

# A New Mode of Classifying the Medicaments by Using the Electrochemical Impedance Spectroscopy

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**Abstract:** In this paper an "Electrochemical Impedance Spectroscopy (EIS)" method has been elaborated for classifying the medicaments (especially those from the God pharmacy) with respect to their capacitive and inductive properties. The method uses the following reference dielectrode: Pt | [Fe(CN)<sub>6</sub>]<sup>3-</sup> / [Fe(CN)<sub>6</sub>]<sup>4+</sup>, KCl (in excess), O<sub>2</sub> physically dissolved. The medicament is introduced in the electrolytic solution of this reference dielectrode, and the Nyquist plots are recorded according to a schedule described in the paper. Unlike Warburg, we have considered that the interface has both capacitive and inductive properties. Consequently, we have substituted the Warburg pseudo-capacitance C<sub>W</sub>, either by a pseudo-capacitance C<sub>W</sub><sup>\*</sup> put in series with a pseudo-inductance L<sub>W</sub><sup>\*</sup>, or by a pseudo-capacitance C<sub>W</sub><sup>\*\*</sup> put in parallel with a pseudo-inductance L<sub>W</sub><sup>\*\*</sup>. In this way, it was possible to propose a criterion which permits to compare the inductive properties of two medicaments, and therefore to classify the medicaments with respect to a reference medicament (e.g. the Swedish Bitter).

**Keywords:** Electrochemical Impedance Spectroscopy, pseudo-capacitance, cyclic voltammetry

## 1. Introduction

In preceding papers, Bonciocat et al., have shown that the faradic current density of an electrode redox reaction occurring with combined limitations of charge transfer and nonstationary, linear, semiinfinite diffusion, is the solution of an integral equation of Volterra type [1-7]. To each electrochemical method used in the experimental electrochemistry corresponds such an integral equation and by solving it an expression for the faradic current density characterizing the respective method. On the basis of these

current densities expressions, it was possible to develop new methods of direct and cyclic voltammetry, applicable in aqueous electrolytic solutions or in molten salts [8-18], new chronoamperometric methods [19, 29] and new Electrochemical Impedance Spectroscopy methods when only charge transfer and diffusion limitations are present [21].

The developments given in this paper are based on the equations deduced very recently [21, 22] for the Nyquist plots of redox multielectrodes in the domain of very small frequencies (round  $\nu = 0.2$ Hz). These equations are:

$$\operatorname{Re}(P) = R_{sol} + (\gamma^* R_{is}^*) + \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (1)$$

$$-\operatorname{Im}(P) - \frac{J_1^2[\omega(t-\tau)] + J_2^2[\omega(t-\tau)]}{2\pi} (\gamma^{**} \sigma^{**})^2 C_d = \frac{J_2[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (1')$$

*Re* and *Im* represent the real and imaginary part of the impedance of the measuring cell, i.e.,  $Z_{cell} = Re + Imj$ ,  $\omega = 2\pi\nu$  represents the radial frequency of the alternating current,  $R_{sol}$  the solution resistance,  $\tau$  the moment of time when the *alternating overvoltage* is superimposed over the *constant overvoltage* applied at  $t=0$ , and  $t$  is the time when the Nyquist plot recording ends.  $C_d$  is the double layer capacity, and  $J_1[\omega(t-\tau)]$ ,  $J_2[\omega(t-\tau)]$  are the Fresnel integrals:

$$J_1[\omega(t-\tau)] = \int_0^{\omega(t-\tau)} \frac{\cos x}{x^{1/2}} dx,$$

respective:

$$J_2[\omega(t-\tau)] = \int_0^{\omega(t-\tau)} \frac{\sin x}{x^{1/2}} dx \quad (2)$$

whose values tend to  $\sqrt{\pi/2} \cong 1.253$  for sufficiently great values of the product  $\omega(t-\tau)$ .  $P$  is a point on the Nyquist plot, and its coordinates given by eqs.(1 and 1'), depend on both  $\omega$  and the product  $\omega(t-\tau)$ . In a Nyquist plot, the points should be enumerated from right to left. Then, considering a record with 10 points per decade, starting with  $\nu_1 = 0.02$  Hz and ending at  $10^5$  Hz, the first point  $P_1$  corresponds to the radial frequency  $\omega_1 = 2\pi\nu_1 = 1.256 s^{-1}$ , and the second point  $P_2$  to the radial frequency  $\omega_2$  given by equation

$\log(\omega_2/\omega_1) = 0.1$ , i.e.,  $\omega_2 = \omega_1 \cdot 10^{0.1} = 1.582 \text{ s}^{-1}$ .

