INVESTIGATION OF THE ADSORPTION PROCESSES BY RADIO-SPECTROSCOPIC METHOD

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The processes of electromagnetic radiation of radio-waves range in electrochemical systems are the matter of consideration in the present study. Two potentials, constant potential and low variable potential (with amplitude of 10 mV) are applied simultaneously in these systems to the metal-solution interface. The aim of the present work is: investigation of the adsorption processes in electrochemical systems by radio-spectroscopic method. The adsorption processes of the organic molecules are of great importance for creation of optochemotronic sensors, for electrochemiluminescence and various other processes. The analytical expressions for coordinates and rate of particles in such system are received. Moreover, expressions for vector-potential of the electromagnetic radiation of the system, which is connected with this motion, are also considered. The main outcome is existence of nonlinear, quadratic dependence between the signal of the electromagnetic radiation of the radio-wave range U and amplitude of a variable potential E, which is applied to the interface. The same dependence exist in electrochemical systems, where there is no current. Obtained theoretical results are used for the analysis of the experimental data, which was received for adsorption-desorption of aliphatic alcohols. Although there is no charge transfer between the alcohol molecules and electrode during the adsorption, quadratic dependence between U and E is investigated for all peaks on desorption SHS(second harmonic signal) - curves of butanol-1, butanol-2, hexanol, pentanol and isoamyl molecules on mercury electrode. For different concentrations of alcohols, different frequencies and values of the amplitude of variable potential were applied. Experimental results confirm the accuracy of proposed theoretical model.

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Introduction

The new method based on recording of the electromagnetic radiation in radio-wave frequency band has been in practice by electrochemical systems researches since last 10 to 15 years.[1-10] This method allows to record electromagnetic radiation connected to adsorption - desorption processes by removal so-called SHS, E (signal of the second harmonic, potential) curves. The peaks located at the left on these curves and on the right of significance of the potential are well selected when the maximum on the curve C, E (differential capacity, potential) is reached for the same process. It is possible to find out the detailed description of a method and obtained results in the work done by the previous workers.[2,3,9] Fundamentals of the classical theory generated by an electrochemical system of oscillations with the double frequency $2\omega_0$, when an external variable signal of ω_0 frequency acts on a system may also be find in these reports.[11,12] The base of the working mechanism of such nonlinear electrochemical generator is essentially nonlinear form of volt-ampere curve. At the same time it is important that a charge transfer from discharged (regenerated) or adsorbed (desorbed) particle on an electrode (from an electrode) in an electrochemical system takes place. In the reports[3,9,10] desorption process was investigated by the registration method of the second harmonic signal (SHS). The measurements were conducted on frequency 800 Hz, when the system is acted by a variable signal with frequency 400 Hz, and amplitude 50 mV. Measurements of dependence of differential capacity from a potential were conducted simultaneously. As it was indicated in this work on a curve SHS, E the minimum near to a maximum of desorption peak of a curve SHS, E is observed. At the Left and to the right of this minimum on a curve SHS,E, the left and right peaks are observed. In reports[3,9,10] the correlation between $\partial C / \partial E$, E and SHS, E curves for an adsorption of a number of organic substances was investigated, though it was indicated[10], that this correlation is sometimes disturbed. In article[7] the model description for electromagnetic radiation of an electrochemical system is represented when an adsorption on a mercury electrode of various organic substances from aqueous and non-aqueous solutions takes place. It was shown, that during the simultaneous registration of electromagnetic radiation in one system, SHS and C method of a measurement of SHS most accurate and informative. It allows extract parameters of a double electrical layer, which cannot be defined by other methods. In article[18] the experimental data obtained by SHS method for process of desorption of aliphatic alcohols (butanol and hexanol) on a mercury electrode are indicated. For these systems it is supposed, that during the adsorption and desorption process the charge transfer from a particle on the electrode and on the other hand does not take place. Nevertheless, this system is investigated experimentally just by a SHS method. It means that when there is no charge transfer between a particle and electrode this method also can successfully be applied, and it is more informative, as it was presumed.

In earlier reports[13,14] we were depend upon separate mechanisms, which explain electromagnetic radiation of a range of radio-waves in non-stationary, heterogeneous, in

particular, electrochemical systems. Unfortunately, the phenomena connected with a radiation of the electromagnetic waves of a range of radio-waves, has rather complicated in nature. The full theoretical analysis of all processes causing in the issue to this radiation does not always manage to be finished in analytical form. Because of this, it is important that the experimental study of such systems would be conducted in broader band of parameters describing an electrochemical system.

