Quasi-Periodic Noise Oscillations in Oxyhydrates of Rare-Earth Elements

Yuri I. Sucharev[1*], Boris A. Markov[2], Tatiana I. Prolubnikova1, Irina I. Lebedeva[1]

[1]Chelyabinsk State University 129 Bratiev Kashirinyh St., Chelyabinsk 454001 Russia
[2]South Ural State University 76 Lenin St., Chelyabinsk 454080 Russia

Abstract

The present paper dwells upon the chemical foundations of formation of a gel nanostructure (by the example of zirconium oxyhydrate) at the time of formation of oxyhydrate polymer chain and develops electrophoretic (diffusional) conceptions related to the phenomenon of self-organization of non-equilibrium oxyhydrate gel. Adduced are the experimental data (measurements of spontaneous current induced by the alterations in capacity of the polarized double electrical layer of the gel) that permit to claim that the mathematical model of the phenomenon is not in contradiction with the experiment. On the ground of the experimental data and calculations it is concluded that the constant magnetic field alters the character of geometrical configuration of chemical interaction of the oxyhydrate gel fragments with each other, which affects the value of nano-current measured in the course of the experiment.

Introduction

Let us contemplate general colloid conceptions first in order to further consider behavior of the ion fluxes in colloidal matter under conditions that are far from equilibrium. All macromolecular colloid structures of oxyhydrates are surrounded with a polarized diffuse double electrical layer [1]. A gel often contains an electrolyte, e.g., a solution of its own salt, and, as it was formulated in [2], the oxyhydrate gel interacts with both that solution of its own salt and the water molecules. The interaction may lead to formation and absorption of a certain number of ions. The double electrical layer is formed because some of the ions are absorbed by the gels' matrix (potential-determining layer), while ions of the opposite sign stay in the intermicelle liquid to form the double electrical layer around the macromolecule.

The macromolecules of an oxyhydrate gel, as it was proven by quantum chemical calculations [2, 4], form a great number of varied conformers, and their shapes and structures can change under the effect of the surrounding medium even at room temperature [2]. At that phenomena of destruction and polymerization play not a small role as they also create a variety of conformers. That is why the macromolecular structures are capable of nearly instantaneous realignments at the temperature 298 K as a consequence of low potential barrier.

There are many oxyhydrate forms of zirconium having the shared formula $ZrO_2(H_2O)_n$ that can be a monomer link of an oxyhydrate systems' non-equilibrium polymer chain. The detailed analysis of possible links carried out by means of the ZINDO/1, a semi-empirical quantum chemistry method, proved that the dependence of the ΔH_h hydration enthalpy on the *n* hydration degree had an extreme nature, as shown on Fig. 1. This dependence is not contrary to the experimental data. It is a generally accepted belief [4], that it is zirconic acid $ZrO(OH)_2$ (or $ZrO_2(H_2O)$), or its hydrated form $ZrO(OH)_2$ H_2O (or $ZrO_2(H_2O)_2$) that makes the basis for the zirconium oxyhydrate polymer structures. The water is valence-bound in those compounds; and it is the coordination sphere that another water molecule is added to.

---

[*] corresponding author. E-mail: sucharev74@mail.ru

Printed in Kazakhstan

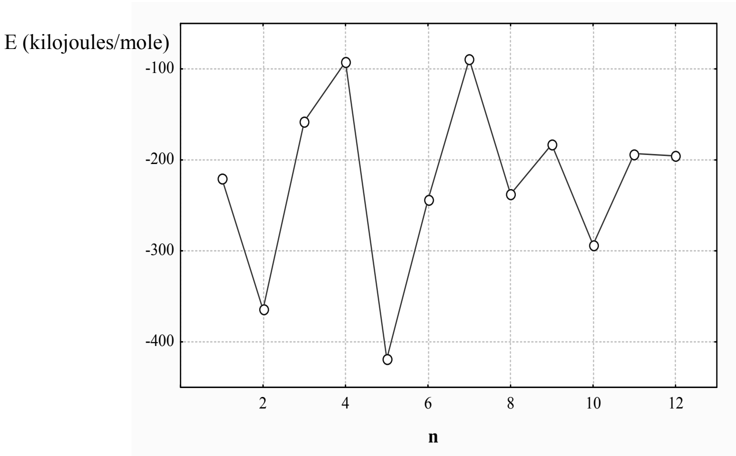


Fig. 1. The hydration enthalpy (ΔH_h) of a polymer chain versus the hydration degree

Formation of a polymer chain is an interaction between couples of monomer links. In this case, one should consider three types of interaction. The first type may be produces as follows:

1_1. $2\ ZrO_2(H_2O) \rightarrow (ZrO_2(H_2O))_2$ - 105.89

1_2. $ZrO_2(H_2O)_2 + ZrO_2(H_2O) \rightarrow ZrO_2(H_2O)_2 \bullet ZrO_2(H_2O)$ - 58.75

1_3. $2\ ZrO_2(H_2O)_2 \rightarrow (ZrO_2(H_2O)_2)_2$ - 17.01

1_4. $ZrO_2(H_2O)_2 + ZrO_2(H_2O)_3 \rightarrow ZrO_2(H_2O)_2 \bullet ZrO_2(H_2O)_3$ - 49.01

1_5. $2\ ZrO_2(H_2O)_3 \rightarrow (ZrO_2(H_2O)_3)_2$ - 81.90

1_6. $ZrO_2(H_2O)_3 + ZrO_2(H_2O)_4 \rightarrow ZrO_2(H_2O)_3 \bullet ZrO_2(H_2O)_4$ - 118.50

1_7. $2\ ZrO_2(H_2O)_4 \rightarrow (ZrO_2(H_2O)_4)_2$ - 121.62

The continued growth of the polymer chains goes through a series of processes listed below:

2_1. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_2 \rightarrow (ZrO_2(H_2O)_3)_2 \cdot ZrO_2(H_2O)_2$; $\Delta H = -80.99$;

2_2. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_3 \rightarrow (ZrO_2(H_2O)_3)_3$; $\Delta H = -85.35$

2_3. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_4 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_4$; $\Delta H = -180.84$;

2_4. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_5 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_5$; $\Delta H = -123.22$;

2_5. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_6 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6$; $\Delta H = -108.50$;

2_6. $(ZrO_2(H_2O)_3)_2 + ZrO_2(H_2O)_7 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_7$; $\Delta H = -111.70$.

