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ABOUT THE POSSIBILITY OF USING THE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AS A METHOD OF CLASSIFYING THE DRUGS

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ABSTRACT. The proposed EIS method uses the *reference redox dielectrode*: $\mathrm{Pt}\left|\left[\mathrm{Fe(CN)_6}\right]^{3-}/\left[\mathrm{Fe(CN)_6}\right]^{4-},\mathrm{KCl}\right.$ (in excess), O_2 physically dissolved (1) which, e.g., in weak acidic media, has the reactions:

$$\frac{1}{4}\mathrm{O_2}+\mathrm{H^+}+e\rightarrow\frac{1}{2}\mathrm{H_2O} \quad (2a)$$

$$\left[\mathrm{Fe(CN)_6}\right]^{4-}\rightarrow\left[\mathrm{Fe(CN)_6}\right]^{3-}+e \quad (2b)$$

In the case of the *reference redox dielectrode* (1), the *pseudo-capacitance* $C_W(\omega)$, introduced by Warburg to explain the phase difference between the current and the tension, has led to expressions of the Nyquist plots, obtaned in the domain of very small radial frequencies ω, in good agreement with the experimetal data. Consider now the *multielectrode*:

$\mathrm{Pt}\left|\left[\mathrm{Fe(CN)_6}\right]^{3-}/\left[\mathrm{Fe(CN)_6}\right]^{4-},\mathrm{KCl}\right.$ (in excess), v ml (LD), O_2 physically dissolved (3), where LD= liquid drug.

New additional reactions appear, and we don't know them. Therefore, it is necessary to give a criterion of classifying the drugs which doesn't imply the knowledge of the additional reactions. Consequently, we have considered that to explain the phase difference between the current and the tension, it is also correct to replace $C_W(\omega)$, either by a series arrangement $C^*_W(\omega)$, $L^*_W(\omega)$, or by a parallel one $C^{**}_W(\omega), L^{**}_W(\omega)$ of course, if one maintains the value of the impedance of $C_W(\omega)$. The quantities $C^*_W(\omega)$, $L^*_W(\omega)$, as well as $C^{**}_W(\omega), L^{**}_W(\omega)$ are *theoretical quantities* (i.e., not *real quantities*), but they permit to determine what values must have the quotients $L^*_W(\omega)/\ C^*_W(\omega)$, or $L^{**}_W(\omega)/\ C^{**}_W(\omega)$, for both, the *charge transfer*, and the *diffusion*, resistances of the multielectrode [3] regain the values corresponding to the dielectrode (1). In this way, *a criterion of classifying the medicaments, based on the values of above-mentioned quotients, has resulted*.

Keywords*: electrochemical impedance spectroscopy, drug analysis*

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INTRODUCTION

In a series of papers, Bonciocat at al., have shown that the faradaic current density of an electrode redox reaction occuring with combined limitations of charge transfer and nonstationary, linear, semiinfinite diffusion, is the solution of an integral equation of Volterra type [1-7]. By solving this integral equation, new methods of direct and cyclic voltammetry, applicable in aqueous electrolytic solution, or in molten salts, have been developed [8-20]. Similarly, the above mentioned integral equation has led to a new approach to the Electrochemical Impedance Spectroscopy when only the charge transfer and diffusion limitations are present[21-23]. Very recently has been shown that the (E I S) method may have important applications in drug research [24,25].

Some results already obtained are needed to understand the development given in this paper. We briefly remind them, and for details, see [22,24]. They refer to *redox multielectrodes* and give the *parametric equation* of their Nyquist plots in the domain of very small frequencies (round $\nu = \frac{\omega}{2\pi}$ = 0.2Hz). The equation which we are interested in, is:

$$Re = R_{sol} + (\gamma R_{ct}) + \frac{J_1[\omega(t-\tau)]}{\sqrt{2\pi\tau}}(\gamma\sigma)\omega^{-1/2} \tag{4}$$

Re represents the real part of the impedance of the measuring cell, ω the radial frequency of the alternating current, R_{sol} the solution resistance, τ the moment of the time when the *alternating overtension* is superposed over the *constant overtension* η, applied at t=0, and t is the time when the Nyquist plot recording ends. C_d represents the double layer capacity, and $J_1[\omega(t-\tau)]$ the Fresnel integral:

$$J_1[\omega(t-\tau)] = \int_0^{\omega(t-\tau)} \frac{\cos x}{x^{1/2}}\,dx \tag{4'}$$

whose value tends to $\sqrt{\pi/2} \cong 1.253$ for sufficiently great values of the product ω(t – τ).

