

THE MATHEMATICAL DESCRIPTION OF PERIODIC SORPTION BEHAVIOR OF RARE METALS OXYHYDRATE GELS (THE ISOTHERMS OF ADSORPTION)

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Abstract

The analytical equation for the Liesegang operator has been obtained. The genetic relation between the Liesegang operator describing the behavior of the non-equilibrium oxyhydrate gel and the Hamiltonian of the vibrating sorption system is shown.

Having applied the principle of separability and having used the Liesegang operator we succeeded in giving the analytical description (to suggest the periodic sorption isotherms) of the sorption states of gel systems in coordinates $u = f(t)$ and $u = f(c_p)$, where u is the value of sorption.

Introduction

Sorption of ions by non-linear oxyhydrates able to add the oxyhydrate matrix (sorption with further copolymerization) is, in general case, of quite complex periodic character during long periods. Such periodic curves describe the state of the far-from-equilibrium sorption system (Figure1). For such systems it seems reasonable either to experimentally define or theoretically calculate two-dimensional sorption isotherms in two coordinates: “equilibrium specific sorption - equilibrium sorbate concentration” as well as to introduce one more coordinate, namely “time” (Figure1).

The Liesegang operator and the Hamilton-Jacobi equation

The time coordinate describes not only the kinetics of sorption process but determines the change of some internal recurring states of a sorbent solid phase, i.e. its self-organization. Hence, it is the constituent of the sorption isotherm. The task is to mathematically describe the change in these sorbate system states using the time coordinate since classical sorption isotherms don't give us such a possibility.

In our previous works [1,2] we introduced the so-called process evolution operator, the Liesegang operator, to describe the periodic self-organizing systems. To describe the self-organizing processes in gel we will use a simple one-dimensional model which makes it possible to illustrate the behavior of the Liesegang operator and, hence, the change in the sorbate concentration. To describe the above self-organization we will use the diffusion equation introducing the Liesegang operator:

$$\begin{cases} \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + L[u] \\ u \Big|_{x=0} = u_0, u \Big|_{t=0} = u_0 = const, \\ u \Big|_{x=l} = u_0 \end{cases} \quad (1)$$

where D is the diffusion coefficient, l is the line length for a given equation, $L[u]$ is the Liesegang operator, u, u_0 are some current and initial values of concentration of structuring fragments.

For the purpose of our work it is necessary to derive an approximate formula for the Liesegang operator. It is shown in [2] that the Liesegang operator $L[u]$ is equal to αu , if the concentration of sorbate in gel has not reached the upper critical value of concentration u_{max} , and it is equal to $-\alpha u$, if the concentration of sorbate in gel has exceeded the value u_{max} and started to decrease but has not yet reached the lower critical value u_{min} . The analytic formula for a general case has not been found yet but it is quite possible to write a program for calculating this operator.

A clear idea of the possible Liesegang operator formulas can be inferred from a simple case. Earlier we used the simplified equation of form (1) where the diffusion was neglected:

$$\frac{\partial u}{\partial t} = aL[u].$$

Let us consider the different forms of the Liesegang operators. In the simplest case the Liesegang operator may be expressed in the form of the well-known periodic function $L[u] = \alpha \cos \omega t$. Then, the differential equation will take the form: $\frac{\partial u}{\partial t} = \alpha \cos \omega t$. As a result, we may write the concentration of the structuring

fragments in the form $u = \frac{\alpha}{\omega} \sin \omega t$, assuming that the initial condition equals zero.

This is the simplest way of the vibrating system modelling.

In our research we used the other forms of the Liesegang operator for the vibrating system modelling, which are given further in the article.

We neglect the diffusion in (1) in order to simplify the Liesegang operator and write it as $L[u] = \alpha Sgn[u]$, where α is some constant coefficient. The operator $Sgn[u]$ is determined as follows: we have two values of concentration: u_{max} and u_{min} , with $u_{min} < u_{max}$. When u reaches u_{max} , $Sgn[u] = -1$, when u reaches u_{min} , $-Sgn[u] = +1$.

Equation (1) takes the following form: $\frac{du}{dt} = \alpha Sgn[u]$. Now we calculate the absolute values for both members. As a result the absolute values of time are α , i.e. the rate of concentration change for the model is constant. Hence, since in our case both the upper critical value u_{max} and the lower critical value u_{min} (the so-called oscillations return points) remain unchanged, the Liesegang operator takes the form:

$$Sgn[u] = \alpha \operatorname{sgn}\left(\sin\left(\frac{\pi \alpha t}{u_{max} - u_{min}}\right)\right). \tag{2}$$

Then the concentration of self-organized gel (sorbed ion) is:

$$u = u_{\min} + \frac{u_{\max} - u_{\min}}{\pi} \arccos\left(\sin\left(\frac{\pi\alpha t}{u_{\max} - u_{\min}}\right)\right). \quad (3)$$

In our model we use the concentration coordinate that describes some ideal periodic vibration law of sorbtion variation in non-linear oxyhydrate gels. Energy component of this periodic process is lacking. The Liesegang operator only implicitly includes the energy component. It enters into the constants of integration.

