SQUARE WAVE VOLTAMMETRY OF SURFACE-ACTIVE, ELECTROINACTIVE COMPOUNDS

Dijana JADREŠKO, *Marina* ZELIĆ, *Milivoj* LOVRIĆ
"Ruđer Bošković" Institute, Center for Marine and Environmental Research, Zagreb, Croatia/Hrvatska

Square wave voltammetry (SWV) is generally considered as being insensitive to capacitive currents, which is true if it is compared to alternating current voltammetry, but less so if the comparison is made to pulse and differential pulse voltammetry [1]. In fact, the sensitivity of SWV to capacitive current depends on the frequency of signal, particularly in the case of electrode reactions complicated by the reactant adsorption [2].

The aim of these investigation was to show that in tensametry SWV appears as useful alternative to phase selective *ac* polarography, as well as develop a basic theory of SW voltammetry of surface-active, electroinactive compounds.

1. V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, Square-wave voltammetry, Springer, Berlin, 2007.
2. M. Lovrić, Electroanalysis, 14 (2002) 405.

THE MODEL

Adsorption and desorption of a simple electroinactive substance on the surface of planar electrode is considered:

$$A \leftrightarrow (A)_{ads} \quad (1)$$

The mass transfer is described by the Fick's 2nd law for linear diffusion:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad (2)$$

$$t = 0, \quad x \geq 0: \quad c = c^*, \quad \Gamma = 0 \quad (3)$$

$$t > 0, \quad x \to \infty: \quad c \to c^* \quad (4)$$

$$x = 0: \quad D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{d\Gamma}{dt} \quad (5)$$

1. Assumption: A) between adsorbed molecules there are neither attractive nor repulsive forces. The adsorption can be described by Langmuir isotherm:

$$\beta_E (c)_{x=0} = \frac{\theta}{1-\theta} \quad (6)$$

The charge of the electrical double layer at the electrode surface is $Q = C_E \cdot (E - E_{pzc}) \cdot S$, and the charging current is:

$$i = \frac{dQ}{dt} = C_E \cdot S \cdot \frac{d}{dt}(E - E_{pzc}) + S \cdot (E - E_{pzc}) \cdot \frac{dC_E}{dt} \quad (7)$$

where C_E is the capacitance per unit area and E_{pzc} is the potential of zero charge:

$$C_E = C_{\theta=1} \cdot \theta + C_{\theta=0} \cdot (1-\theta) \quad (8)$$

$$E_{pzc} = E_{pzc,\theta=1} \cdot \theta + E_{pzc,\theta=0} \cdot (1-\theta) \quad (9)$$

The application of Laplace transforms to eq. (2) gives the equation for surface concentration of substance A:

$$c_{x=0,m} = c^* - \frac{2\Gamma_{max}}{\sqrt{\pi d D}}\left[\theta_m + \sum_{j=1}^{m-1}\theta_j (Z_{m-j+1} - Z_{m-j})\right] \quad (10)$$

where $Z_k = \sqrt{k} - \sqrt{k-1}$. Introducing equation (10) into eq. (6), yields the expression for degree of electrode surface coverage:

$$\theta_m^2 + B\theta_m + \omega_m = 0 \quad (11)$$

$$\theta_m = -\frac{B}{2} - \frac{\sqrt{B^2 - 4\omega_m}}{2} \quad (12)$$

where θ_m is the surface coverage in the moment $t = m \cdot d$ and d is the time increment. The meanings of other symbols are:

$$B = -1 - \frac{c^*\sqrt{\pi d D}}{2\Gamma_{max}} - \frac{\sqrt{\pi d D}}{2\beta_E \Gamma_{max}} + \sum_{j=1}^{m-1}\theta_j\left(Z_{m-j+1} - Z_{m-j}\right) \quad (13)$$

$$\omega_m = \frac{c^*\sqrt{\pi d D}}{2\Gamma_{max}} - \sum_{j=1}^{m-1}\theta_j\left(Z_{m-j+1} - Z_{m-j}\right) \quad (14)$$

$$d = \frac{1}{50 f} \quad (15)$$

$$\theta_1 = \frac{\beta_E \cdot c^*}{1 + \frac{2\beta_E \Gamma_{max}}{\sqrt{\pi d D}}} \quad (16)$$