In eqs.(1,1') are two unknowns:  $(\gamma^* R_{ts}^*)$  and  $(\gamma^{**} \sigma^{**})$  expressing the charge transfer, respective diffusion,

where:

$$\gamma_k R_{tsk} = \frac{RT}{n_k F I_k^0} \{ \beta_k \exp[-\beta_k n_k f \eta_k(0)] + (1 - \beta_k) \exp[(1 - \beta_k) n_k f \eta_k(0)] \}^{-1} \quad (4)$$

respective:

$$(\gamma_k \sigma_k) = \frac{RT}{\sqrt{2} n_k^2 F^2 A} \left\{ \frac{1}{\sqrt{D_{O_k}} \cdot c_{O_k}} \exp[-\beta_k n_k f \eta_k(0)] + \frac{1}{\sqrt{D_{R_k}} \cdot c_{R_k}} \exp[(1 - \beta_k) n_k f \eta_k(0)] \right\} \times \\ \times \{ \beta_k \exp[-\beta_k n_k f \eta_k(0)] + (1 - \beta_k) \exp[(1 - \beta_k) n_k f \eta_k(0)] \}^{-1}; \quad f = \frac{F}{RT} \quad (4')$$

In equations (4, 4'),  $I_k^0$ ,  $\beta_k$ ,  $n_k$  refer to the electrode redox reaction  $k$ , and represent the exchange current intensity, the symmetry factor, and the number of electrons participating in the reaction.  $\eta_k(0)$  represents the initial overpotential at which the  $k$  electrode reaction occurs, and is given by:

$$\eta_k(0) = g_m + \eta - g_{Nernst,k} \quad (5)$$

where  $g_m$  represents the mixed potential of the interface,  $g_{Nernst,k}$  the equilibrium potential of the electrode reaction  $k$ , and  $\eta$  the constant overpotential applied at the initial moment  $t=0$ .  $A$  is the free area of the interface and the other quantities have the usual meanings.

The last term in equation (1) represents the Warburg diffusion resistance of the interface  $R_W(P)$ , while the last term in equation (1') represents the magnitude of the capacitive reactance of the interface  $|X_{C_W}(P)|$ , and is due to the Warburg pseudo-capacitance of the interface:

$$C_W(P) = \frac{1}{\omega |X_{C_W}(P)|}$$

Therefore equations (1, 1') it follows:

$$R_W(P) C_W(P) = \frac{J_1[\omega(t-\tau)]}{J_2[\omega(t-\tau)]} \cdot \frac{1}{\omega} \quad (6)$$

The pseudo-capacitance  $C_W(P)$  has been introduced by Warburg to explain the phase difference that appears between the current and the tension.

Unlike Warburg, we shall consider that the interface has both capacitive and inductive properties. Consequently, we shall substitute the Warburg pseudo-capacitance  $C_W(P)$ , either by a pseudo-capacitance  $C_W^*(P)$  put in series with a pseudo-inductance  $L_W^*(P)$ , or by a pseudo-capacitance  $C_W^{**}(P)$  put in parallel with a pseudo-inductance  $L_W^{**}(P)$ .

limitations of the interface. Their expressions are:

$$\frac{1}{(\gamma^* R_{ts}^*)} = \sum_k \frac{1}{(\gamma_k R_{tsk})}; \quad \frac{1}{(\gamma^{**} \sigma^{**})} = \frac{1}{2} \sum_k \frac{1}{(\gamma_k \sigma_k)} \quad (3)$$

In this substitution, two conditions must be fulfilled:  
- the impedance of the corresponding arrangement (i.e., in series, or in parallel) must be equal with the Warburg pseudo-capacitance impedance.

- of course, these substitutions will change the Warburg diffusion resistance, but eq.(6) must remain valid, i.e.,

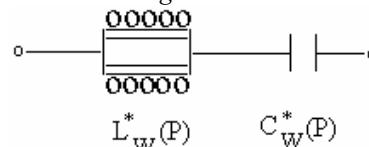
$$R_W(P) \cdot C_W(P) = R_W^*(P) \cdot C_W^*(P) = R_W^{**}(P) \cdot C_W^{**}(P) \quad (7)$$

because the second member of eq.(6) is practically equal to  $1/\omega$  (i.e., is not dependent on these substitutions).