In these reactions, the hydration is likely to compete with the growth of the trimers, as it is in dimerization. The hydration is represented by the equation:

$(ZrO_2(H_2O)_3)_2 + H_2O \rightarrow ZrO_2(H_2O)_3 \bullet ZrO_2(H_2O)_4$; $\Delta H_{hyd.}$ - 58.54

Enthalpies of the monomers hydrations are given in Fig.1. Enthalpies of the competing dimer chain growth and the cumulative hydration of the monomers and the dimers are listed in Table 1.

Table 1

Enthalpy of the trimerization (the growth of the chain ΔH) and the cumulative hydration of the dimer and the monomer links (ΔH_H)

No.	ΔH, kcal/mole	ΔH_H, kcal/mole	$\Delta H - \Delta H_H$, kcal/mole
2_1	-80.99	-96.03	15.04
2_2	-85.35	-80.48	-4.87
2_3	-180.84	-158.23	-22.61
2_4	-123.22	-116.62	-6.60
2_5	-108.50	-79.82	-28.68
2_6	-111.70	-115.13	3.43

It is obvious that the trimerization process competes with the hydration reaction while interaction of the $(ZrO_2(H_2O)_3)_2$ with the monomer links from the trihydrate to the hexahydrate (that is, from the $ZrO_2(H_2O)_3$ to the $ZrO_2(H_2O)_6$). In other cases, it is more energetically advantageous for the dimer and the monomer to be in the solution in the shape of independent hydrated compounds. The joining of the hexa- and tetrahydrate forms of the monomer to the dimer are the most energetically advantageous. Nevertheless, the tetrahydrate and the hexahydrate forms are not among the compounds that are commonly found in the solution.

The joining of the predominant hydrate form – a pentahydrate (reaction 2_4) is the most thermodynamically probable in this case, but it leads to the formation of a metastable (that is, not the most probable) product $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_5$.

This compound is expected to join the water, thus forming a more energetically advantageous compound $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_6$. But, due to the structural parameters of the trimers $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_5$ and $(ZrO_2(H_2O)_3)_2 \cdot ZrO_2(H_2O)_6$, it is far from being so.

The hydrate water is located in the inner bindings region, between the zirconium oxide molecules, providing the bindings between the monomer links. While the hydration of the compound $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_5$, the water molecule cannot go straight into the inner region, that is why a hydration of such a chain is not equivalent to a simple joining of hexahydrate to a dimer. A complicated hydration like this entails an isomerization including an opening of the inner region where the water's molecule is supposed to go to, and its subsequent closing. This process is too complicated and therefore unlikely to happen.

A more probable process is that including the destruction of the $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_5$ trimer together with the hydration of the dimer and the pentahydrate form of the polymer. This process only takes 6.60 kcal/mole, a reaction contrary to 2_4. Further on, the freshly formed hexahydrate joins the dimer and emits 28.68 kcal/mole, process 2_5. In this case, the enthalpy of the destruction of $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_5$ can be regarded as the activation energy for the formation of a more advantageous chain $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_6$. The value of the energy barrier (6.60 kcal/mole) is low and is equal to the activation energy of the diffusion.

If we keep considering the further growth of the oxyhydrate chain in comparison with the trimer $(ZrO_2(H_2O)_3)_2{\cdot}ZrO_2(H_2O)_6$ which is the most advantageous of all the previously formed ones, then we will seen the continued interaction reactions between the trimer and the various hydrated forms of the monomer links:

3_1. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 \cdot ZrO_2$ - 139.51

3_2. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O) \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 \cdot ZrO_2(H_2O)$ - 180.34

3_3. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_2 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 \cdot ZrO_2(H_2O)_2$ -146.32

3_4. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_3 \rightarrow (ZrO_2(H_2O)_3)_3\ ZrO_2(H_2O)_6$ –168.68

3_5. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_4 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6ZrO_2(H_2O)_4$ - 190.66

3_6. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_5 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6ZrO_2(H_2O)_5$ 134.01

3_7. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_6 \rightarrow (ZrO_2(H_2O)_3)_2\ (ZrO_2(H_2O)_6)_2$ - 152.58

3_8. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_7 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6\ ZrO_2(H_2O)_7$ - 371.28

3_9. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_8 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6\ ZrO_2(H_2O)_8$ - 153.02

3_10. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_9 \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6\ ZrO_2(H_2O)_9$207.72

3_11. $(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + ZrO_2(H_2O)_{10} \rightarrow (ZrO_2(H_2O)_3)_2ZrO_2(H_2O)_6\ ZrO_2(H_2O)_{10}$143.08

The competing hydration reaction is described by the equation below:

$$(ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_6 + H_2O \rightarrow (ZrO_2(H_2O)_3)_2\ ZrO_2(H_2O)_7 - 24.48$$

It is obvious from the aforementioned reactions that the joining of the predominant pentahydrate form to the growing chain, except for stage one in the formation of the dimer, is thermodynamically advantageous, but it leads to the formation of metastable forms. The structural difficulties brought about by the hydration of the latter forms require a structural realignment of the chain for the transition to a more stable state. The transition includes the destruction, the hydration, and the repeated restructuring of the chain. The destruction requires the activation energy, but this energy is comparable with that of the hydrogen bonds. The destruction rate of the chain is therefore rather rapid, and is expected to increases as the number of the links increases. The growth of the chain is thermodynamically advantageous and is only defined by the rate at which the monomer links are supplied. Meanwhile, the diffusion in the gel phase is considerably slow. That is why the interaction between the pentahydrate form and the oxyhydrate chain is the most probable. However, the polymer chain thus formed is metastable. The interaction between the pentahydrate and the dimer $(ZrO_2(H_2O)_3)_2$ is supposed to produce a trimer with the overall number of the water molecules equal to 11. But the stable form contains 12 water molecules, and is more advantageous than the metastable one by 22.28 kcal/mole. The subsequent interaction between the pentahydrate and the $(ZrO_2(H_2O)_3)_2 \cdot ZrO_2(H_2O)_5$ metastable trimer results in the formation of a metastable tetramer with 16 water's molecules, while a stable tetramer is supposed to contain 19 water molecules and be more advantageous by 223.72 kcal/mole.