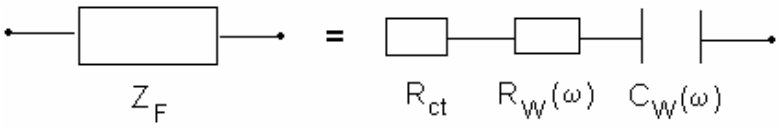
(γ R_{ct}) and (γ σ) express the *charge transfer*, respective *diffusion*, limitations, and they have the meanings:

$$\frac{1}{(\gamma R_{ct})} = \frac{1}{\gamma_1 R_{ct1}} + \frac{1}{\gamma_2 R_{ct2}} + ... \tag{5}$$

$$\frac{1}{(\gamma\sigma)} = \frac{1}{2}\left(\frac{1}{\gamma_1\sigma_1} + \frac{1}{\gamma_2\sigma_2} .....\right) \tag{5'}$$

where the terms in the right-hand sides of eqs.(5,5') refer to the individual electrode reactions occuring simultaneously at the interface. For the aim of this paper, it is not important to give their expressions.

The last term in eq.(4), represents the *Warburg diffusion resistance* $R_W(\omega)$ of the interface. It is an ohmical term that *doesn't introduce* a phase difference between the current and the tension. To explain the phase difference between the current and the tension, Warburg has introduced a *pseudo-capacitance* $C_W(\omega)$ in the series circuit by which represents the Faraday impedance of the interface:



(6)

$C_W(\omega)$ introduces a Warburg capacitive reactance $X_{C_W}(\omega)$ situated along the imaginary axes of the complex plane, and having the expression:

$$X_{C_W}(\omega) = -\frac{J_2[\omega(t-\tau)]}{\sqrt{2\pi}}(\gamma\sigma)\omega^{-1/2}j \qquad (7)$$

where:

$$J_2[\omega(t-\tau)] = \int_0^{\omega(t-\tau)} \frac{\sin x}{x^{1/2}}dx \qquad (7')$$

Like the Fresnel integral (4'), also this Fresnel integral tends to $\sqrt{\pi/2}$, for sufficiently great values of $\omega(t-\tau)$.

From eq.(7) it fallows:

$$C_W(\omega) = \frac{1}{\omega\left|X_{C_W}(\omega)\right|} = \frac{\sqrt{2\pi}}{J_2[\omega(t-\tau)]}\cdot\frac{1}{(\gamma\sigma)\omega^{-1/2}}\cdot\frac{1}{\omega} \qquad (8)$$

From the expressions of $R_W(\omega)$ (i.e., the last term in eq.(4)) and $C_W(\omega)$ one gets:

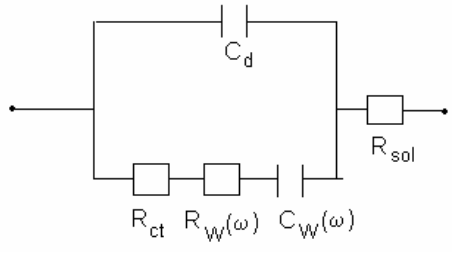
$$R_W(\omega)C_W(\omega) \cong \frac{J_1[\omega(t-\tau)]}{J_2[\omega(t-\tau)]}\cdot\frac{1}{\omega} \cong \frac{1}{\omega} \qquad (9)$$

for times of recording sufficiently large

Concerning the electric scheme of the measuring cell needed to obtain the Nyquist plots, it refers only to the electrode under study, because the impedance of the reference electrode is practically equal to zero. Consequently,

in the scheme one must enter excepting the Faraday impedance Z_F (see (6)), the double layer capacity C_d and the resistance of the solution. Of course, this is an oversimplifyed scheme, but as we shall see, for the aim of this paper it is adequate.

Thus:



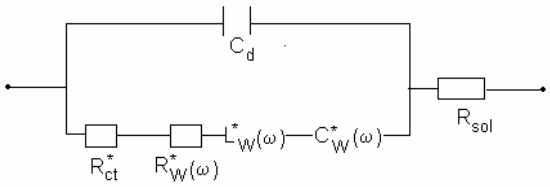
(I)

This scheme is considered to be adequate for the *reference redox dielectrode*; because the expressions of the Nyquist plots in the domain of very small values ω, obtained on its basis, have proved to be in good agreement with the experimental data.