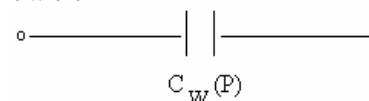
## 2. Theoretical Section

### 1. Substitution of the Warburg pseudo-capacitance $C_W(P)$

a) By a series arrangement



is equivalent with:



The equality of the impedances writes:

$$Z^* = \left( \omega L_W^*(P) - \frac{1}{\omega C_W^*(P)} \right) j = - \frac{1}{\omega C_W(P)} j = Z \quad (9)$$

$$\text{i.e.,} \quad \omega L_W^*(P) = |X_{C_W^*}(P)| - |X_{C_W}(P)| \quad (10)$$

where (see eq.(1')):

$$|X_{C_W^*}(P)| = -\text{Im}^*(P) - \frac{J_1^2[\omega(t-\tau)] + J_2^2[\omega(t-\tau)] (\gamma^{**} \sigma^{**})^2 C_d}{2\pi} \quad (11)$$

$$|X_{C_W}(P)| = -\text{Im}(P) - \frac{J_1^2[\omega(t-\tau)] + J_2^2[\omega(t-\tau)] (\gamma^{**} \sigma^{**})^2 C_d}{2\pi} \quad (11')$$

because the quantity  $(\gamma^{**}\sigma^{**})^2 C_d$  is not dependent on the way the charge transfer occurs.

The inductive reactance being a positive quantity, it results from eq.(10), and the meaning of a capacitive reactance (i.e.,  $|X_C| = \frac{1}{\omega C}$ ):

$$\omega C_W(P) \gg \omega C_W^*(P) \quad (12)$$

and:

$$L_W^*(P) = \frac{C_W(P) - C_W^*(P)}{\omega^2 C_W(P) C_W^*(P)} \quad (12')$$

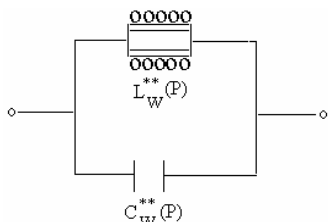
Equation (12) shows that in a series arrangement, the pseudo-capacitance  $C_W^*(P)$  is smaller than the Warburg pseudo-capacitance  $C_W(P)$ . The two equations (12,12') may be written in the form:

$$C_W^*(P) = \alpha C_W(P); \quad \alpha < 1$$

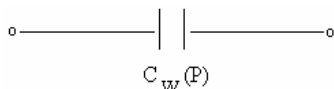
and

$$\omega L_W^*(P) = \frac{1 - \alpha}{\alpha} \cdot \frac{1}{\omega C_W(P)} \quad (13)$$

b. By a parallel arrangement



is equivalent with: (14)



Then:

$$\frac{1}{Z^{**}} = \omega C_W^{**}(P)j + \frac{1}{\omega L_W^{**}(P)j}; Z = \frac{1}{\omega C_W(P)j} \quad (15)$$

From the condition:

$$Z^{**} = Z \quad (16)$$

it follows:

$$\frac{1}{\omega L_W^{**}(P)} = \frac{1}{|X_{C_W^{**}(P)}|} - \frac{1}{|X_{C_W(P)}|} \quad (17)$$

$\omega L_W^{**}(P)$  being positive, eq.(17) leads to the conclusions:

$$\omega C_W^{**}(P) \gg \omega C_W(P) \quad (18)$$

$$L_W^{**}(P) = 1/\omega^2 [C_W^{**}(P) - C_W(P)] \quad (18')$$

Equation (18) shows that in a parallel arrangement, the pseudo-capacitance  $C_W^{**}(P)$  is greater than the Warburg pseudo-capacitance  $C_W(P)$ . The two equations (18) may be written in the form:

$$C_W^{**}(P) = \beta C_W(P); \quad \beta > 1$$

and

$$\omega L_W^{**}(P) = \frac{1}{\beta - 1} \cdot \frac{1}{\omega C_W(P)} \quad (19)$$

Taking  $\beta = 1/\alpha$ , one gets:

$$\boxed{C_W^{**}(P) = \frac{1}{\alpha} C_W(P) \text{ and } \omega L_W^{**}(P) = \frac{\alpha}{1 - \alpha} \cdot \frac{1}{\omega C_W(P)}} \quad (20)$$

## 2. Relation between the real oscillating period $T = 2\pi/\omega$ and the Thomson oscillating periods associated to the two arrangements

a. Series arrangement

From the two equations (13) it follows:

$$T = \frac{1}{\sqrt{1 - \alpha}} 2\pi \sqrt{L_W^*(P) C_W^*(P)} \quad (21)$$

But :

$$T_{\text{Thomson, series}} = 2\pi \sqrt{L_W^*(P) C_W^*(P)} \quad (21')$$

and thus:

$$T_{\text{Thomson, series}} = \sqrt{1 - \alpha} \cdot T; \omega_{\text{Thomson, series}} = \frac{1}{\sqrt{1 - \alpha}} \omega \quad (21'')$$

b. Parallel arrangement

From the two equations (20) it follows:

$$T = \sqrt{1 - \alpha} 2\pi \sqrt{L_W^{**}(P) C_W^{**}(P)} \quad (22)$$

i.e.,

$$T_{\text{Thomson, parallel}} = 2\pi \sqrt{L_W^{**}(P) C_W^{**}(P)} = \frac{1}{\sqrt{1 - \alpha}} T;$$

$$\omega_{\text{Thomson, parallel}} = \sqrt{1 - \alpha} \cdot \omega \quad (22')$$