Another form of the Liesegang operator leads to the following decision $u = A \exp(\arcsin(\sin(\omega t)))$. The graphs of the functions are presented in Figure 2, 3.

It **should** be noted, that we use another form of the Liesegang operator, conjugated to the first one (Figure 5), as in many cases we have to make calculations against a certain system “background” under which we understand the precipitation dissolving in the dispersed medium. So we have to take into account some gel component transformed from the precipitation into the solution, which is a general case. Then, the formula for the Liesegang operator will take the form:

$$u = U_0 - U_{\max} \exp\left(\alpha \sin\left(\sin\left(\frac{\pi}{u_{\max} - u_{\min}} \int_0^t u(\tau) d\tau\right)\right)\right), \quad (4)$$

where u is the gel quantity in the solution, U_0 is the total gel quantity, U_{\max} is the maximum gel quantity capable of transforming into solution.

The vibrations of a simple harmonic oscillator may be an actual analogue of periodic sorbtion. The oxyhydrate quasi-liquid-crystal gel (due to the particular properties of liquid crystals) [2,5] can be likened to some oscillator, which absorbs and then, by virtue of some physical-chemical reasons, desorbs, which naturally causes the vibration process. From the analysis of bounded Hamiltonian systems [3] it follows that the trajectories of the oscillator containing the sorbate have the form of closed invariant curves in the phase plane.

Thus, motion is periodic and the return to the same point (p, q) of space takes place after the cycle with a period of $2\pi/\omega$ is completed, where ω is the

frequency of motion, p, q are the generalized impulse and the generalized coordinates.

The very idea of introducing the “action - angle” variables lies in finding such a pair of costate variables, assuming that the costate “coordinate” increases by 2π with each complete cycle of motion. The “action-angle” variables are defined by I, θ , where I is the constant conjugate momentum. The following expression for the generating function $S(q, I)$ can be written:

$$\begin{aligned} p &= \frac{\partial}{\partial q} S(q, I), \\ \theta &= \frac{\partial}{\partial I} S(q, I). \end{aligned} \tag{5}$$

The generating function for the model of a simple harmonic oscillator with the Hamiltonian $H = \frac{1}{2}(p^2 + \omega^2 q^2)$ is expressed by:

$$S(q, I) = \int_{q_0}^q \sqrt{2(I\omega - \frac{1}{2}\omega^2 q^2)} dq. \tag{6}$$

The equation for the generalized coordinates relationship $q = q(I, \theta)$ can be written as:

$$q = \sqrt{\frac{2I}{\omega}} \sin(\omega t + \delta). \tag{7}$$

It can be easily demonstrated that in some actual vibration process the vibration period is the difference of the vibration process return points $u_{\max} - u_{\min}$ but in the sorbtion process theory the process evolution operator or the Liesegang operator is used. The Hamilton – Jacobi equation [3] is genetically equivalent to the Liesegang operator.

Gel systems are metastable systems developing with time. In previous articles [6,7] we showed that the development of these systems occurs in helical fashion. It is natural that the spiral fragments form complex systems of double electrical layers on their surface.

Let us consider in theory the way Van der Waals forces act in polymer gel fragments against the background of self-organizing pulsating-autosoliton

processes of structuring. We will describe these processes with the help of the Liesegang operator [1,2]. Thus, we will try to give the colloid-chemical interpretation of the Liesegang operator, supposing that the Liesegang operator determines the processes of gel self-organization.

Let us consider the colloid particle movement in the field of Lennard-Jones potential (intermolecular forces of London – Van der Waals). Let's perform the procedure of Lennard-Jones potential demasurement. It is known that the Lennard-Jones potential has the form:

$$\Delta U = -\frac{C}{r^6} + \frac{B}{r^{12}} \quad (8)$$

Let's demeasure the potential ΔU by means of the following operations. Let U_0 be the dimensional and scale constant (suppose that the potential is measured in joules); U' is certain dimensionless quantity. In that case we can write the following product for the potential $\Delta U = U_0 U'$, so the product for the radius will take the form $r = r_0 r'$. Let us drop the primes. As a result we obtain the Lennard-