To propose a criterion of classifying the drugs, we have considered other two schemes. In one, the pseudo-capacitance $C_W(\omega)$ is replaced by a series arrangement, $C^*_W(\omega)$, $L^*_W(\omega)$, in the other, by a parallel arrangement $C^{**}_W(\omega), L^{**}_W(\omega)$, but maintaining the impedance of the Warburg pseudo-capacitance, i.e.,

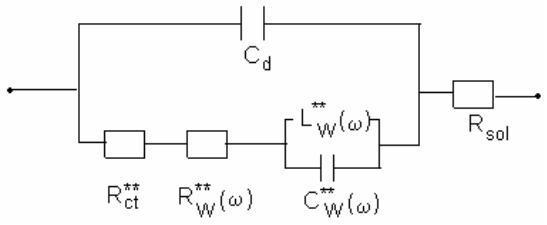
$$Z_{C_W} = Z^*_{series} = Z^{**}_{parallel} \tag{10}$$

of course, the *charge transfer* resistance R_{ct}, and the *Warburg diffusion* resistance, $R_W(\omega)$ will change, becoming R^*_{ct}, $R^*_W(\omega)$, respective R^{**}_{ct}, $C^{**}_W(\omega)$. Therefore, these two schemes are:



(I*)

respective



(I**)

In addition, we shall consider that also the *total ohmical resistance* $R_{ct} + R_W(\omega)$ preserves its value, i.e.,

$$R_{ct} + + R_W(\omega) = R^*_{ct} + R^*_W(\omega) = R^{**}_{ct} + R^{**}_W(\omega) \tag{11}$$

THEORETICAL SECTION

The theoretical development given in this paper is based on the following idea: to explain the phase difference between the current and the tension, we shall use instead of *one theoretical quantity* (as the *pseudo-capacitance* $C_W(\omega)$ introduced by Warburg, *two theoretical quantities*, namely, a *pseudo-capacitance*, and a *pseudo-inductance*.

Because the phase differences introduced by these physical quantities are different, and depend on their arrangement, i.e., in series or in parallel, we shall analyse separately these two possibilities.

1. Characteristic quantities of the scheme (I^*) for very small ω

As one knowns, in the complex plane, the impedance of an inductance L is ωLj, and of a capacitance C is $-\frac{1}{\omega C}j$. Then from the equality $Z_{CW}(\omega) = Z_{series}(\omega)$ (see eqs.(10), one gets:

$$\left(\omega L^*_W(\omega) - \frac{1}{\omega C^*_W(\omega)}\right) j = -\frac{1}{\omega C_W(\omega)} j \tag{12}$$

i.e.,

$$\omega L^*_W(\omega) = \frac{1}{\omega C^*_W(\omega)} - \frac{1}{\omega C_W(\omega)} \tag{12'}$$

Because $\omega L^*_W(\omega)$ is a positive quantity, it follows:

$$\boxed{C^*_W(\omega) = \alpha^* C_W(\omega);\ \alpha^* < 1,\ \text{and}\ \ \omega L^*_W(\omega) = \frac{1-\alpha^*}{\alpha^*} \cdot \frac{1}{\omega C_W(\omega)}} \tag{13}$$

Further, the product $R_W(\omega)\, C_W(\omega)$ depending only on ω (see eq. (9)), it is normal to consider that eq.(9) remains valid for the scheme (I^*) too. Then:

$$R^*_W(\omega) C^*_W(\omega) = R_W(\omega) C_W(\omega) \tag{14}$$

and therefore:

$$R_W^*(\omega) = \frac{1}{\alpha^*} R_W(\omega) \tag{15}$$

Coming back to eqs.(11) and using eq.(15), it results:

$$R_{ct}^* = \left(1 - \frac{1}{\alpha^*}\right) R_W(\omega) + R_{ct} \tag{16}$$

Let's write eq.(16) for multielectrodes and for $\omega_1 = 1.256 s^{-1}$. In addition, using the approximation:

$J_1[\omega_1(t-\tau)] \cong \sqrt{\frac{\pi}{2}}$, one gets:

$$(\gamma R_{ct})^* = -\left(\frac{1-\alpha^*}{\alpha^*}\right)\frac{(\gamma\sigma)}{2\omega_1^{1/2}} + (\gamma R_{ct}) \tag{16'}$$

or:

$$\boxed{R_{sol} + (\gamma R_{ct})^* = -\left(\frac{1-\alpha^*}{\alpha^*}\right)[0.446(\gamma\sigma)] + R_{sol} + (\gamma R_{ct})} \tag{17}$$

if one introduces the solution resistance too.