From equations (21'' and 22') results a very important conclusion: *the real period (or radial frequency) of the alternating current is the geometric mean of the Thomson periods (or radial frequencies) associated to the two arrangements, i.e.,*

$$T = \sqrt{T_{\text{Thomson, series}} T_{\text{Thomson, parallel}}}; \quad (23)$$

$$\omega = \sqrt{\omega_{\text{Thomson, series}} \omega_{\text{Thomson, parallel}}}$$

## 3. The new expressions of the Warburg diffusion resistances, and capacitive reactances of the interface

a. Series arrangement

From condition (7) results:

$$R_W^*(P) = R_W(P) \cdot \frac{C_W(P)}{C_W^*(P)} = \frac{1}{\alpha} R_W(P) \quad (24)$$

and explicating *the Warburg diffusion resistance* (see the

last term in equation (1)):

$$R_w^*(P) = \frac{1}{\alpha} \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (24')$$

$$\left| X_{C_w^*}(P) \right| = \frac{1}{\alpha} \frac{J_2[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (25')$$

As for the magnitude of the capacitive reactance, it is given by:

$$\left| X_{C_w^*}(P) \right| = \left| X_{C_w}(P) \right| \cdot \frac{\left| X_{C_w^*}(P) \right|}{\left| X_{C_w}(P) \right|} = \left| X_{C_w}(P) \right| \cdot \frac{C_w(P)}{C_w^*(P)} = \frac{1}{\alpha} \left| X_{C_w}(P) \right| \quad (25)$$

and explicitating the magnitude of the capacitive reactance:

$$\left| X_{C_w^*}(P) \right| = \left| X_{C_w}(P) \right| \cdot \frac{\left| X_{C_w^*}(P) \right|}{\left| X_{C_w}(P) \right|} = \left| X_{C_w}(P) \right| \cdot \frac{C_w(P)}{C_w^*(P)} = \alpha \left| X_{C_w}(P) \right| \quad (27)$$

i.e.,

$$\left| X_{C_w^*}(P) \right| = \alpha \frac{J_2[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (27')$$

#### 4. Estimation of the unknowns $R_{sol.} + (\gamma^* R_{ts}^*)$ and $(\gamma^{**} \sigma^{**})$

a) By using the equations of the series arrangement

The first parametric equation of the Nyquist plot writes:

$$\text{Re}(P) = R_{sol.} + \left[ (\gamma^{**} R_{ts}^*) \right]^* + R_w^*(P) = R_{sol.} + \left[ (\gamma^* R_{ts}^*) \right]^* + \frac{1}{\alpha} R_w(P) \quad (28)$$

and may be put in the form:

$$\text{Re}(P) = R_{sol.} + \left[ (\gamma^* R_{ts}^*) \right]^* + \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} + \frac{1-\alpha}{\alpha} \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (28')$$

Let's introduce the quantity:

$$Y^*(P) = R_{sol.} + \left[ (\gamma^* R_{ts}^*) \right]^* + \frac{1-\alpha}{\alpha} \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (29)$$

when equation (28') takes the form:

$$\text{Re}(P) - Y^*(P) = \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (30)$$

$$Y^* \left( \frac{\omega_1 + \omega_2}{2} \right) \cong \left[ \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \quad (32)$$

For sufficiently great values of the recording time, one may consider:

$$\text{Re}(P) - Y^*(P) \cong \frac{1}{2} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (30')$$

and thus:

$$\frac{\text{Re}(P_1) - Y^*(P_1)}{\text{Re}(P_2) - Y^*(P_2)} \cong \left( \frac{\omega_1}{\omega_2} \right)^{-1/2} = 1.122 \quad (31)$$

Further, one may accept:

$$Y^*(P_1) \cong Y^*(P_2) \cong Y^* \left( \frac{\omega_1 + \omega_2}{2} \right) \quad (31')$$

and then, equation (31) leads to:

b) Parallel arrangement

The same condition (7) leads to:

$$R_w^{**}(P) = R_w(P) \cdot \frac{C_w(P)}{C_w^{**}(P)} = \alpha R_w(P) \quad (26)$$

i.e.,

$$R_w^{**}(P) = \alpha \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (26')$$

Similarly:

Therefore (see equation (29)):

$$R_{sol.} + \left[ (\gamma^* R_{ts}^*) \right]^* = Y^* \left( \frac{\omega_1 + \omega_2}{2} \right) - \frac{1-\alpha}{\alpha} \frac{(\gamma^{**} \sigma^{**})}{2 \left( \frac{\omega_1 + \omega_2}{2} \right)^{1/2}}$$

and finally:

$$R_{sol.} + \left[ (\gamma^* R_{ts}^*) \right]^* = -0.42 \frac{1-\alpha}{\alpha} (\gamma^{**} \sigma^{**}) + \left[ \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \quad (33)$$