Presently it is possible today to propose a number of the theoretical approaches for the description of the phenomenon of electromagnetic radiation in electrochemical systems, especially in the most interesting part of experimentally obtained outcomes [18] in the field of the nonlinear phenomena.

Theoretical part

For mathematical description of electromagnetic phenomenon in electrochemical system we'll use method of temporal Green functions at finite temperature.

We will describe liquid phase by polarization operator:[15]

$$\vec{P}\left(\vec{r}\,,\,\vec{t}\right)$$

In this case electrolyte can be described in linear approximation by one-particle retarded Green's function when finite temperatures:

$$G_{\mathrm{ik}}^{\mathrm{R}}\left(\vec{r},\vec{r}',t,t'\right)=-\frac{i}{\hbar}\theta(t-t')\left\langle\left[P_{\mathrm{i}}\left(\vec{r},t\right)P_{\mathrm{k}}\left(\vec{r}',t'\right)\right]\right\rangle_0 \quad (1)$$

where angular brackets mean quantum-statistical averaging, $\theta(t\text{-}t')=1$, for $t\text{-}t'>0$; $\theta(t\text{-}t')=0$, for $t\text{-}t'<0$. For homogeneous isotropic systems (in volume of electrolyte) this Green's function can be easily connected with complex dielectric permeability of electrolyte:

$$\varepsilon = 1+4\pi G^{\mathrm{R}} \quad (2)$$

Homogeneity and isotropy of medium near the electrode is disturbed and dependence between G^{R} and ε has much more complicated character.[16,17]

In the existing approach it is possible to take into account effects of a frequent and space dispersion of a liquid phase within the framework of various models. We shall use an approximation of separation of dependence on space and temporary coordinates for Green function:

$$G_{\mathrm{ik}}^{\mathrm{R}}\left(\vec{r},\vec{r}',\omega\right)=G_{\mathrm{ik}}^{\mathrm{R}}\left(\vec{r},\vec{r}')\right)G^{\mathrm{R}}(\omega) \quad (3)$$

As to dependence of G from ω, formally it would be possible to determine this dependence on the base of experimental data in absorption spectra of a system in corresponding region of frequencies. For determination of the form of function

$$G\left(\vec{r},\vec{r}'\right)$$

the conduction of complicated quantum mechanical calculations is necessary. Instead of it is possible to simulate this function by various damping oscillating functions. The corresponding parameters (characteristic size of damping and period of oscillations) for these models can be determined, for example, by free energies of solvation. If in a system round positive ions in first solvated shell the dipole molecules of a solvent of one type would only be collected, the characteristic size for polarization oscillations would be approximately equal to a diameter of a molecule of a solvent. Unfortunately, in our case the picture is more complicated and it is possible to consider this parameter only as observable fact.

We shall imply, that solvated particle moves in a liquid phase and radiates an electromagnetic field. Effective mass, charge and size of this particle will be determined by corresponding approximate parameters.

When making concrete calculations it is possible to use some models for a Green function describing a liquid phase (for simplicity we shall reduce functions in $\varphi\rho$ representation):

$$G_{\rho\varphi}\left(\vec{r}\,\vec{r}'\right)=-\frac{C_0}{4\pi}\delta\left(\vec{r}-\vec{r}'\right) \quad (4)$$

$$G_{\rho\varphi}^{(\lambda)}\left(\vec{r}\,\vec{r}'\right)=-\frac{C_0}{32\pi^2\lambda^3}e^{-\frac{\left(\vec{r}-\vec{r}'\right)}{\lambda}} \quad (5)$$

$$G_{\rho\varphi}^{(\lambda)}\left(\vec{r}\,\vec{r}'\right)=-\frac{C_0}{32\pi^2}\nu(\nu^2-3\lambda^2)e^{-\nu\left(\vec{r}-\vec{r}'\right)}\cos\left(\gamma\left|\vec{r}-\vec{r}'\right|\right) \quad (6)$$

where C_0 is constant connected with the dielectric properties of the system, λ and ν are parameters.

Depending on an electrode potential the distribution of different charged particles will vary in liquid phase. Dependence of concentration, as function of a distance from an electrode, we shall describe by model damping functions.