The high kinetic probability of the pentahydrate zirconium oxide's joining therefore leads to the formation of thermodynamically metastable chains. As the chain grows longer, its instability increases, thus increasing the probability of a relaxation of the metastable state, that is, the destruction of the chain. The chain is expected to break apart as soon as it reaches a certain length. The two resulting fragments are more stable and may resume their growth separately.

Upon disruption of the polymer chains structural water rises to the surface to have a share in formation of the double electrical layer. Clear is the recurrent and oscillatory nature of these phenomena. Thus, the successive growth of the polymer chain fragments and their destruction both contribute to the temporal periodicity of the gel's properties as well as energetically to the pulsating power noise.

Gel as it is has a reticulate structure that tends to change, probably due to the polymerization of gel's fragments. Not all of gel fragments are capable of moving around freely within the gel space. There are formative conditions for osmotic pressure that affects the charged particles.

Therefore, there is a complex system of cluster motions – both linear traveling and oscillatory rotations – as well as motions of the sizeable oxo-olic molecules (microelectrophoresis [3-9]). Meanwhile electrical fields appear spontaneously provided that presumptions of osmotic influence of the nanoclusters' charged particles are valid [3]. Dynamical systems like that evolve due to the polymerization processes going on in the zirconium oxyhydrate, e.g., destruction and oxolation. It is remarkable that geometry of gel (that is shape of the electrochemical cell) considerably, may be totally, determines the value of electric potential difference in the gel system, as the linear velocity of ion flow depends on the regular cross-section of the cell.

Experimental

Zirconium oxyhydrate gels had been synthesized from zirconium oxychloride salts by adding caustic liquor to the solution upon certain conditions, e.g., pH = 9.25; quantity of added zirconium being n = 0.00094 mole.

The current monitoring electrolytic cell consists of a hollow glass tube with round platinum electrodes (R=0.4 cm) attached at either end, and an electrical unit that registers current alterations on the electrodes. The cell was filled with a fresh gel oxyhydrate. The span between the electrodes altered within the range of 1 to 70 mm. The gel-filled cell was factually short-circuited, that is the output resistance was very low. The current formed inside the system was registered by the digital equipment [5, 8] at the report rate 5 times per second. The experiment lasted for 6 hours. For the instrument layout see Fig. 2.

The tube filled with the oxyhydrate was placed in a system of annular stationary magnets (the field's intensity in the system of magnets A was H_A = 900 Oe, in the system if magnets B it was H_B = 600 Oe), then the cell was fastened to an oscillatory-type mechanical agitator. The experiment was thermostated (T = 303 K). All the current-carrying bus bars have been protected from external electromagnetic blasts.

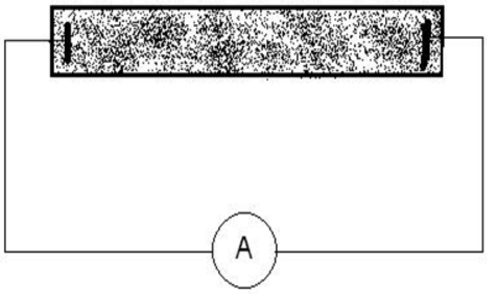


Fig. 2. The electrochemical cell containing an oxyhydrate residue.

Analysis of the results

It was experimentally revealed (Fig. 3 a, b, c), that there was a spontaneous pulsating current formed between the electrodes. In oxyhydrate gel systems of zirconium oxyhydrate, as it has already been mentioned in [1-5], oscillatory rotary ionic molecular flows are caused by a great number of relatively rare stochastic transformations of the gel macromolecules (conformer transitions at the temperature 298K) that, while remaining almost motionless within their coordinates (their mass centers coordinates that is) inside the cell space (due to their enormous masses), continuously pumped the repeated oscillatory diffused ionic flows into the extended gel space. Those flows were formed by the double electrical layers that surrounded the conformers. This is the meaning of the Arnold diffusion's mechanism in gel systems [9]. Those transitions could be viewed as periodical impacts or perturbations of the gel system under the conditions that are far from equilibrium.

It is common knowledge [11, 12] that any dynamical system generally has an irremovable stochasticity region in the phase space in all cases. In fact, those are Langevin's classical ideas [11]. The Hamiltonian function of such an oscillatory rotary ionic molecular colloid chemical system can be represented as:

$$H = H_0 (I) + \varepsilon V (I, \theta, t), \qquad (1)$$

where I, θ - N_0 are for the measurement vectors.

Such a system has $N = N_0 + 1/2$ degrees of freedom, 1/2 of them belongs to the *t* variable (time). Generally, some extent of the H_0 (I). Hamiltonian has separatrixes, that is why a εV perturbation, destroying them, creates stochastic layers at any ε. The stochastic trajectories are further on defined by the weak chaos topology of the colloid chemical system in the phase space.

In practice, the hyperbolic growth of the polarization current is registered in the samples placed into the magnet that has the highest intensity (Table 2). Zirconium hydroxide samples placed into a lower intensity magnet demonstrate the same hyperbolic current increase and surge, but in the latter case, the polarization current starts to decrease rapidly as soon as it reaches a certain maximum. The current sign changes to the opposite, and there is a charge exchange between the electrodes or in the gel phase double electric layer (Fig. 3c). The charge exchange effect is much stronger in the double electric layer of the gel that was not exposed to the magnetic effect.