2. Characteristic quantities of the scheme (I^{**}), for very small ω

From the same eqs.(10) it follows $1/Z_{C_W} = 1/Z_{parallel}$, and thus:

$$\frac{1}{\omega L_W^{**}(\omega) j} + \omega C_W^{**}(\omega) j = \omega C_W(\omega) j \tag{18}$$

i.e.,

$$\frac{1}{\omega L_W^{**}(\omega)} = \omega C_W^{**}(\omega) - \omega C_W(\omega) \tag{18'}$$

$1/\omega L_W^{**}(\omega)$ being a positive quantity:

$$\boxed{C_W^{**}(\omega) = \frac{1}{\alpha^{**}} C_W(\omega);\ \ \alpha^{**} < 1,\ \text{and}}$$

$$\boxed{\omega L_W^{**}(\omega) = \frac{\alpha^{**}}{1-\alpha^{**}} \cdot \frac{1}{\omega C_W(\omega)}} \tag{19}$$

Further, eq.(9) remains valid for the scheme (I^{**}) too, and gives:

$$R_W^{**}(\omega)C_W^{**}(\omega) = R_W(\omega)C_W(\omega) \tag{20}$$

i.e.,

$$R_W^{**}(\omega) = \alpha^{**}R_W(\omega) \tag{20'}$$

Using eq.(20') to express the term $R_W^{**}(\omega)$, eq.(11) leads to:

$$R_{ct}^{**} = \left(1-\alpha^{**}\right)R_W(\omega) + R_{ct} \tag{21}$$

For ω_1= 1.256s^{-1} and $J_1[\omega_1(t-\tau)] \cong \sqrt{\pi/2}$, eq.(21), written for multielectrodes, takes the final form:

$$\boxed{R_{sol} + (\gamma R_{ct})^{**} = \left(1-\alpha^{**}\right)[0.446(\gamma\sigma)] + R_{sol} + (\gamma R_{ct})} \tag{22}$$

3. Estimation of $R_{sol} + (\gamma R_{ct})$ and $(\gamma\sigma)$

Suppose that the Nyquist plots are recorded using 10 points per decade, starting with ν_1= 0.2Hz and ending at 10^5 Hz. Then, the first point P_1 corresponds to $\omega_1 = 2\pi\nu_1$ = 1.256 s^{-1}, and the second point P_2 to $\omega_2 = \omega_1\, 10^{0.1}$= 1.582$s^{-1}$.

Let's suppose that the intervals of time (t - τ) required to record the Nyquist plots are sufficiently great to be permitted the approximation $J_1[\omega_1(t-\tau)] \cong J_2[\omega_1(t-\tau)] \cong 1.253$. Then, writing eq.(4) for the two points P_1 and P_2, one gets:

$$\frac{Re(P_1) - X}{Re(P_2) - X} = \left(\frac{\omega_1}{\omega_2}\right)^{-1/2}; \qquad X = R_{sol} + (\gamma R_{ct}) \tag{23}$$

and consequently:

$$\boxed{R_{sol} + (\gamma R_{ct}) \cong \left[Re(P_2) - \frac{Re(P_1) - Re(P_2)}{0.122}\right]} \tag{24}$$

where: 0.122 = $(\omega_1 / \omega_2)^{-1/2}$ -1.

Coming back to eq.(4), and using the expression(24) of $R_{sol} + (\gamma R_{ct})$, one gets:

$$(\gamma\sigma) \cong \frac{\sqrt{2\pi}\,\omega_1^{1/2}}{J_1[\omega_1(t-\tau)]}\left[Re(P_1) - Re(P_2) + \frac{Re(P_1) - Re(P_2)}{0.122}\right] \tag{26}$$

i.e.,

$$\boxed{(\gamma\,\sigma) \cong 20.6\,[\mathrm{Re}(P_1) - \mathrm{Re}(P_2)]} \qquad (26')$$