In connection with a strain of solvate shell of the charged particles near to a surface of the electrode, in accordance with growth of the electrode potential, the distance from the particle up to the surface of the electrode decreases.

We consider a system, in which two potentials are enclosed in the interface: constant (E) and variable (with amplitude E_{V1} and frequency ω_0).

In researched region of frequencies we can register electromagnetic radiation connected with non-uniform translation movement of the charged solvated particles. The equation of motion for these particles we shall present as[13]:

$$m\frac{d\vec{v}\left(\vec{r},t\right)}{dt} = q\vec{D}(\vec{r},t) - \kappa\vec{v}(\vec{r},t) \qquad (7)$$

where

$\vec{v}\left(\vec{r},t\right)$	is rate of the particle in point *r* and time point *t*,
m	is mass of this particle,
q	is charge,
κ	is factor of friction for the electrolyte,
D	is induction of an electromagnetic field applied at the interface.

The corresponding potential has a form:

$$E_z(z') = E(z') + E_{V1}(z')\cos(\omega_0 t) \qquad (8)$$
$$E_x + E_y = 0$$

For plane-parallel electrodes the solution of the equation (7) results in following expressions for coordinates and velocity of a particle:

$$z' = z'_0 + qD(z')\left[\frac{\kappa}{mt} + e^{-\frac{\kappa}{mt}} - 1\right] + \\ + q\frac{D_{V1}(z')}{\frac{\kappa^2}{m^2} + \omega_0}\left[\frac{\kappa}{m\omega_0}\sin(\omega_0 t) - \cos(\omega_0 t) + e^{-\frac{\kappa}{mt}}\right] \qquad (9)$$
$$x' = x'_0; y' = y'_0$$

$$\frac{dz'}{dt} = q\frac{\kappa}{mt}D(z')\left(1 - e^{-\frac{\kappa}{mt}}\right) + \\ + \frac{qD_{V1}(z')}{\frac{\kappa^2}{m^2} + \omega_0^2}\left[\frac{\kappa}{m}\cos(\omega_0 t) - \omega_0\sin(\omega_0 t) + \frac{\kappa}{m}e^{-\frac{\kappa}{mt}}\right] \qquad (10)$$

$$\frac{dx}{dt} = 0; \quad \frac{dy}{dt} = 0.$$

where *z* is direction perpendicular to a surface of the electrode.

As approaching a surface of an electrode the part of particles passes in an adsorbed condition, at that time the redistribution of an electronic density on a particle takes place. Under an action of an external variable field the particle makes non-uniform movement near to an adsorbed condition and as the corollary radiates an electromagnetic field. The expression for vector potential of this field has a form (see article [13]):

$$Az(x,y,z,\omega) = \frac{q}{c}\int dz' S_\varepsilon(z')\Phi(z')\varepsilon(\omega)\left\{\frac{\kappa}{m}I(z')\left[\frac{1}{\gamma - i\omega} - \frac{1}{\frac{\kappa}{m} - i\omega}\right] + \frac{I_{V1}(z')}{\frac{\kappa^2}{m^2} + \omega_0^2}\left[\frac{\kappa}{m}\frac{\gamma - i\omega}{\omega_0^2 + (\gamma - i\omega)^2} + \frac{\omega_0^2}{\omega_0^2 + (\gamma - i\omega)^2} - \frac{\kappa}{m}\frac{1}{\frac{\kappa}{m} - i\omega}\right]\right\} \qquad (11)$$
$$\gamma \to 0$$

where ε is dielectric permeability of an electrolyte on frequency ω, *I* and I_{V1} are electric field strengths of constant and variable components.

The approximation of particles when an adsorption takes place corresponds to emerging of peak on a capacity curve as function of parameters describing a field of an electrode. The corresponding radiation of electromagnetic waves (SHS) will depend on ω.

In accordance with growth of negative significance of an electrode potential, desorption of adsorbed particles takes place. Redistribution of an electron density and change of the charge density on a particle takes place at the moment of desorption. The expression for a vector potential will look like similar to the equation (11), with corresponding boundary conditions. One peak on a curve of capacity and two peaks on a curve of electromagnetic radiation as function of potential corresponds to each adsorption - desorption process in this case. The directed movement of charged particles under the influence of an external field results in modification of current, flowing through a system. This modification can be connected with three processes:

1. Electron transfer from a particle to an electrode and vica versa;
2. Relaxation process connected with transition of charged particles;
3. Transition of the charged particles under the influence of an external field, rate of which is determined by the Eqn. (10).