B) during adsorption of surface active, electro-inactive substance, the change of the potential of zero charge is negligible. The solution of equation (7):

$$\frac{i_m}{S \cdot C_{\theta=0} \cdot f} = E_m \cdot \left(\frac{C_{\theta=1}}{C_{\theta=0}} - 1\right) \cdot 50 \cdot (\theta_{m-1} - \theta_m) \quad (17)$$

and the dependence of the adsorption constant β_E on the electrode potential is:

$$\beta_E = \beta_0 \exp\left[-\frac{C_{\theta=0}\left(1 - \frac{C_{\theta=1}}{C_{\theta=0}}\right)(E - E_{pzc})^2}{2RT\ \Gamma_{max}}\right] \quad (18)$$

2. Assumption: between adsorbed molecules the attractive forces exist. The adsorption is described by Frumkin isotherm, with the coefficient $a < 0$:

$$\beta_E (c)_{x=0} = \frac{\theta}{1-\theta}\exp(a\theta) \quad (19)$$

Introducing equation (10) into eq. (19), yields the expression for the degree of electrode surface coverage ($0 \leq \theta_m \leq 1$):

$$(\theta_m - \omega_m) \cdot (\theta_m - 1) = \frac{\sqrt{dD\pi}}{2\Gamma_{max}\beta_m} \cdot \theta_m \cdot \exp(a \cdot \theta_m) \quad (20)$$

3. Assumption: the reaction (1) changed the potential of zero charge:

$$\frac{i_m}{S \cdot C_{\theta=0} \cdot f} = \left\{(E_m - E_{pzc,\theta=0}) \cdot \left(\frac{C_{\theta=1}}{C_{\theta=0}} - 1\right) - 2\Delta E_{pzc} \cdot \left(\frac{C_{\theta=1}}{C_{\theta=0}} - 1\right) \cdot \theta_m - \Delta E_{pzc}\right\} \cdot 50 \cdot (\theta_{m-1} - \theta_m) \quad (21)$$

where $\Delta E_{pzc} = E_{pzc,\theta=1} - E_{pzc,\theta=0}$ and the relationship between the adsorption constant and the electrode potential is:

$$\beta_E = \beta_0 \exp\left[-\frac{C_{\theta=0}\left(1 - \frac{C_{\theta=1}}{C_{\theta=0}}\right)(E - E_{pzc,\theta=0})^2}{2RT\ \Gamma_{max}}\right]\exp\left[-\frac{C_{\theta=0}\frac{C_{\theta=1}}{C_{\theta=0}}(E - E_{pzc,\theta=0})\Delta E_{pzc}}{RT\ \Gamma_{max}}\right] \quad (22)$$

In SWV the normalized response of the reaction (1) depends on four parameters, which are related to the bulk concentration of the reactant ($y = \frac{c^*\sqrt{D}}{\Gamma_{max}\sqrt{f}}$), the maximum adsorption constant ($b_0 = \frac{\beta_0 \Gamma_{max}\sqrt{f}}{\sqrt{D}}$), the capacity of a double layer on the free electrode surface ($k_c = \frac{C_{\theta=0}\left(1 - \frac{C_{\theta=1}}{C_{\theta=0}}\right)}{2RT\Gamma_{max}}$) and the ratio of capacities of totally covered and free electrode surfaces ($C_{\theta=1}/C_{\theta=0}$).