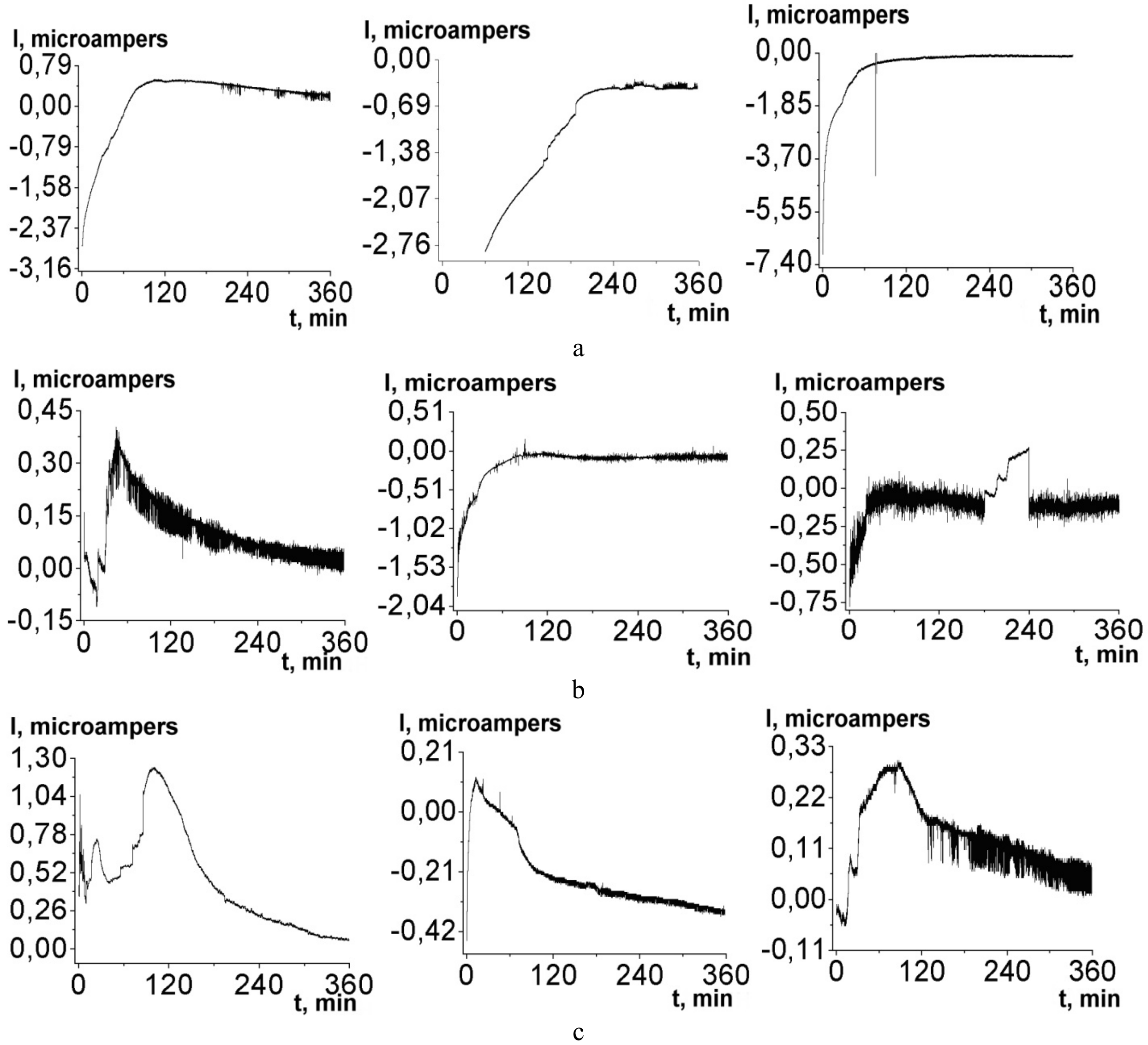
The quantitative evaluation of a current surge in the zirconium gel oxyhydrate required the calculation of the ΔI value, microamperes, the upper and the lower currents surge values, as shown on the diagrams and Table. 2.

Table 2
Difference of the maximum and the minimum values of the self-organization current by the modulus

Intensity of the magnetic field H, Oe	ΔI, mcA		
0	1.18	0.57	0.35
600	0.49	1.84	0.99
900	13.46	3.21	6.94

Thus, the range of the ΔI value grows in microamperes as the intensity of the magnetic field increases. The phenomenon is probably caused by the orientation effect of the mesophase-like regions of the gel exposed to a magnetic field, which leads to a one-way ejection of charged particles connected to the double electrical layer and producing the current. Therefore, we see an ionic surge effect. Alternatively, we see extended bound dipoles of the gel fragments that have a considerable polarization in the double electric layer.

The extended current surges are shown on Fig.4. Let us attempt to analytically picture the phenomenon of current expulsions by making the algorithmic model of the given problem, meanwhile without the magnetic field.



a

b

c

Fig.3. Alterations in the gels polarization current in zirconium hydroxide that were synthesized in three parallels, where a) the gels were studied in a magnetic field with the intensity 900 Oe, b) in a magnetic field with the intensity 600 Oe, and c) with the magnetic field off; the sample was synthesized at the pH = 9.25; length of the rube L = 70 mm; the quantity of the zirconium oxyhydrate in the tube n = 0.00094 moles.

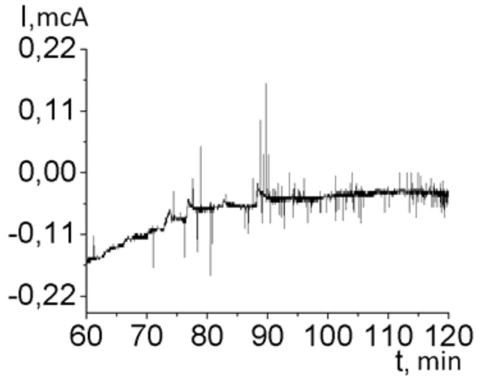


Fig. 4. A part of the experimental curve representing large currents surges. The selected kinetic curve of the self-organization current in the zirconium oxyhydrate, pH = 9.00, n = 0.00235 moles, L = 10 mm, T = 284 K.