Jones potential in the form of the proportion $U U_0 = -\frac{C}{r_0^6 r^6} + \frac{B}{r_0^{12} r^{12}}$. The equation

of the colloid particle affected by the Lennard-Jones potential has the form:

$$\frac{r_0^2}{t_0^2} \frac{d^2 r}{dt^2} = -U_0 \frac{dU}{dr}, \quad \text{or} \quad \frac{m r_0}{t_0^2} \frac{d^2 r}{dt^2} = \left(-\frac{C'}{r_0^7 r^7} + \frac{B'}{r_0^{13} r^{13}} \right), \quad \text{where primed and}$$

unprimed quantities are connected by the relationship $C' = 6C$, $B' = 12B$. As a result we get the relationship of the following form:

$$\frac{m r_0^8}{C t_0^2} \frac{d^2 r}{dt^2} = \left(-\frac{1}{r^7} + \frac{1}{r^{13}} \right). \quad (9)$$

The dimensionless equation has the form:

$$\frac{d^2r}{dt^2} = \left(-\frac{1}{r^7} + \frac{1}{r^{13}} \right). \quad (10)$$

Unfortunately, it is impossible to define the exact solution of the equation. That is why we have to solve this equation numerically.

In Figure 4 the particle is shown “to get stuck” in the field of potential attraction, performing cyclic vibrations close to the point $r = 1$.

If we compare the change of density or the change curve of polymer gel fragments concentration determined by the Liesegang operator in [2,8,9] shown in Figure 5 with the moving curve of colloid particle shown in Figure 4, it is easy to observe the visual identity of these curves.

The remarkable fact is that the particles forming the gel in the field of Van der Waals forces are pulsating with time, that is, they perform complex vibrating movements, thus, periodically changing some dimensionless spherical radius (Figure 4). These particle movements have two consequences, namely:

- 1) the particles acquire the physical possibility to rearrange themselves at some state or at some point of time, that is they change their spatial orientation and surrounding (in that case the fragment will have the minimum energy for barrier turns);
- 2) the period of gel particles vibration is a certain constant of the system of oxyhydrate particles (pacemakers), organized in the oxyhydrate gel which is a certain system of attractors.

The Liesegang operator describes the self-organization of gel system with time. The periodicity of spherical radii changing in the field of Van der Waals forces and the geometrical identity of these curves (Figure 4) to the Liesegang operator changing with time (Figure 5) surely, indicate that the forces determining the Liesegang operator (the operator of system self-organization) and the forces determining the Lennard-Jones potential are similar. The intermolecular forces initiate an instant “splash” of ions into the external environment, which happens after the ion sorbtion by gel swirl is finished. When the particle acquires large

potential, its movement in the Lennard-Jones potential may sharply change with time.

Thus, the introduction of the Liesegang operator as the reflection of the Hamilton-Jacobi equation is proved in terms of energy.

Such correlations are made to address not only the Hamilton-Jacobi equation but the conditions of the Liesegang operator separability. In case of separable systems it is solvable and written as:

$$H_k\left(\frac{\partial S}{\partial q_k}, q_k\right) = \alpha_k, \quad k = 1, \dots, n. \quad (11)$$

Where α_k are interconnected by the relationship $\alpha = \alpha_1 + \alpha_2 + \dots + \alpha_n = H'$, and a is the value of the transformed Hamiltonian H' .

In case of the Liesegang operator the similar relationship can be written as:

$$\frac{\partial U}{\partial t} = a_1 L_1[u_1] + a_2 L_2[u_2] + a_3 L_3[u_3] + \dots \quad (12)$$

Periodic isotherm of state

The introduction of the Liesegang operator is justified by the possibility it (the Liesegang operator) gives to mathematically describe periodically developing complex processes of sorbtion with time. In this case we don't need to find the analytical form of the complex sorbtion Hamiltonians of the system.

It is possible to make such a description for the mesophaselike systems, when a certain group of exchange centers (domains) acts as a liquid crystal one, i.e. it works coherently [4,5]. Therefore describing the isotherms of sorbtion one may deal with some energetically averaged functional domains conferred on the property the experimental of separability.

In study of the sorption behavior of gel the isotherm of sorbtion with time ($u = f(t)$) often has a not-simple vibration nature (Figure1), which can't be limited to the frequency of vibrations of some form. The graphs are more complex and even non-periodical. It should be noted that from our point of view stated in our previous works [2], there is the only frequency of vibrations, which we modeled by

three different equations. In the first case it has the form of a sine (or a cosine, or the sum of a sine and a cosine depending on the phase).

From graphs: $u = A \sin(\omega t)$, $u = A \arcsin(\sin(\omega t))$, $u = A \exp(\arcsin(\sin(\omega t)))$ it follows that the experimental data (e.g., Figures 2,3,4) coincide with neither of them at any frequency and any amplitude.