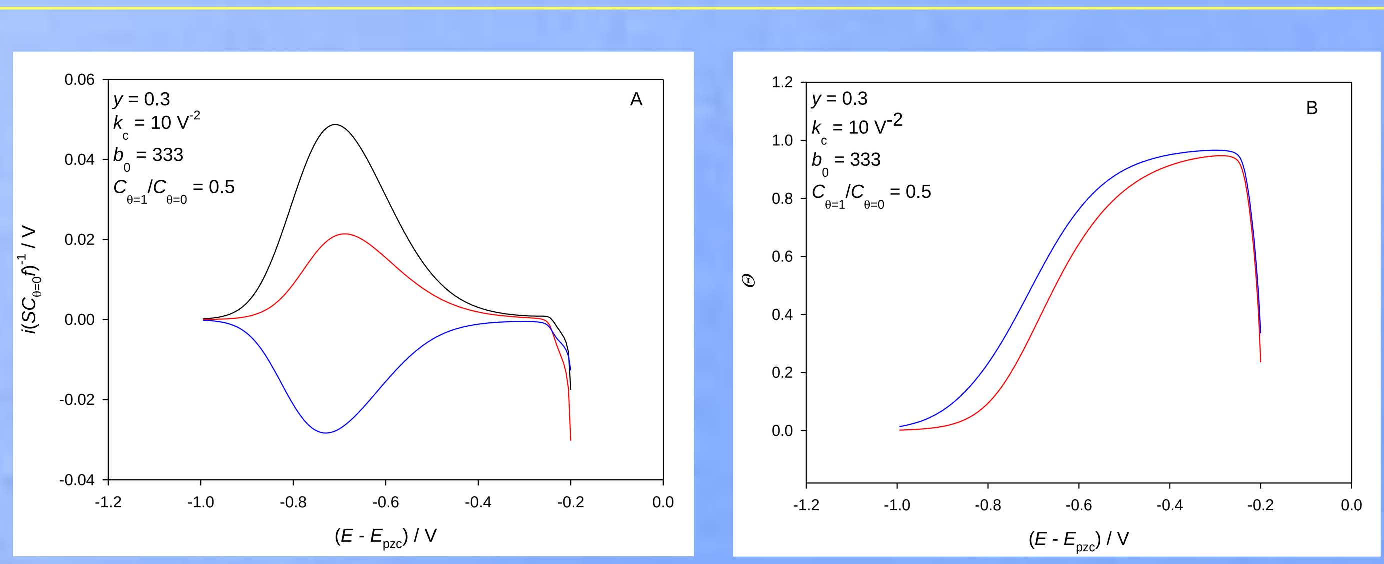


Fig 1. Normalized SW voltammogram (A) (with its forward (red), backward (blue) and net (black) components) and the dependence of electrode surface coverage on the electrode potential (B). E_{in} = -0.2 V vs. E_{pzc}, ΔE = -5 mV and E_{SWV} = 50 mV.

For given values of parameters (y, k_c, b_0, $C_{\theta=1}/C_{\theta=0}$), the saturation of electrode surface area is obtained within a small interval of potential, starting from the initial value.

THE EFFECT OF :

a) *dimensionless adsorption constant, b_0, and capacity parameter, k_c, on the electrode surface coverage (A, C) and appearance of normalized SW voltammogram (B, D):*

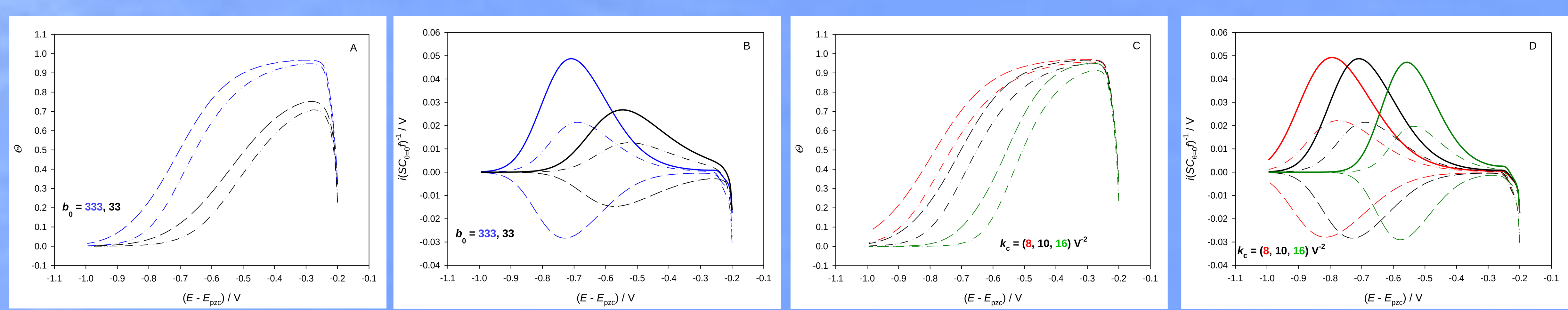


Figure 2. Forward (— · · —), backward (— —) and net (—) components. All other parameters as in Figure 1.

b) *Frumkin adsorption coefficient, a, on normalized SWV responses (A) and electrode surface coverage (B). Dependence of net peak potential (C) and half-peak width (D) on Frumkin coefficient:*