Mathematical simulation

Let there be an electrolyte, e.g., a solution of the gel's own salt, added to a fresh gel. Opposite sign ions will be subsiding on large fragments of colloid particles (or rather, they will be absorbed by them), canceling each other's charges. The number of the freely traveling ions will thus be limited, or the effect of the electrical field on the movement of the charged particles will not be noticeable. What we are interested in is the very possibility of the phenomenon, not a precise quantitative result, nor the measurements of the parameters. Therefore, we will be considering all the parameters related to the movement of the ions as either constant or as linear (linearized). That is why we are going to confine our discourse to a simple linear model. As it will be proven below, this approach makes some forecasting sense.

According to [8, 11], the I_+ and the I_- charge flows in the absence of temperature gradients and chemical potentials are defined by the relations:

$$\begin{aligned} I_+ &= L_{11}\, grad\, \varphi + L_{12}\, grad\, P \\ I_- &= \tilde{L}_{11}\, grad\, \varphi + \tilde{L}_{12}\, grad\, P \end{aligned} \qquad (2)$$

where φ is for the electrical potential, P is for the osmotic pressure that forms due to the reticulate structure of the gel, L_{11} is for the conductivity coefficient for the flow of freshly charged '+' particles, L_{12} is for the electroosmotic flow of positively charged particles, and $\tilde{L}_{11}$ and $\tilde{L}_{12}$ are the respective negatively charged ions' coefficients.

The I_+ and the I_- currents can be of various natures, and it can lead to an accumulation of a charge.

The continuity equation of the concentrations with a separated diffusion looks like:

$$\begin{aligned} \frac{\partial n_+}{\partial t} + div\vec{j}_+ &= D\Delta n_+ \\ \frac{\partial n_-}{\partial t} + div\vec{j}_- &= D\Delta n_- \end{aligned} \qquad (3)$$

where $\vec{j}_+$ and $\vec{j}_-$ are for the ionic currents' density with the respective signs, $D\Delta_n$ is for the contribution made by the diffusion, D is for the diffusion coefficient, Δ is for the Laplace operator, and $n_\pm$ is for the concentration of the positive and negative particles.

It is remarkable that the J's and the I's dimensions are not the same. So let us divide the I_+ and the I_- by the sections' area that we will consider to be constant, and, from (3) we will derive the relations:

$$\begin{aligned} \vec{j}_+ &= l_{11}\, grad\, \varphi + l_{12}\, grad\, P \\ \vec{j}_- &= l_{21}\, grad\, \varphi + l_{22}\, grad\, P \end{aligned} \qquad (4)$$

where all the coefficients are in relation to the area of the cross section.

Now let us substitute the currents density expressions (4) to the continuity equations (3):

$$\begin{cases} \dfrac{\partial n_+}{\partial t} + l_{11}\Delta\varphi + l_{12}\Delta P = D\Delta n_+ \\ \dfrac{\partial n_-}{\partial t} + l_{21}\Delta\varphi + l_{22}\Delta P = D\Delta n_- \end{cases} \qquad (5)$$

The osmotic pressure P is defined by the formula $P = inRT$, where i is a number, n is for the concentration of the substance that forms the osmotic pressure, $R = k_B N_A$ is for the universal gas constant, and T is for the temperature. Only the concentration changes in the course of the experiment, consequently, we can consider the pressure proportional to the remainder of the ions' concentrations, $P = \alpha\,(n_+ - n_-)$.

$$\begin{cases} \dfrac{\partial n_+}{\partial t} + l_{11}\Delta\varphi + \tilde{l}_{12}\Delta\left(n_+ - n_-\right) = D\Delta n_+ \\ \dfrac{\partial n_-}{\partial t} + l_{21}\Delta\varphi + \tilde{l}_{22}\Delta\left(n_+ - n_-\right) = D\Delta n_- \end{cases} \qquad (6)$$

where the constant factor α is present in the new coefficients $\tilde{l}_{12}$ and $\tilde{l}_{22}$.

The Poisson equation without the boundary conditions will look like: $\Delta\varphi = 4\pi\,(n_+ - n_-)$. Substituting this expression to (6), we will obtain:

$$\begin{cases} \dfrac{\partial n_+}{\partial t} + \tilde{l}_{11}\left(n_+ - n_-\right) + \tilde{l}_{12}\Delta\left(n_+ - n_-\right) = D\Delta n_+ \\ \dfrac{\partial n_-}{\partial t} + \tilde{l}_{21}\left(n_+ - n_-\right) + \tilde{l}_{22}\Delta\left(n_+ - n_-\right) = D\Delta n_- \end{cases} \qquad (7)$$

Let us now subtract the equations of the system (2.3.6) from each other and introduce notation $u = n_+ - n_-$. The result will be the expression

$$\frac{\partial u}{\partial t} + (\tilde{l}_{11} - \tilde{l}_{21})u + (\tilde{l}_{12} - \tilde{l}_{22})\Delta u = D\Delta u\,.$$

Adding the boundary conditions and the initial conditions to this equation, we will derive a closed boundary-value problem.

We will regard the ionic flow as moving towards the electrode and forming an instantaneous potentials difference on it (within the closed circuit of first-class conductors, Fig.2).