In case, when redistribution of the charge density between particles and electrode takes place throughout particle motion, the density is determined by the following equation (for brevity this ratio and number of others are adduced in operator form):

$$\rho(\omega_0) = -G_{\rho p}(\omega_n)I(\omega_n)$$
$$\omega_n = 2\pi kT; \quad n = 0, \pm 1, \pm 2 \qquad (12)$$

where *k* is Boltzmann's constant, ρ is modification of an electron density under the influence of an external field, $G_{\rho p}(\omega_n)$ is Fourier representation of a temperature Green function of operators ρ and *p*.

Micro-currents which appear in the described system have the form:

$$\vec{i}(\omega) = \int \rho\left(\vec{r},\omega\right)\vec{v}\left(\vec{r},\omega\right)d\vec{r} \qquad (13)$$

where, ρ is charge density of a particle, v is rate of particle's motion. The equation of motion for a particle differs from the equation (7) and takes the form:

$$m\frac{d\vec{v}\left(\vec{r},t\right)}{dt} = q(t)D\left(\vec{r},t\right) - \kappa\vec{v}\left(\vec{r},t\right) \qquad (7a)$$

where $q(t)$ is charge on the particle at the moment.

In frames of a simple model, when the particles move perpendicularly to an electrode surface (10), the expression for micro-currents takes a form:

$$i(\omega) = P(\omega) + M(\omega)E_{V1} + N(\omega)E_{V1}^2 \qquad (14)$$

where $P(\omega)$, $M(\omega)$ and $N(\omega)$ are the coefficients.

In case when an electron transfer from a particle on an electrode does not take place, dependence of micro-currents on quadrate of voltage amplitude of an external variable field is also possible (polarization of any chemical bond of a particle is enough for this). The dipole moment induced under an action of an external field is equal:

$$\delta d = \alpha E_{V1} \qquad (15)$$

where α is polarizability of molecules along this chemical bond.

If length of a dipole moment is equal to 1, then for micro-currents we shall receive expression similar to the equation (13), where the density of a charge ρ can be received from the following expression:

$$\rho = \frac{\alpha}{l}E_{V1} \qquad (16)$$

In a general form the coefficients $P(\omega)$, $M(\omega)$and $N(\omega)$ have a rather complicated form. However, for the double frequency $\omega=2\omega_n$ the form of factors $P(\omega)$, $M(\omega)$ and $N(\omega)$ essentially becomes simpler. The expression for a signal of the second harmonics, which can be registered in a system, contains square-law dependence on amplitude E_{V1}:

$$U(2\omega_0) = \frac{1}{2}L\frac{m}{\kappa}\frac{\alpha}{l}\frac{\varepsilon(2\omega_0)}{R(2\omega_0)}E_{V1}^2 \qquad (17)$$

where $R(2\omega_n)$ is resistance of a measuring circuit, L - factor connected to geometry of electrodes and parameters of a space dispersion of a dielectric permeability of the electrolyte.

In works[11,12] is shown, that when sinusoidal variable voltage of ω frequency is applied on an electrode, except of variable current of ω frequency a constant component of the current and second harmonic - component of the current with 2ω frequency arises in an electrochemical circuit. The emerging of these additional components is connected with the nonlinear and asymmetrical form of dependence of a current from an overstress.

The work of such "nonlinear" electrochemical generator has a quantum character. Expression for secondary harmonic's voltage includes such characteristics of an electrochemical system as: factor of friction of an electrolyte near to a electrode's surface, significance of a dielectric permeability at the frequency of a secondary harmonic, effective length of the dipole of some chemical bond of adsorbed-desorbed particle, polarization of which ensures "work" of this nonlinear generator.

Results and Discussions

In work[18] the outcomes of an experimental research of desorption process of aliphatic spirits butanol-1 and hexanol-1 on a mercury electrode obtained by SHS method are represented. In same work the data for dependence of a differential capacity of an electrode potential is given.

As can be seen from the experimental data, given in work[18], the adsorption - desorption process is accompanied by two peaks of electromagnetic radiation: the "left" peak, maximum of which is on the left side of a potential of a maximum of capacity peak (see Fig.3b, 4b in work[18]) and "right" peak, maximum of which is on the right side of maximum potential.