For  $\alpha = 1$ , equation (33) particularizes in the equation giving the unknown  $R_{sol.} + (\gamma^* R_{ts}^*)$ :

$$R_{sol.} + (\gamma^* R_{ts}^*) = \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \quad (\Omega) \quad (34)$$

Further, equations (30' and 32) give:

$$(\gamma^{**} \sigma^{**}) = 2 \omega_1^{1/2} \left[ \text{Re}(P_1) - \text{Re}(P_2) + \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \text{ i.e.,} \\ \boxed{(\gamma^{**} \sigma^{**}) \approx 20.6 [\text{Re}(P_1) - \text{Re}(P_2)] (\Omega s^{-1/2})} \quad (35)$$

b. By using the equations of the parallel arrangement

The first parametric equation is now

$$\text{Re}(P) = R_{sol} + [(\gamma^* R_{ts}^*)]^{**} + R_W^{**}(P) = \\ = R_{sol} + [(\gamma^* R_{ts}^*)]^{**} + \alpha R_W(P) \quad (36)$$

and may be put in the form:

$$\text{Re}(P) = R_{sol} + [(\gamma^* R_{ts}^*)]^{**} + \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} + \\ + (\alpha - 1) \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (36')$$

With the aid of the quantity:

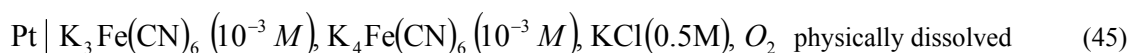
$$Y^{**}(P) = R_{sol} + [(\gamma^* R_{ts}^*)]^{**} + (\alpha - 1) \cdot \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (37)$$

equation (36') takes the form:

$$\text{Re}(P) - Y^{**}(P) = \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi}} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \cong \frac{1}{2} (\gamma^{**} \sigma^{**}) \omega^{-1/2} \quad (38)$$

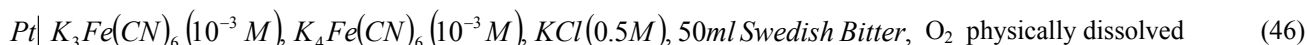
and thus:

$$\frac{\text{Re}(P_1) - Y^{**}(P_1)}{\text{Re}(P_2) - Y^{**}(P_2)} \cong \left( \frac{\omega_1}{\omega_2} \right)^{-1/2} = 1.122 \quad (39)$$

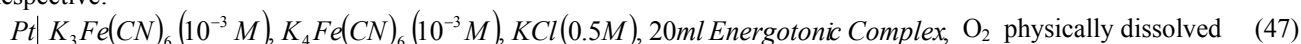


has only capacitive properties, and for explaining them suffice to introduce the Warburg pseudo-capacitance in the Faraday impedance of the interface.

In this paper, one analyzes the effect that two medicaments, namely the Swedish Bitter, original Schweden Tropfen, BANO, and the Energotonic multivitamin complex Plant Extrakt- Radaia, Cluj, have



Respective:



The concentrations are given with respect to the same total volume of V= 300ml.

To perform the experiments, three values of the constant overpotential  $\eta$  have been used, namely 0.00V; -0.05V and 0.05V and for each overpotential, four Nyquist

Accepting the approximation:

$$Y^{**}(P_1) \cong Y^{**}(P_2) \cong Y^{**} \left( \frac{\omega_1 + \omega_2}{2} \right) \quad (39')$$

one gets:

$$Y^{**} \left( \frac{\omega_1 + \omega_2}{2} \right) \cong \left[ \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \quad (40)$$

and further:

$$R_{sol} + [(\gamma^* R_{ts}^*)]^{**} = 0.42(1 - \alpha)(\gamma^{**} \sigma^{**}) + \\ + \left[ \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \quad (41)$$

and for  $\alpha = 1$ :

$$R_{sol} + (\gamma^* R_{ts}^*) = \left[ \text{Re}(P_2) - \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] (\Omega) \quad (42) \equiv (34)$$

As for the expression of  $(\gamma^{**} \cdot \sigma^{**})$ , it is obtain from eqs. (38 and 40):

$$(\gamma^{**} \sigma^{**}) = 2 \omega_1^{1/2} \left[ \text{Re}(P_1) - \text{Re}(P_2) + \frac{\text{Re}(P_1) - \text{Re}(P_2)}{0.122} \right] \quad (43)$$

i.e.,

$$\boxed{(\gamma^{**} \sigma^{**}) \cong 20.6 [\text{Re}(P_1) - \text{Re}(P_2)] (\Omega s^{-1/2})} \quad (44) \equiv (35)$$

### 3. Experimental Section

In a very recent paper<sup>[25]</sup> it has been proved that the interface of the dielectrode:

upon the electrochemical properties of the reference dielectrode [45]. These medicaments have been introduced in the electrolytic solution of the reference dielectrode[45], maintaining the total volume of the solution at V= 300ml.