The adequate description of the isotherms of sorption in non-linear oxyhydrate gels can be performed using the above principle of separability for the oxyhydrate systems. In our case this principle has a definite physical meaning. As it has been found out before [10], there is a certain number of pacemakers (аттракторов) in gel, i.e. some discrete particles (fragmentarily quantified) of gel not interacting with each other and defining the significant number n of the Liesegang operators. They also give the additive effect of sorbtion. In case of zirconium oxyhydrate gels the number of pacemakers is 3-5 [10]. Large diameter pacemakers are little different from the amorphous non- structured phase of gel.

In this connection a supposition arises: if autowave vibration in gel are exclusively determined by the forming of the attractors (pacemakers), then there may be the infinite number of attractors. Therefore it seems reasonable to find the frequencies and amplitudes of vibrations for these attractors.

The concentration of the sorbate in gel can be presented in one of the three ways. It depends on the method used to define the attractor vibrations, i.e. we choose the Liesegang operator as follows, namely

$$\begin{aligned}
 1a) \quad u &= \sum_{i=1}^N u_i \sin(\omega_i t); \quad \text{or} \quad 1b) \quad u(t) = \int_0^{+\infty} u_\omega \sin(\omega t) d\omega \\
 2a) \quad u &= \sum_{i=1}^N u_i \arcsin(\sin(\omega_i t)); \quad \text{or} \quad 2b) \quad u(t) = \int_0^{+\infty} u_\omega \sin(\arcsin(\omega t)) d\omega \\
 3a) \quad u &= \sum_{i=1}^N u_i \exp(\arcsin(\sin(\omega_i t))); \quad \text{or} \quad 3b) \quad u(t) = \int_0^{+\infty} u_\omega \exp(\sin(\arcsin(\omega t))) d\omega.
 \end{aligned} \tag{13}$$

Note, that in the left equations (13 (1a, 2a, 3a)) the number of attractors is considered to be equal to N , in the right equations it is equal to infinity.

In case of the finite number of attractors it is necessary to find the parameters of u_i manually. In case of the infinite number of attractors (1b) it is necessary to solve the integral equation (9,1b). The spectrum of solutions is determined by:

$$u_\omega = \frac{2}{\pi} \int_0^{+\infty} u(t) \sin(\omega t) dt. \quad (14)$$

The spectrum of frequencies, for the experimental data presented in Figure 4, is diagramed in Figure 5. In case we consider the attractor, vibrating according to the 2nd and 3rd integral laws, it is necessary to solve the Fredholm's integral equation of the first kind, presented by the equations (13, 2b) and (13, 3b). This problem is incorrect, so the regularization is needed. We used the Fridman's method of iterative regularization [11]. The calculations made indicate that the quantity of the important frequencies constitute 5 at most. The values of u_ω for the other frequencies are about zero. This is another argument for the fact that the number of pacemakers in the considered gels is equal to 5 or less than 5.

The calculations of the isotherms of sorbtion of yttrium (3) ions by the zirconium oxyhydrate gels under conditions of saturation of gel phase by the yttrium (3) ions were performed on the assumption that the maximum number of pacemakers is 5 and the Liesegang operator (13, 1a) is valid. The conditions of saturations were chosen on the assumption that the processes of peptization (destruction) of the gel phase under such conditions manifest themselves to the maximum degree, Fig.1. For a general case the isotherm of state is written:

$$u = u_0 + \sum_{i=1}^n A_i \arcsin(\sin(\omega_i t + \varphi_i)), \quad (15)$$

where u_0 is some average value of the sorbtion, mmole/g, ω_i is the frequency of variations, φ_i is the phase deviation, value i may vary between 1 and 5.

It is reasonable to consider the isotherms of sorbtion state in terms of a non-linear dynamic sorbtion system far from equilibrium as some section surfaces in coordinates $u = f(t)$ and $u = f(c_p)$. The isotherm states of the type $u = f(c_p)$ are written as:

$$u = u_0 + \sum_{i=1}^n A_i \arcsin(\sin(\omega_i c_p + \varphi_i)). \quad (16)$$

For the comparison purposes the nature of experimental and calculated isotherms is given in appendix. We observe the satisfactory agreement between the experimental and calculated isotherms of sorbtion (**Appendix**).

Conclusions

The analytical equation for the Liesegang operator has been obtained. The genetic relation between the Liesegang operator describing the behavior of the non-equilibrium oxyhydrate gel and the Hamiltonian of the vibrating sorption system is shown.

Having applied the principle of separability and having used the Liesegang operator we succeeded in giving the analytical description (to suggest the periodic sorption isotherms) of the sorption states of gel systems in coordinates $u = f(t)$ and $u = f(c_p)$, where u is the value of sorbtion.

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Figures.