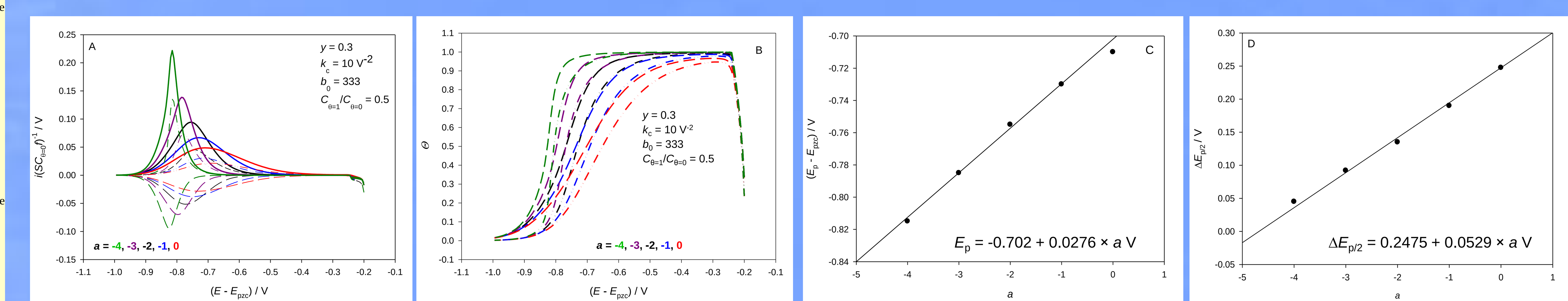


Figure 3. Forward (— · · —), backward (— —) and net (—) components. Other parameters as in Fig. 1.

c) *the change of the potential of zero charge, ΔE_{pzc}, on normalized SWV responses (A) and electrode surface coverage (B):*

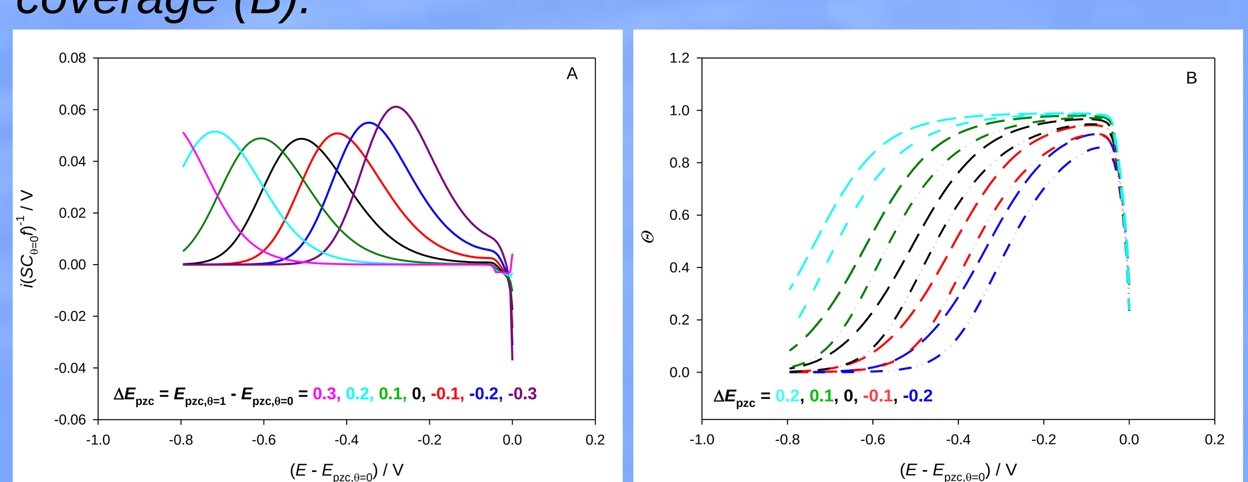
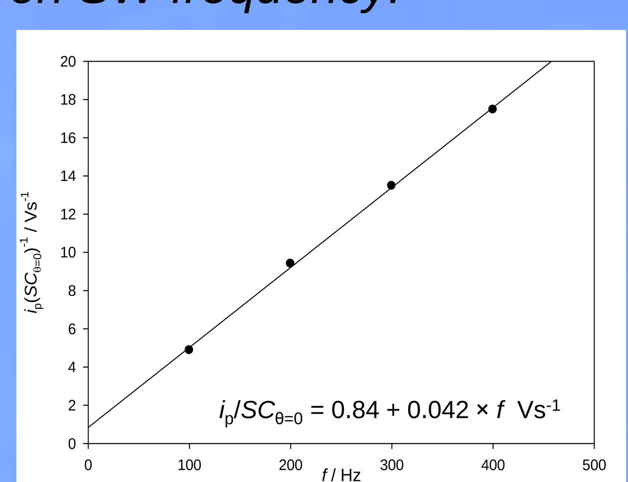


Figure 4. Forward (— · · —), backward (— —) and net (—) components. All other parameters as in Figure 1.

Dependence of the normalized net peak current on SW frequency:



CONCLUSIONS:

- •The SW response is caused by the difference in surface coverage during the forward and backward series of square-wave pulses.
- •The maximum SW net response appears at the potential at which the difference in the surface coverage is the biggest.
- •The net peak potential and the half-peak width of SWV response are a linear function of the Frumkin coefficient.
- •The normalized net peak current is a linear function of the SW frequency.