The two electrochemical systems that have been analyzed are:

plots have been recorded, corresponding to four values of the time  $\tau$ , i.e., 0s, 10s, 100s, and 1000s. In this way, 12 Nyquist plots have been obtained, for each medicament, and from each Nyquist plot, the coordinates of the two points  $P_1$  and  $P_2$  have resulted. These coordinates have

served to estimate, by means of equations (34 and 35), the values of  $R_{sol} + (\gamma^* R_{ts}^*)$ , respective  $(\gamma^{**} \sigma^{**})$ .

The resulted values are given in Table 1.

TABLE I. Estimation of the quantities  $R_{sol} + (\gamma^* R_{ts}^*)$  and  $(\gamma^{**} \sigma^{**})$  characterizing the charge transfer an diffusion limitations of the electrochemical systems (46) and (47)

	$\eta$ (V)	$\tau$ (s)	Re(P <sub>1</sub> ) ( $\Omega$ )	Re(P <sub>2</sub> ) ( $\Omega$ )	$\gamma^{**} \sigma^{**}$ ( $\Omega s^{-1/2}$ )	$R_{sol} + (\gamma^* R_{ts}^*)$ ( $\Omega$ )
Swedish Bitter	0	0	4236	3791	9173	143
	0	10	4297	3851	9194	195
	0	100	4419	3932	10039	-60
	0	1000	4595	4054	11152	-380
	-0.05	0	6495	5676	16883	-1037
	-0.05	10	6559	5707	17563	-1277
	-0.05	100	6559	5739	16903	-982
	-0.05	1000	6527	5739	16244	-720
	0.05	0	5676	4973	14492	-789
	0.05	10	5946	5243	14492	-519
	0.05	100	5946	5243	14492	-519
	0.05	1000	5838	5135	14492	-627
Energotonic complex	0	0	1358	1273	1752	576
	0	10	1325	1240	1752	543
	0	100	1287	1197	1855	459
	0	1000	1263	1178	1752	481
	-0.05	0	2525	2323	4164	667
	-0.05	10	2525	2313	4370	575
	-0.05	100	2535	2333	4164	677
	-0.05	1000	2535	2354	3731	870
	0.05	0	1912	1771	2907	615
	0.05	10	1926	1785	2907	629
	0.05	100	1933	1798	2783	691
	0.05	1000	1946	1805	2907	649

The fact that in the case of Energotonic multivitamin complex the values obtained for  $R_{sol} + (\gamma^* R_{ts}^*)$  and  $(\gamma^{**} \sigma^{**})$  are all positive and mutual compatible for each value of the overtenion  $\eta$ , shows that the electrochemical system [47] must be considered as having only capacitive properties. Consequently, in the case of the system containing the Energotonic complex, the Warburg pseudo-capacitance  $C_w(P)$  accounts for its electrochemical properties, and there is no need to introduce something else in its Faraday impedance.

As for the negative values resulted for  $R_{sol} + (\gamma^* R_{ts}^*)$  in the case of the system [46], they are unacceptable and shows that the Swedish Bitter has transformed the reference dielectrode [45] in a multielectrode whose electrochemical properties may not be explained by a Faraday impedance containing only a capacitive reactance.

To account for this transformation, we have considered that the Faraday impedance must contain a Warburg pseudo-inductance too.

The values of  $C_w(\omega_1)$ ,  $C_w^{**}(\omega_1)$  and  $L_w^{**}(\omega_1)$  have been obtained by means of the formulae:

$$C_w(\omega_1) = \frac{1}{\omega_1 |X_{C_w}(\omega_1)|} = \frac{\sqrt{2\pi}}{J_2[\omega_1(t-\tau)](\gamma^{**} \sigma^{**}) \omega_1^{-1/2}} \cdot \frac{1}{\omega_1} \cong \frac{2}{(\gamma^{**} \sigma^{**}) \omega_1^{1/2}} \tag{49}$$

respective:

$$C_w^{**}(\omega_1) = \frac{1}{\alpha} C_w(\omega_1); L_w^{**}(\omega_1) = \frac{\alpha}{1-\alpha} \cdot \frac{1}{\omega_1^2 C_w(\omega_1)}; \alpha = 0.8, \omega_1 = 1.256 s^{-1} \tag{50}$$

and 1H(henry) = 1 $\Omega$ s.