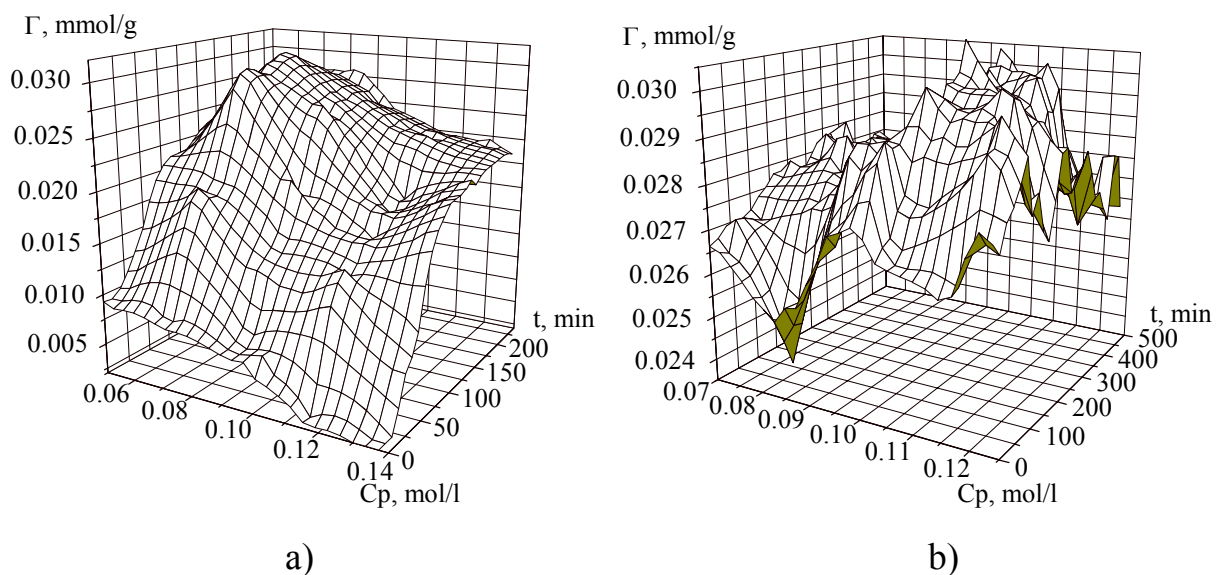


Figure 1.

The three-dimensional sorption isotherms of the yttrium ions (3) in the coordinates $\Gamma = f(C_p, t)$, where Γ – is the value of the sorption, C_p – is the quasi-equilibrium sorbate concentration, t – is the time;

a) the isotherm got after the contact of the fresh gel with the yttrium ions sorbate;

b) the isotherm got after the 24 hours gel standing in sorbate.

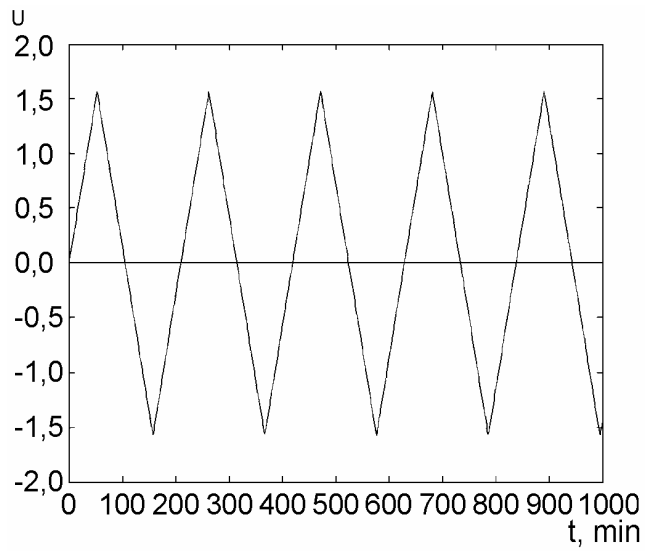


Figure 2

Function $u = f(t)$ written by the equation $u = A\arcsin(\sin(\omega t))$.