Consequently, we are to stipulate the boundary convection condition on the region's boundary – a third-class condition: $\left(\frac{\partial u}{\partial x} - \lambda u\right)\Big|_{x=0} = 0$, where λ is for a number, for we believe that the electrode is located at the $x = 0$. The whole region where we are going to solve the problem will be regarded as an unlimited one, $x \epsilon$ [0; + ∞]. It is convenient to ascribe such geometrical dimensions to a limited region because all the phenomena listed in the introduction and that we are able to register are onlyconfined to a narrow laminar layer adjacent to the electrode that has the thickness 10^{-5} m. The geometrical dimensions of the double electrical layer region of the macromolecules is approximately 10^{-7} m [8, 9]), that is the dimensions of the double electric layer are small in comparison with the infinitely large near-wall laminar region. Talking of the initial condition, it is something that we already know and it is represented by the function $u|_{t=0} = u_0 (x)$. This is how the problem looks now:

$$\begin{cases} \frac{\partial u}{\partial t} + au = (D-b)\Delta u, \quad x \in [0;+\infty),\ t \in [0;+\infty) \\ \frac{\partial u}{\partial x}\Big|_{x=0} = \lambda u\ |_{x=0},\ u\ |_{x\to+\infty} = 0,\ \frac{\partial u}{\partial x}\Big|_{x\to+\infty} = 0 \\ u\ |_{t=0} = u_0(x) \end{cases} \tag{8}$$

where $a = \tilde{l}_{11} - \tilde{l}_{21}$, $b = \tilde{l}_{12} - \tilde{l}_{22}$.

Now let us accept D – b = B. It deserves a mention that in the (8), the difference *D - b* can be either positive or negative. The positive difference means that the diffusion of the ions suppresses the charges separation due to the osmotic pressure. The negative ones means that the osmotic pressure is stronger than the diffusion, and if there is even a slightest difference between the charges that is different from zero, then that difference will be only increasing.

We will confine our studies to an instance whenD – b > 0. The problem presupposes that the a number is positive. The problem (8) has been studied inside and out. The uniqueness theorem and the existence theorem, and the solutions can be found in [10].

The flow is the concentrations difference gradient: $\vec{j} = grad\left(n_+ - n_-\right)$.

At the region's boundary $j = \frac{\partial u}{\partial x}\Big|_{x=0}$.

To begin with, let us consider the modeled problem: let the initial deflection be $u_0 = A\delta (x-x_0)$, where $x_0 > 0$. Then the whole problem (8) will look like:

$$\begin{cases} \frac{\partial u}{\partial t} + au = B\Delta u,\ B > 0, a > 0,\ x \in [0;\infty), t \in [0;+\infty) \\ \frac{\partial u}{\partial x}\Big|_{x=0} = \lambda u\ |_{x=0},\ \frac{\partial u}{\partial x}\Big|_{x\to+\infty} = 0,\ u\ |_{x\to+\infty} = 0 \\ u\ |_{t=0} = A\delta(x - x_0) \end{cases} \tag{9}$$

We will be seeking a solution that looks like: u = ν exp (-at), where ν is for a novelty unknown function. The solution (9) for the ν function can be represented as [10]:

$$v(x,t)=\frac{A}{\sqrt{4\pi Bt}}\left\{\exp\left(-\frac{(x-x_0)^2}{4Bt}\right)+\exp\left(-\frac{(x-x_0)^2}{4Bt}\right)-2\lambda\int_0^{+\infty}\exp\left(-\frac{(x+x_0+\xi)^2}{4Bt}-\lambda\xi\right)d\xi\right\}$$

We can only register currents when the x = 0, consequently, in order to draw a comparison with the experiment, we are to find

$$v(x,t)=\frac{A}{\sqrt{\pi Bt}}\left\{\exp\left(-\frac{x_0^2}{4Bt}\right)-\lambda\int_0^{+\infty}\exp\left(-\frac{(x_0+\xi)^2}{4Bt}-\lambda\xi\right)d\xi\right\}$$

Calculating the integral, we will derive:

$$v(x,t)=\frac{A}{\sqrt{\pi Bt}}\left\{\exp\left(-\frac{x_0^2}{4Bt}\right)-\frac{\lambda}{2}\left(1+erf\left(\frac{x_0}{4\lambda Bt}+\frac{1}{2}\right)\right)\exp\left(-\lambda x_0-\lambda^2 Bt\right)\right\}.$$

Let us note that the second component rapidly decreases, as there is a growth in time. The component can be neglected, at least to make simple and rough evaluations easier, seeing as the experiment's time is normally not too short.

Seeing as at the boundary $\left.\frac{\partial u}{\partial x}\right|_{x=0}=\lambda u\,|_{x=0}$, the current $j=\frac{\partial u}{\partial x}$, then $j=\frac{v(t)e^{-at}}{\lambda}$ can be represented as: $j\approx\frac{A}{\lambda\sqrt{\pi B}}\frac{\exp\left(-\frac{x_0^2}{4Bt}-at\right)}{\sqrt{t}}$. In terms of the experimental curves diagrams (Fig. 3, 4) that represent the dependences of the registered currents or the ionic cluster flow on time and considering it as only containing the "aftereffects" of the charge fluctuation, we can calculate the *a* and the $\frac{x_0^2}{4B}$ coefficients.

Let us represent them as $K_1=\frac{x_0^2}{4B}$ and $K_2=-a$ respectively, and resort to the least square technique to fit them. The K_2 coefficient can hardly be negative, for it looks like a case when the charges traveling in an electric field (that is moving towards their compensation) start to separate. The positive K_1 coefficient is for the case when the charges separate, affected by the osmotic pressure.

An instance of the K_1, K_2 coefficients computations by means of the least square technique is represented on Fig. 5.

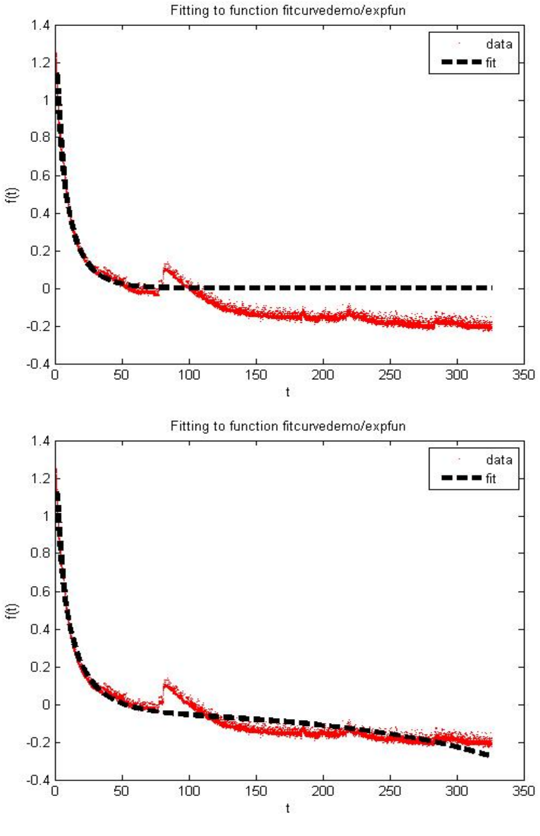


Fig. 5. Coefficient fitings by means of the least square technique. The dotted line is for the fiting of the values, the gray dots are for the experimental data. The X axes of the both diagrams represent the time in minutes, the Y axes the currents values is dimensionless units.