EXPERIMENTAL SECTION

Two liquid drugs have been tested: the Swedish Bitter (Original Schweden Tropfen, BANO) and the Energotonic complex (ENERGOTONIC-multivitamin complex, Plant Extract). The *reference redox dielectrode*(RRD) and the *multieletrodes* (i.e., RRD containing the respective liquid drug: Bitter or Energotonic) had the compositions given above (see (1 and 3)) we only mention that in all three cases the total volume has been V=300ml and v_{Bitter} = 50ml, respective $v_{Energotonic}$ = 20ml. In Table 1-3 are reproduced from the papers[24, 25] the horizontal coordinates of the points $P_1(\omega_1)$, $P_2(\omega_2)$ corresponding to the 12 Nyquist plots obtained experimentally (three values for the constant overtension η, and for each value of η four values for τ). Of course, these coordinates represent the real parts $Re(P_1)$, $Re(P_2)$, of the corresponding Niquist plots: -Im vs Re, and permit to get the values of $R_{sol} + (\gamma\, R_{ct})$, respective of $(\gamma\, \sigma)$, by using the formulae (24 and 26'). As one sees, there is a good compatibility betwen the values corresponding to a given value of η , but appear differences when one passes to an other value of η. However, in this paper we are not interested in explaining the origin of these differences. We are interested only in comparing the effect that the too drugs investigated have in changing the values $R_{sol} + (\gamma\, R_{ct})$ and $(\gamma\, \sigma)$ of the *reference redox dielectrode*. For this reason, and because the thee values of η are close values, we shall compare the mean values resulted by using all Nyquist plots.

Table 1.

Reference Redox Dielectrode R R D

η (V)	τ (s)	$Re(\omega_1)$ (Ω)	$Re(\omega_2)$ (Ω)	$R_{sol} + (\gamma R_{ct})_{RRD}$ (Ω)	$(\gamma\,\sigma)_{RRD}$ ($\Omega\, s^{-1/2}$)
0	0	1368	1274	504	1938
0	10	1343	1242	414	2082
0	100	1324	1230	460	1938
0	1000	1299	1211	490	1814
-0.05	0	1838	1712	679	2597
-0.05	10	1838	1685	431	3154
-0.05	100	1820	1676	496	2968
-0.05	1000	1784	1646	515	2845
0.05	0	2703	2486	707	4473
0.05	10	2703	2486	707	4473
0.05	100	2703	2486	707	4473
0.05	1000	2689	2473	703	4453
			Mean= 572		Mean= 3101

Table 2.

R R D Containing Swedish Bitter (B)

η (V)	τ (s)	$Re(\omega_1)$ (Ω)	$Re(\omega_2)$ (Ω)	$R_{sol} + (\gamma R_{ct})_B$ (Ω)	$(\gamma \sigma)_B$ ($\Omega\ s^{-1/2}$)
0	0	4236	3791	143	9173
0	10	4297	3851	195	9194
0	100	4419	3932	- 60	10039
0	1000	4595	4054	- 380	11152
-0.05	0	6495	5676	- 1037	16883
-0.05	10	6559	5707	- 1277	17563
-0.05	100	6559	5739	- 982	16903
-0.05	1000	6527	5739	- 720	16244
0.05	0	5676	4973	- 789	14492
0.05	10	5946	5243	- 519	14492
0.05	100	5946	5243	- 519	14492
0.05	1000	5838	5135	- 627	14492
				Mean= - 548	Mean= 13760

Table 3.

R R D Containing Energotonic Complex (E)

η (V)	τ (s)	$Re(\omega_1)$ (Ω)	$Re(\omega_2)$ (Ω)	$R_{sol} + (\gamma R_{ct})_E$ (Ω)	$(\gamma \sigma)_E$ ($\Omega\ s^{-1/2}$)
0	0	1358	1273	576	1752
0	10	1325	1240	543	1752
0	100	1287	1197	459	1855
0	1000	1263	1178	481	1752
-0.05	0	2525	2323	667	4164
-0.05	10	2525	2313	575	4370
-0.05	100	2535	2333	677	4164
-0.05	1000	2535	2354	870	3731
0.05	0	1912	1771	615	2907
0.05	10	1926	1785	629	2907
0.05	100	1933	1798	691	2783
0.05	1000	1946	1805	649	2907
				Mean= 619	Mean= 2920

1. Estimation of drugs effects

As one sees from the Tables1-3, the effects of the investigated drugs consist in changing the values of $R_{sol} + (\gamma R_{ct})_{RRD}$ and $(\gamma \sigma)_{RRD}$.

Because the RRD containing the drug investigated corresponds, either to a scheme of type (I^*), or to one of type (I^{**}), we shall estimate the effects of drugs by the values of the quotients $L^*_W(\omega_1)/C^*_W(\omega_1)$, or $L^{**}_W(\omega_1)/C^{**}_W(\omega_1)$ for which these schemes become equivalent to the scheme (I) corresponding to the RRD electrode.