For butanol-1 (when the concentration is 0.47 mol L^{-1}) and hexanol-1 (when the concentration is 0.015-0.030 mol L^{-1}) for left and right peaks the dependence of an electromagnetic signal $U(\omega)$ from quadrate of amplitude of variable component E_{V1} of an electrode's field is well visible. So that, the signal of the second harmonic of electromagnetic radiation will be square-law function of a voltage amplitude of a variable component of a field applied to an interface:

$$U(\omega) = C(\omega)E_{V1}^2 \qquad (18)$$

During adsorption process the molecule of spirit comes nearer to a surface of an electrode, and molecules of water – move away from a surface of an electrode. Redistribution of a density of a charge on OH groups at this time takes place.

Table 1. Experimental significances of voltage difference corresponding to microcurrents.

Alcohol	Concentra-tion, mol L^{-1}	*E*, mV	Left peak frequency, kHz			Right peak frequency, kHz		
			1.3	12.6	125.6	1.3	12.6	125.6
Butanol-1	0.07	5	40.0	35.7	26.4	8.2	7.9	5.3
		10	157.9	142.9	116.4	31.4	28.6	26.4
		15	364.3	321.4	264.3	72.9	82.1	64.3
	0.5	5	89.3	85.7	80.1	54.3	52.1	47.1
		10	350.0	335.7	300.0	217.9	214.3	185.7
		15	821.4	792.9	714.3	492.9	458.1	428.6
	0.7	5	95.0	102.1	85.0	71.4	75.0	57.5
		10	378.6	364.3	328.6	264.3	235.7	219.6
		15	878.6	842.9	721.4	635.7	642.9	478.6
Butanol-2	0.07	5	40.0	35.7		7.5	5.7	
		10	158.6	144.3		24.3	22.9	
		15	364.3	321.4	235.7	57.1	46.4	31.4
	0.5	5	94.3	88.6	85.7	46.1	45.0	42.1
		10	360.7	350.0	322.0	194.3	178.6	165.7
		15	821.4	821.4	720.0	425.0	414.4	364.3
	0.7	5	96.4	94.3	84.3	52.1	51.4	43.9
		10	457.1	364.3	324.3	235.7	207.1	182.1
		15	871.4	842.5	828.6	471.4	457.1	432.1
Hexanol	0.03	5	173.6	123.6	75.0	137.9	93.6	42.9
		10	721.4	485.7	285.7	564.3	350.0	173.6
		15	1592.9	1085.7	714.3	1264.3	821.4	382.1
Pentanol	0.1	5	131.4	120.0	89.29	93.6	84.3	55.0
		10	514.3	464.3	350.0	353.6	314.3	217.9
		15	1150.0	1050.0	785.0	800.0	750.0	496.4
Isoamyl alcohol	0.1	5	119.3	104.3	82.1	78.6	67.9	42.9
		10	457.1	407.1	303.6	292.9	242.9	167.9
		15	1050.0	950.0	721.4	700.0	571.4	385.7

The implications of $C(\omega)$, which are obtained with the help of formula (18) for left and right peaks of electromagnetic radiation (on SHS, *E* - curves) are given in the Table 1. As may be seen from this table, for both spirits the dependence of $U(\omega)$ from $E_{V1}(\omega)$ with a good exactness is described by the formula (18). For amplitudes of 2.5 and 10 mV we receive implications of $C(\omega)$ coefficient, distinguished from average value (at given ω frequency and concentration of spirit) less than on 10 % (except for one experiment for hexanol at frequency 1.3 kHz and concentration 0.03 mol L^{-1}, where the deviation reaches 17 %).

Thus, the registration of an electromagnetic signal reveals the interesting phenomenon in electrochemical systems - nonlinear dependence between a variable potential, influencing a system, and corresponding response when charge transfer between an adsorbed particle and electrode does not take place.

The square-law dependence between a registered signal of electromagnetic radiation and amplitude of the variable potential, applied to a system, takes a place both for left, and for right peaks of SHS, *E* - curves. Heights of right and left peaks are different, because during desorption the redistribution of an electronic density takes place in a system, that in it's turn induces both modification of a particle's rate, and redistribution of a charge on OH groups of spirit and water molecules.