The results given in Table 2, show that a substitution of the Warburg pseudo-capacitance  $C_w(P)$  by a parallel arrangement:  $C_w^{**}(P) = \frac{1}{\alpha} C_w(P)$  in parallel with a Warburg pseudo-inductance  $L_w^{**}(P) = \frac{\alpha}{1-\alpha} \frac{1}{\omega^2 C_w(P)}$  (see equations (20)), leads to acceptable values for  $R_{sol} + [(\gamma^* R_{ts}^*)]^{**}$ .

The value of  $\alpha$  has been chosen taking into account the condition:

$$0.42 (1-\alpha) 17563 > 1277 \tag{48}$$

which gives  $\alpha < 0.827$ . To be not far away from  $\alpha = 1$ , when the substitution of the Warburg capacitance is not necessary, we have chosen the value  $\alpha = 0.8$ . The corresponding values  $C_w^{**}(\omega_1)$  and  $L_w^{**}(\omega_1)$  are given in Table 3.

TABLE 2. Estimation of the quantities  $R_{sol} + [(\gamma^* \cdot R_{ts}^*)]^{**}$ , characterizing the charge transfer limitations of the electrochemical system [46],  $\alpha = 0.8$ 

$\eta$ (V)	$\tau$ (s)	$\gamma^{**} \cdot \sigma^{**}$ ( $\Omega \text{ s}^{-1/2}$ )	$0.42 \cdot (1-\alpha) \cdot (\gamma^{**} \cdot \sigma^{**})$ ( $\Omega$ )	$R_{sol} + (\gamma^* \cdot R_{ts}^*)$ ( $\Omega$ )	$R_{sol} + [(\gamma^* \cdot R_{ts}^*)]^{**}$ ( $\Omega$ )
0	0	9173	771	143	934
0	10	9194	772	195	967
0	100	10039	843	-60	783
0	1000	11152	937	-380	557
-0.05	0	16883	1418	-1037	381
-0.05	10	17563	1475	-1277	198
-0.05	100	16903	1420	-982	438
-0.05	1000	16244	1364	-720	644
0.05	0	14492	1217	-789	428
0.05	10	14492	1217	-519	698
0.05	100	14492	1217	-519	698
0.05	1000	14492	1217	-627	590

TABLE 3. Estimation of the components of the parallel arrangement by which one may explain the inductive effect of the Swedish Bitter

$\eta$ (V)	$\tau$ (s)	$\gamma^{**} \cdot \sigma^{**}$ ( $\Omega \text{ s}^{-1/2}$ )	$10^3 \cdot C_W(\omega_1)$ (s/ $\Omega$ )	$10^3 \cdot C_W^{**}(\omega_1)$ (s/ $\Omega$ )	$10^3 \cdot L_W^{**}(\omega_1)$	$T_{Th,p}$ (s)	$T = \sqrt{1-\alpha} T_{Th,p}$ (s)
0	0	9173	0.195	0.244	13.01	11.19	5.00
0	10	9194	0.194	0.243	13.07	11.19	5.00
0	100	10039	0.178	0.223	14.25	11.19	5.00
0	1000	11152	0.160	0.200	15.85	11.18	5.00
-0.05	0	16883	0.106	0.133	23.92	11.20	5.01
-0.05	10	17563	0.102	0.128	24.86	11.20	5.01
-0.05	100	16903	0.106	0.133	23.92	11.20	5.01
-0.05	1000	16244	0.110	0.138	23.05	11.20	5.01
0.05	0	14492	0.123	0.154	20.62	11.19	5.00
0.05	10	14492	0.123	0.154	20.62	11.19	5.00
0.05	100	14492	0.123	0.154	20.62	11.19	5.00
0.05	1000	14492	0.123	0.154	20.62	11.19	5.00

To verify the correctness of the values obtained for  $C_W^{**}(\omega_1)$  and  $L_W^{**}(\omega_1)$  in the last two columns are given the Thomson periods corresponding to the parallel arrangement and the values resulted for the real time  $T = 2\pi / \omega_1 = 5s$ , by applying the first equation (22').

#### 4. Conclusions

The Energotonic multivitamin complex transforms the reference redox dielectrode(45), which has only *capacitive* properties, in the mutielectrode(47), having practically only *capacitive* properties too. The Farady impedances of both systems have only Warburg *capacitive reactances*.

