{\text{P,tot}} / c_{\text{L,tot}}^* \quad (16)$$

$$c_{\text{PL}} = c_{\text{P,tot}} \quad (17)$$

where:  $K_{\text{P}} = c_{\text{PL}} / (c_{\text{P}} \cdot c_{\text{L,tot}}^*)$  and  $K_{\text{P}} c_{\text{L,tot}}^* \gg 1$ .

In the second reaction scheme, it is assumed that the reduction destroys the adsorbed complex:



The product  $P$  does not form any complex species with the ligand  $L^-$ .

Differential Eqs. (14) and (15) have to be solved under the following initial and boundary conditions:

a) the scheme (A):

$$t = 0, x \geq 0: c_{\text{M,tot}} = c_{\text{M,tot}}^*, c_{\text{P,tot}} = 0, \Gamma_{\text{ML}} = \Gamma_{\text{PL}} = 0 \quad (\text{a})$$

$$t \geq 0, x \geq 0: c_{\text{L,tot}} = c_{\text{L,tot}}^* \quad (\text{b})$$

$$t > 0, x \rightarrow \infty: c_{\text{M,tot}} \rightarrow c_{\text{M,tot}}^*, c_{\text{P,tot}} \rightarrow 0 \quad (\text{c})$$

$$x = 0: \Gamma_{\text{ML}} = \beta_{\text{ex,l}} \Gamma_{\text{max}} (c_{\text{L,tot}}^*)^{-1} c_{\text{M,tot}, x=0} \quad (\text{d})$$

$$\Gamma_{\text{PL}} = \beta_{\text{ex,P}} \Gamma_{\text{max}} (c_{\text{L,tot}}^*)^{-1} c_{\text{P,tot}, x=0} \quad (\text{e})$$

$$D(\partial c_{\text{M,tot}} / \partial x)_{x=0} = d\Gamma_{\text{ML}} / dt + i / nFS \quad (\text{f})$$

$$D(\partial c_{\text{P,tot}} / \partial x)_{x=0} = d\Gamma_{\text{PL}} / dt - i / nFS \quad (\text{g})$$

$$i / nFS = k_{\text{SA}} \exp(-\alpha_{\text{A}} \varphi_{\text{A}}) (\Gamma_{\text{ML}} - \Gamma_{\text{PL}} \exp(\varphi_{\text{A}})) \quad (\text{h})$$

where:  $\varphi_{\text{A}} = \varphi_0 + \ln(K_1 \beta_{\text{ex,l}} / K_{\text{P}} \beta_{\text{ex,P}})$ ,  $\varphi_0 = nF(E - E^\circ) / RT$ ,  $E^\circ$  is a standard potential of a simple redox reaction  $M^+ + e^- \rightleftharpoons P$ ,  $k_{\text{SA}}$  is a standard reaction rate constant and  $\alpha_{\text{A}}$  is a transfer coefficient.