Let's start with the Swedish Bitter. From table2, one sees that the mean value of $R_{sol} + (\gamma R_{ct})_B$, i.e., -548Ω, is less than the mean value of $R_{sol} + (\gamma R_{ct})_{RRD}$, equal to 572Ω (se Table 1). Consequently, it must *increase* to 572Ω, and equation (22) shows that this increase implies *a parallel arrangement* (i.e., a *scheme* I**) and a value α_B^{**} given by:

$$1-\alpha_B^* = \frac{[R_{sol}+(\gamma R_{ct})_{RRD}]-[R_{sol}+(\gamma R_{ct})_B]}{0.446(\gamma\sigma)_{RRD}} =$$

$$\frac{572+548}{0.446\cdot 3101} = 0.810 \qquad (27)$$

In the case of Energotonic complex, Table 2 shows that the mean value $R_{sol} + (\gamma R_{ct})_E$ =619Ω must *decrease* to 572Ω, and equation (17) shows that this decrease implies *a series arrangement* (i.e., a *scheme* I**), and a value α_E^* given by:

$$1-\frac{1}{\alpha_E^*} = \frac{[R_{sol}+(\gamma R_{ct})_{RRD}]-[R_{sol}+(\gamma R_{ct})_E]}{0.446\cdot(\gamma\sigma)_{RRD}} =$$

$$\frac{572-619}{0.446\cdot 3101} = -0.034 \qquad (28)$$

Therefore, eqs.(27 and 28) give: $\alpha_B^{**} = 0.190$ and $\alpha_E^* = 0.967$

2. The proposed criterion of classifying the drugs

From eqs.(13) written for $\alpha^* = \alpha_E^*$, $\omega = \omega_1$ and $J_1[\omega_1(t-\tau)] \cong \sqrt{\pi/2}$ one gets:

$$\lambda_E^*(\omega_1) = \frac{L_W^*(\omega_1)}{C_W^*(\omega_1)} = \frac{1-\alpha_E^*}{(\alpha_E^*)^2}\cdot\left[\frac{1}{\omega_1 C_W(\omega_1)}\right]^2 =$$

$$\frac{1-\alpha_E^*}{(\alpha_E^*)^2}\cdot[0.446(\gamma\sigma)_{RRD}]^2 \qquad (29)$$

and similarly, from eqs.(19), results:

$$\lambda_B^{**}(\omega_1) = \frac{L_W^{**}(\omega_1)}{C_W^{**}(\omega_1)} = \frac{(\alpha_B^{**})^2}{1-\alpha_B^{**}}\cdot[0.446(\gamma\sigma)_{RRD}]^2 \qquad (30)$$

Introducing the values of α_E^* and α_B^{**}, the proposed criterion takes for two drugs investigated the values:

$$\lambda_E^*(\omega_1) = 67505\,\Omega^2; \qquad \lambda_B^{**}(\omega_1) = 85259\,\Omega^2 \tag{31}$$

CONCLUDING REMARKS

1. $L_W^*(\omega_1)$ $C_W^*(\omega_1)$ and $L_W^{**}(\omega_1)$, $C_W^{**}(\omega_1)$ play the role of *theoretical quantities* that have permitted to develop *an advantageous physico-mathematical deduction* of the proposed *criterion of classifying the drugs*.
2. The proposed criterion is a *qualitative* one, because it divides the drugs into two classes, (I^*) or (I^{**}) depending on what type of arrangement is necessary to estimate their action, i.e., a *series* or a *parallel* arrangement; it is also a quantitative criterion, because it estimates numerically these actions by the values $\lambda^*(\omega_1)$ or $\lambda^{**}(\omega_1)$.
3. For a drug that *has no effect*, α^* and α^{**} are equal to unity. Consequently, for such a drug, $\lambda^*(\omega_1) = 0$, and $\lambda^{**}(\omega_1) = \infty$. It fallows that for a drug belonging to the class (I^*), the *greater* the value of $\lambda^*(\omega_1)$, the *greater* is its effect, and for a drug belongingto the class (I^{**}), the *smaller* the value of $\lambda^{**}(\omega_1)$, the *greater* is its effect.

The values resulted for the two drugs investigated, i.e., $\alpha_E^* = 0.957$, respective $\alpha_B^{**} = 0.190$, show that the Energotonic complex has a *much smaller effect than the Swedish Bitter*, because α_E^* is very close to unity, while α_B^{**} is more close to zero than to unity. The values resulted for $\lambda_E^*(\omega_1)$ and $\lambda_B^{**}(\omega_1)$ lead to the same conclusion, because $\lambda_E^*(\omega_1)$ is more close to zero than $\lambda_B^{**}(\omega_1)$ to infinity.

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