The Swedish Bitter transforms the reference redox dielectrode (45) in the mutielectrode (46), having both *capacitive* and *inductive* properties. To account for these properties, it was necessary to substitute the Warburg pseudo-capacitance  $C_W(P)$  by a parallel arrangement:

$$C_W^{**}(P) = \frac{1}{\alpha} C_W(P) \text{ in parallel with a Warburg pseudo-inductance } L_W^{**}(P) = \frac{\alpha}{1-\alpha} \cdot \frac{1}{\omega^2 C_W(P)}, \quad \alpha = 0.8. \quad (51)$$

The ratio:

$$\frac{L_W^{**}(P)}{C_W^{**}(P)} = \frac{\alpha^2}{1-\alpha} \cdot \frac{1}{\omega^2 C_W^2(P)}, \quad \alpha = 0.8.$$

may be used to compare the inductive properties of two medicaments; indeed the fact that the Energotonic multivitamin complex has practically only capacitive properties, must be reflected in a much smaller value of the ratio (51). Therefore, a criterion for comparing the inductive properties of two medicaments may be the quotient:

$$\left[ \frac{L_W^{**}(P)}{C_W^{**}(P)} \right]_B / \left[ \frac{L_W^{**}(P)}{C_W^{**}(P)} \right]_E = \left[ \frac{C_W^2(P)}{C_W^2(P)} \right]_E \quad (52)$$

But, from eq.(49) it results;

$$\left[ \frac{C_W^2(P)}{C_W^2(P)} \right]_E = \left[ \frac{(\gamma^{**} \sigma^{**})_B}{(\gamma^{**} \sigma^{**})_E} \right]^2 \quad (52')$$

and thus, the criterion we are looking for, may be:

$$Q = \left[ \frac{(\gamma^{**} \sigma^{**})_B}{(\gamma^{**} \sigma^{**})_E} \right]^2 \quad (53)$$

In Table 4, are given the values of this criterion for the two medicaments; B= Swedish Bitter and E= Energotonic complex.

The values resulted for this criterion show that the Swedish Bitter has much greater inductive properties than the Energotonic multivitamin complex.

Of course, this criterion may be used for classifying the medicaments (especially those from the God pharmacy) with respect to their *capacitive* and *inductive* properties, by using the Electrochemical Impedance Spectroscopy. The method uses the reference dielectrode (45). The

medicament is introduced in the electrolytic solution of this reference dielectrode, and the Nyquist plots are recorded in the way shown in this paper. From each Nyquist plot, the coordinates of the points  $P_1$ ,  $P_2$ , (corresponding to  $\omega_1 = 1.256s^{-1}$  and  $\omega_2 = 1.582s^{-1}$ ) are obtained. These coordinates permit to get the values of the unknowns  $R_{sol} + (\gamma^* \cdot R_{ts}^*)$  and  $(\gamma^{**} \cdot \sigma^{**})$ .

TABLE 4. The values of the criterion  $Q$  proposed for comparing the inductive properties of the two medicaments investigated.

$\eta$ (V)	$\tau$ (s)	$(\gamma^{**} \cdot \sigma^{**})_B$ ( $\Omega s^{-1/2}$ )	$(\gamma^{**} \cdot \sigma^{**})_E$ ( $\Omega s^{-1/2}$ )	$Q = [( \gamma^{**} \cdot \sigma^{**} )_B / ( \gamma^{**} \cdot \sigma^{**} )_E ]^2$
0	0	9173	1752	27.41
0	10	9194	1752	27.54
0	100	10039	1855	29.29
0	1000	11152	1752	40.52
-0.05	0	16883	4164	16.44
-0.05	10	17563	4370	16.15
-0.05	100	16903	4164	16.48
-0.05	1000	16244	3731	18.96
0.05	0	14492	2907	24.85
0.05	10	14492	2907	24.85
0.05	100	14492	2783	27.12
0.05	1000	14492	2907	24.85

If among the values of  $R_{sol} + (\gamma^* \cdot R_{ts}^*)$  are also negative values, it is a prove that the Warburg pseudo-capacitance must be substituted by a parallel arrangement  $C_W^{**}(P)$ ,  $L_W^{**}(P)$ , and the corrected quantities  $R_{sol} + [(\gamma^* \cdot R_{ts}^*)]^{**}$  are obtained by adding to the values of  $R_{sol} + (\gamma^* \cdot R_{ts}^*)$ , the values  $0.42 \cdot (1-\alpha) \cdot (\gamma^{**} \cdot \sigma^{**})$ . In doing this, the value of  $\alpha$  results from the condition  $R_{sol} + [(\gamma^* \cdot R_{ts}^*)]^{**} > 0$ .

In this way, the unknowns  $[(\gamma^* \cdot R_{ts}^*)]^{**}$  and  $(\gamma^{**} \cdot \sigma^{**})$ , characterizing the *charge transfer and diffusion limitations* of the reference dielectrode in whose electrolytic solution is introduced the medicament, are estimated.

Further, repeating the experiments with a second medicament, results new values for  $(\gamma^{**} \cdot \sigma^{**})$ , and therefore, the *inductive properties* of the two medicaments may be compared by means of the criterion (53).

Choosing, e.g., the Swedish Bitter as a *reference medicament*, the proposed "Electrochemical Impedance Spectroscopy" method permits to classify the other medicaments, by using the criterion (53).

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