The first diagram corresponds to the coefficients values fittings by means of the following formula:

$$j \approx \frac{A}{\lambda\sqrt{\pi B}}\frac{\exp\left(-\frac{x_0^2}{4Bt}-at\right)}{\sqrt{t}}$$

The second one corresponds to the formula

$$\frac{A e^{-at}}{\lambda\sqrt{\pi B t}}\left\{\exp\left(-\frac{x_0^2}{4Bt}\right)-\frac{\lambda}{2}\left(1+erf\left(\frac{x_0}{4\lambda Bt}+\frac{1}{2}\right)\right)\exp\left(-\lambda x_0-\lambda^2 Bt\right)\right\}$$

The numerical evaluations for the first diagram provide the values:

$$\frac{A}{\lambda\sqrt{\pi B}}=2.5183,\ a=0.000923\ \text{(1/sec)},\ \frac{x_0^2}{4B}=46.062\ \text{(sec)}.$$

The second diagram evaluates the value of λ that proves to be negative (corresponds to the repulsion of the charges). The numerical evaluations for the second diagram are the following:

$$\frac{A}{\lambda\sqrt{\pi B}}=2.6198,\ a=0.000595\ \text{(1/sec)},\ \frac{x_0^2}{4B}=37.806\ \text{(sec)},\ \lambda=-0.0957\ \text{(1/m)}.$$

Both the calculations above and the model itself are far from being precise, yet they provide correct evaluations of, e.g., the diffusion coefficients; as it was stated in [1, 2], their value was $x_0 \approx 10^{-5}$ cm. Meanwhile, the ions' diffusion ceofficient in the gel is evaluated to be the $D \approx 10^{-8}$ *cm2/sec* value, which is not contrary to the data provided by the scholars [3].

There are several types of charge separations. In the case in question, we can seek the u_1 that looks like.

$$u_1=\sum_{k=1}^{N}\left(\frac{A_k e^{-at}}{\lambda\sqrt{\pi Bt}}\left\{\exp\left(-\frac{x_{0k}^2}{4Bt}\right)-\frac{\lambda}{2}\left(1+erf\left(\frac{x_{0k}}{4\lambda Bt}+\frac{1}{2}\right)\right)\exp\left(-\lambda x_{0k}-\lambda^2 Bt\right)\right\}\right)$$

The dependence calculations for $N=2$ were made too. The precision we attained in this case was to a certain degree higher, but still we failed to reach any noticeable improvements. The evaluated parameters' values were little or no different from the those on Fig. 5:

$$\frac{A_1}{\lambda\sqrt{\pi B}}=2.5050,\ a=0.000497\ \text{(1/sec)},\ \frac{x_{01}^2}{4B}=43.446\ \text{(sec)},\ \lambda=-0.0921\ \text{(1/m)},$$

$$\frac{A_2}{\lambda\sqrt{\pi B}}=0.8076,\ \frac{x_{02}^2}{4B}=29.418\ \text{(sec)}.$$

The calculations above only meet a certain averaged asymptotic non-oscillatory instance's conditions, Fig.5. The real experimental picture showed a whole range of currents surges in time, that could not have been deduced from the statements above and required a separate description different from the those calculations. It was a physico-chemical phenomenon of a different nature.

When moving towards an electrode, the charges flow sort of "subsides" on graphite or platinum electrodes (or rather, it gets absorbed by them). Then the flow creates a potentials difference, that is, an electrical current, and "trickles back" to the dispersion. The potentials difference is "dissolved," in other words, it simply disappears. This is how oscillatory motions in the ionic flows of the double electric layer appear, forming the general picture of the ion currents surges.

Considering this phenomenon, the problem's representation will be more convenient (9) if put down in a way as follows:

$$\begin{cases} \dfrac{\partial u}{\partial t} + au = B\Delta u,\ B > 0, a > 0,\ x \in [0;\infty), t \in [0;+\infty) \\ \left.\dfrac{\partial u}{\partial x}\right|_{x=0} = -(\lambda + \varepsilon\sin(\omega t + \varphi))u\,|_{x=0},\ \left.\dfrac{\partial u}{\partial x}\right|_{x\to+\infty} = 0,\ u\,|_{x\to+\infty} = 0 \\ u\,|_{t=0} = A\delta(x - x_0) \end{cases} \tag{10}$$

where ε is for a small quantity, an oscillations parameter, ω is for the frequency of the near-electrode oscillations, and φ is for their phase.

We will not go beyond the simplest description of the oscillations – by means of a harmonic function – though the phenomenon deserves a separate and a more detailed consideration.