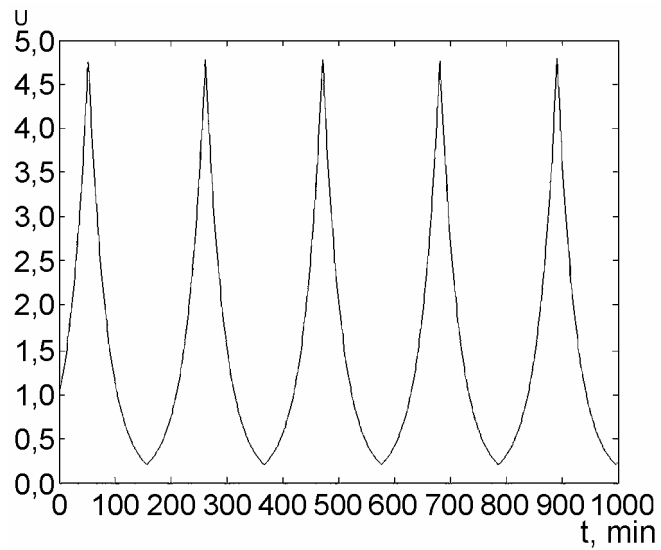


Figure 3

Function $u = f(t)$ written by the equation $u = A\exp(\arcsin(\sin(\omega t)))$

Figure 4

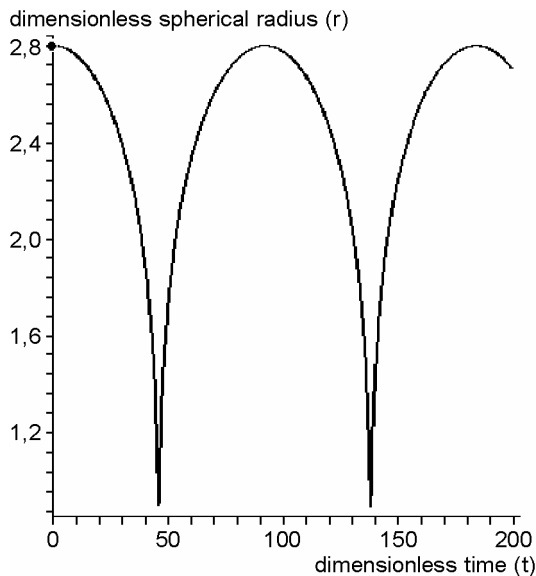


Figure 5

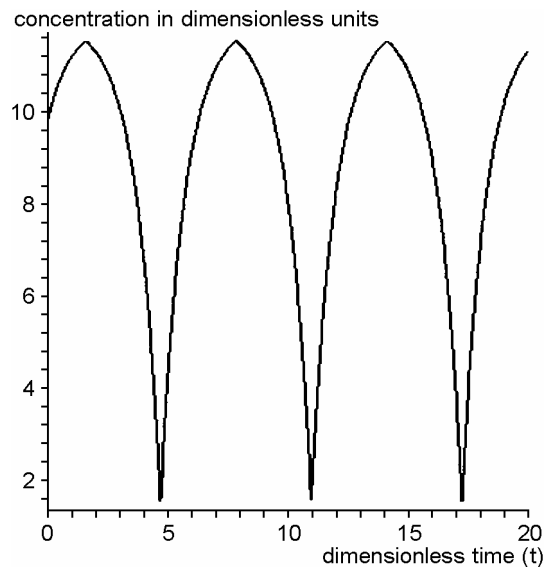


Figure 4. The particle “sticks” in the attraction field, making cyclic movements.

Figure5. Diagram showing the dependence of concentration on time (the Liesegang operator)

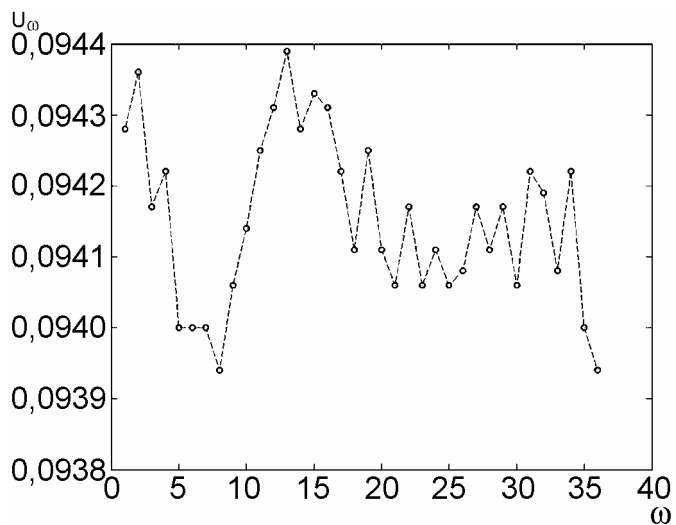


Figure 6.

Experimental data of the function $u = f(t)$.

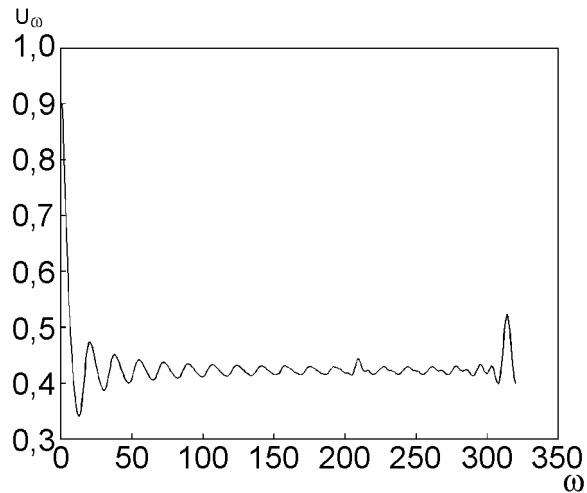


Figure 7.