As the analysis of the experimental data shows, the left peak of micro-current for butanol-2, as a rule, excesses by intensity the corresponding peak for butanol, when for right peaks the intensity for butanol is always lower. It may be assumed, that the left peak of radiation is determined by the motion of electrolyte molecules and the right one by motion of alcohol molecules principally.

The values of $C(\omega)$ coefficient (in μV^{-1}) for different systems at low concentrations are given in the Tables 2-7.

Table 2. The values of $C(\omega)$ coefficient (in μV^{-1}) for ethylene glycol containing 0.01 M NaCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)
min	1450	13.1	1450	15.0	1450	12.1	1430	12.1
max	1250	19.1	1250	19.9	1200	15.3	1100	17.0
min	800	8.0	870	1.35	870	1.5	900	4.0
max	660	17.6	670	17.1	670	15.7	850	26.5
min	540	0.9	540	1.75	540	1.9	750	12.0
max	430	39.0	400	4.1	430	30.0	650	17.2
min	380	4.9	380	7.4	390	9.6	390	87.5
max	270	318.0	270	313	290	228	290	275

Table 3. The values of $C(\omega)$ coefficient (in μV^{-1}) for ethylene glycol containing 0.1 M NaCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)	***E*, mV**	*C*(ω)
min	1400	13.6	1400	12.0	1400	9.7	1450	14.0
max	1100	19.5	1140	19.9	1200	11.1	1140	18.0
min	830	4.7	830	4.3	820	0.3	820	0.5
max	300	204	250	247.5	300	194	300	198

Table 4. The values of $C(\omega)$ coefficient (in μV^{-1}) for ethylene glycol containing 0.01 M KCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**
min	875	0.5	870	0.7	850	4.1	860	1.9
max	660	17.7	650	18.1	650	16.9	660	16.5
min	530	3.0	540	2.55	520	1.6	530	1.8
max	430	42.0	420	42.3	420	35.4	430	34.65
max	380	3.0	380	2.8	380	2.0	380	8.65
min	265	311.0	260	272.0	300	239	280	229.5

Table 5. The values of $C(\omega)$coefficient (in μV^{-1}) for ethylene glycol containing 0.1 M KCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**
min	825	1.1	825	1.0	800	3.0	800	2.8
max	300	214.0	300	212.0	300	197.0	300	187.5

Table 6. The values of $C(\omega)$ coefficient (in μV^{-1}) for ethylene glycol containing 0.01 M CsCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**	***E*, mV**	***C*(ω)**
max	1300	56.9	1300	57.0	1300	43.2	1300	38.3
min	850	2.3	830	0.8	820	1.9	820	1.8
max	660	17.0	640	16.8	640	14.7	640	13.0
min	540	2.1	540	2.4	520	3.6	520	1.45
max	425	44.0	430	44.5	430	34.0	430	28.0
min	380	5.0	400	32.6	380	3.3	380	5.5

Table 7. The values of $C(\omega)$ coefficient (in μV^{-1}) for ethylene glycol containing 0.1 M CsCl at 25 ^{0}C

	Frequency, 20 Hz				Frequency, 200 Hz			
	E=10 mV		E=20 mV		E=10 mV		E=20 mV	
	***E*, mV**	$C(\omega)$	***E*, mV**	$C(\omega)$	***E*, mV**	$C(\omega)$	***E*, mV**	$C(\omega)$
max	1250	58.5	1250	57.0	1260	51.7	1250	50.6
min	800	1.3	800	1.75	780	0.9	790	0.7
max	300	194.0	300	191.0	300	177.0	290	174.0
min	100	220.0	200	170.0	200	101.3	150	148.0

Conclusions

Theoretical model, which shows the existence of nonlinear, quadratic dependence between the signal of electromagnetic radiation of radio-wave range *U* and amplitude of variable potential *E*, which is applied to the interface is proposed. The same dependence exist in electrochemical systems, where is no current. Experimental results confirm the accuracy of proposed theoretical model.

As the analysis of the tables with experimental data reveals, that the quantity of peaks of second harmonic signal increases, with a decrease in concentration of solution. Which mean, that the registration of the radiation, induced by other chemical bonds, or perhaps ions pairs, which can be formed in given system, is possible at low concentrations? It can be observed from the Tables 2-7 also, that mass and size of the cation (K, Na, Cs) does not have influence at the value of the radiated signal. At the same time decrease of concentration leads to increase of the signal (Tables 2-7). This can be explained by increase of friction coefficient κ with decrease of the concentration.

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