If λ > ε, then, using the approach [7, 10], it will be easy to prove that if the solution (10) exists, then it is the unique one. Let us try to develop a solution, and thus prove that the solution (10) does exist. To do so (10), we carry out a Laplace transform for the positive part of the OX axis, solve the derived equation in relation to the *t*, and then invert the Laplace transform. In the derived integral relation, we will go over to the *x* → *0* limit. As a result, we will get the following integral equation:

$$u\,|_{x=0} = A\frac{\exp\left(-\dfrac{x_0^2}{4Bt} - at\right)}{\sqrt{4\pi Bt}} - \int_0^t \frac{\big(\lambda + \varepsilon\sin\big(\omega\tau + \varphi\big)\big)e^{-a\tau}u\,|_{x=0}\,(\tau)}{\sqrt{4\pi B(t-\tau)}}$$

The solution to this equation at the λ>ε does exist, and it is the unique one [13]. The solution for the case ε = 0 can be found in [10]. When the ε values are small, a solution can be developed by means of iterations. Taking in consideration the relation of current

$$\left.\frac{\partial u}{\partial x}\right|_{x=0} = \lambda u\,|_{x=0},$$

the current being $j = \dfrac{\partial u}{\partial x}$, it is not difficult to find the value of current at the border.

The experimental data, the results of the unknown values fittings (including the oscillation frequencies, the oscillation amplitudes, and the phases), and the approximations are listed below on Fig.6.

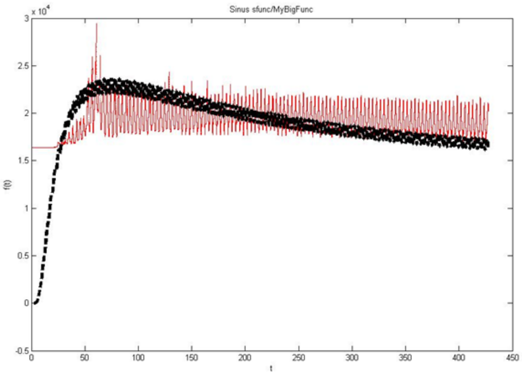


Fig. 6. Coefficient fitings by means of the least square technique. The dotted line is for the fitting of the values, the gray dots are for the experimental data. The X axes of the both diagrams represent the time in minutes, the Y axes the currents values is dimensionless units. *A=2.7962, X0=0.0001(m), λ=1.2909, B=D=2·10⁻¹² (m²/sec), a=0.0005 (1/m), ε=0.0986, ω=0.034(1/sec), φ=0.614.*

The data obtained correspond to the results of an immense number of experiments that we have carried out. The evident modeled approximation of the consideration requires a more detailed consideration in terms of cluster nanophenomena.

Conclusions

For the first time the pulsating character of the current surges in the zirconium oxyhydrate is described as determined by conformational rearrangements of the oxyhydrate matrix. Consequence of the conformational-peptizating instability is the alternation of polarization of the double electrical layer of the gel particles, which manifests itself in the form of periodical electrical current surges. Mathematical model reckons ejective periodical disturbances of the gel system, which determines extended current expulsions a peak character. The vastest range of the ΔI values is observed for those gels that were exposed to the most intensive magnetic field. The phenomenon is probably caused by the orientation effect of the mesophase-like regions of the gel exposed to a magnetic field, which leads to a one-way ejection of charged particles connected to the double electrical layer and producing the current.

Acknowledgements

The present research is a part of the Federal Project “Scientific and pedagogical human resources of innovative Russia” in 2009-2013, sector of “Nanotechnologies and nanomaterials”.

References

1. D.A. Fridrichsberg. Course of colloid chemistr. Moscow: Nauka, 1974. 378p.
2. Yuri I. Sucharev. Nonlinearity of Colloid Systems: Oxyhydrate Systems. Switzerland, UK, USA: Trans Tech Publications. 2007. 433p.
3. B.A. Markov, Y.I. Sucharev, I.Y. Lebedeva, I.Y. Apalikova. Coulomb diffusion model of oxyhydrate gel formation. Butlerov Communications. 2009. Issue 18. №.8. pp.49-54.
4. Y.I. Sucharev and B.A. Markov: Nonlinearity of gel oxyhydrate systems. The Russian Academy of Sciences, Yekaterinburg 2005. 468 p.
5. Y.I. Sucharev, I.Y. Suchareva, A.M. Kostrukova, B.A. Markov. Theoretic treatment of electrophoretic periodic characteristics of oxyhydrate gels of yttrium and zirconium. Chelyabinsk Scientific Center Newsletter issued by the Russian Academy of Sciences. 2003. Issue 21. №4. pp. 125-130.
6. Y.I. Sucharev, I.Y. Suchareva, B.A. Markov. Self-organization of gesl in Lennard- Jones potential. Chelyabinsk Scientific Center Newsletter issued by the Russian Academy of Sciences. 2004. Issue 24. №.3 pp.86-91.
7. Y.I. Sucharev, I.Y. Suchareva, E.P. Yudina. Influence of the electrical and magnetic fields on optical properties of oxyhydrate gels of yttrium and zirconium. Chelyabinsk Scientific Center Newsletter issued by the Russian Academy of Sciences. 2002. №4. pp.127-132.
8. Yu.I. Sukharev, B.A. Markov, A. Yu. Prokhorova, I.Yu. Lebedeva. Spontaneous pulsating current in zirconium oxyhydrate gels. Wseas transactions on circuits and systems. 2005. Vol.4. Issue 11. ISSN: 1109-2734. P.1477-1484.
9. Y.I. Sucharev. Colloid variant of Arnold diffusion mechanism. South Ural State University Newsletter: Mathematics, physics and chemistry series. 2007. Issue 8. №3. 75. pp.89-94
10. A.G. Sveshnikov, A.N. Bogolubov, V.V. Kravtsov. Lectures on mathematical physics. Moscow: Publishing House of Moscow State University. 1993. 352p.
11. V.S. Anischeko, V.V. Astakhov, T.K. Vladivasova and others. Nonlinear effects in chaotic and stochastic systems. Moscow, Izhevsk: Institute of Computer Research. 2003. 544p.
12. Yu.I. Sukharev, T.G. Krupnova, E.P. Yudina, I.Yu. Lebedeva. Concerning the interconnections of self-organizing oxyhydrate gels and their experimental determination. Colloids an Surfaces A: Physicochem. Eng. Aspects. 2007. 300. P.281-286.
13. F.D. Gakhov, Y.I. Chersky. Convolution-type equations. Moscow, 978. 300 p.

Received 16 March 2011