The spectrum of frequencies for the data of Fig.4 in case of equation (9, 1b) solution.

Appendix

The sorbtion isotherms were obtained by the filtration of the yttrium nitrate solution through an ion-exchange column, filled up with the freshly prepared zirconium oxyhydrate gel. In the former case the sorbtion isotherms were obtained by the filtration of the yttrium nitrate solution through an ion-exchange column filled with the zirconium oxyhydrate gel till the moment of the gel saturation. In the latter case the sorbtion isotherms were obtained by the filtration of the yttrium nitrate solution through an ion-exchange column filled with the zirconium oxyhydrate gel after the moment of the gel saturation.

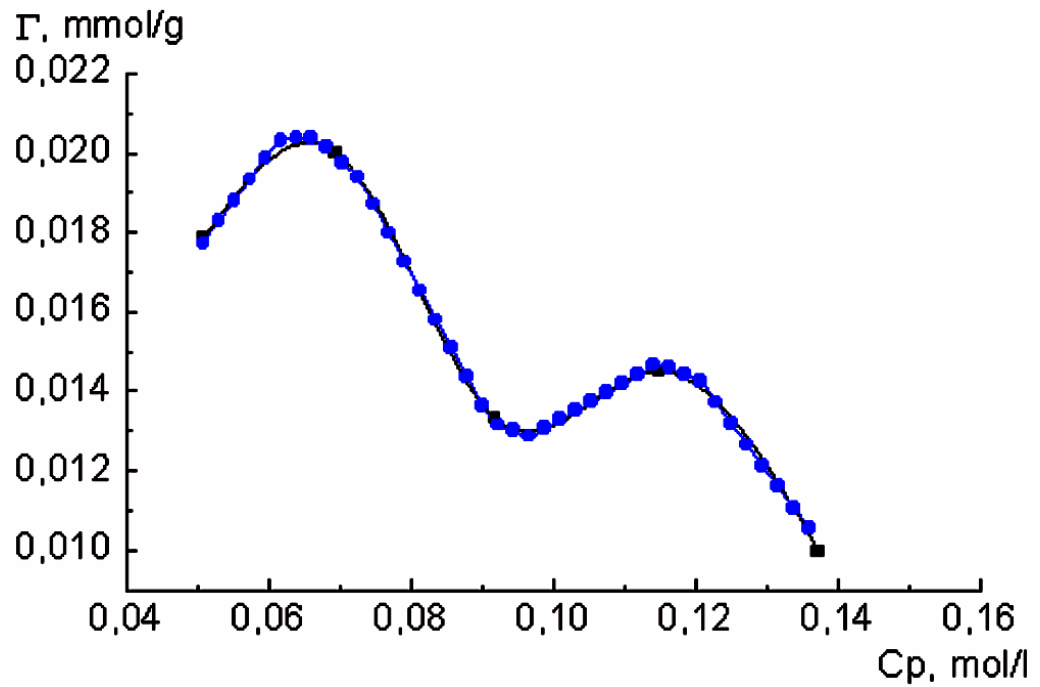
The isotherms were taken off at pH 5.5.

The isotherm of sorbtion for a general case is written as: $u = u_0 + A_1 \arcsin(\sin(\omega_1 t + \varphi_1)) + A_2 \arcsin(\sin(\omega_2 t + \varphi_2)) + A_3 \arcsin(\sin(\omega_3 t + \varphi_3)) + A_4 \arcsin(\sin(\omega_4 t + \varphi_4)) + A_5 \arcsin(\sin(\omega_5 t + \varphi_5));$

1. Ions yttrium sorbtion of the gel before the gel's yttrium saturation.

The experimental points (Fig.1(a)) are marked on the figures as round points.

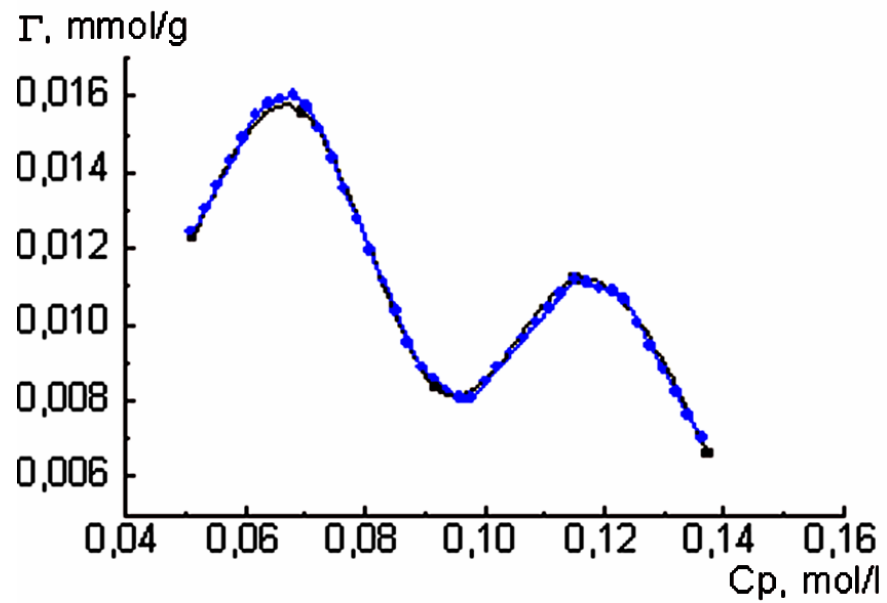
Section: t = 60 min



Calculated isotherm of the sorbtion of the yttrium ions (3):

$$\Gamma = 0.013400 - 0.000610 * \arcsin(\sin(2.88000 * c_p + 1.500000)) + 0.000700 * \arcsin(\sin(2.85000 * c_p - 0.800000)) + 0.004000 * \arcsin(\sin(0.63000 * c_p + 1.200000)) + 0.000900 * \arcsin(\sin(1.10000 * c_p + 2.500000));$$

Section: t = 36 min



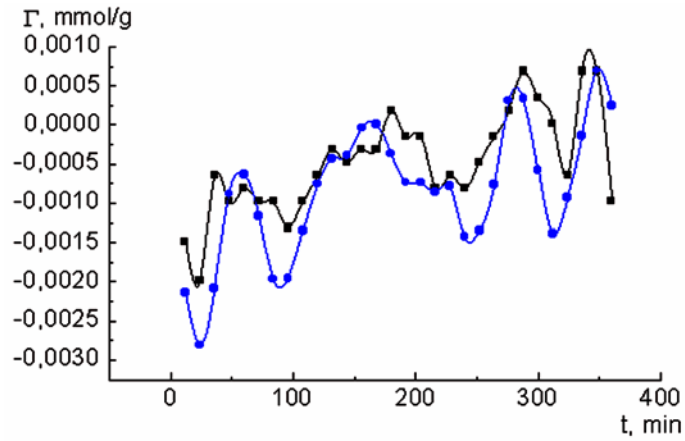
Calculated isotherm of the sorption of the yttrium ions (3):

$$\Gamma = 0.009700 - 0.000950 * \arcsin(\sin(2.58000 * c_p + 2.000000)) + 0.000990 * \arcsin(\sin(2.55000 * c_p - 0.070000)) + 0.002700 * \arcsin(\sin(0.77000 * c_p + 0.880000)) + 0.000730 * \arcsin(\sin(1.30000 * c_p + 1.900000));$$

2. The interaction of the gel with the yttrium ions after the gel's yttrium saturation.

The experimental points (Fig.1(b)) are marked on the figures as square points.

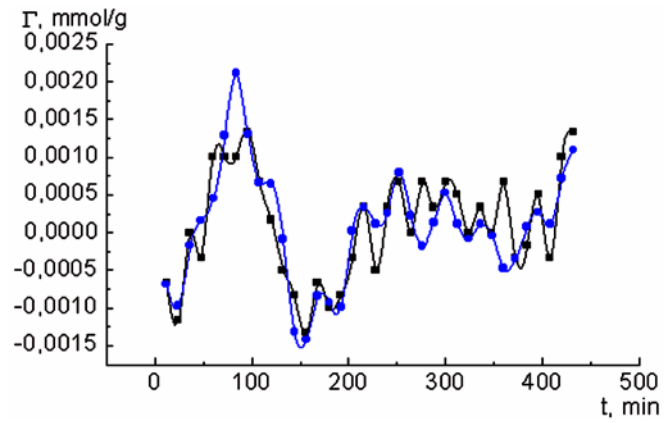
Section: Quasi-equilibrium concentration of sorbate, C = 0,07 mole/l



Calculated isotherm of the sorbtion of the yttrium ions (3):

$$\Gamma = u = 0.000000 - 0.000240 * \arcsin(\sin(13.40000 * t - 1.800000)) + 0.000360 * \arcsin(\sin(3.80000 * t - 3.300000)) - 0.000360 * \arcsin(\sin(6.50000 * t - 4.100000)) + 0.000600 * \arcsin(\sin(0.50000 * t - 1.900000)) - 0.000360 * \arcsin(\sin(11.10000 * t - 1.000000));$$

Section: Quasi-equilibrium concentration of sorbate, C = 0,09 mole/l.



Calculated isotherm of the sorbtion of the yttrium ions (3):

$$\Gamma = u = 0.000005 - 0.000480 * \arcsin(\sin(4.10000*t - 3.800000)) + 0.000360 * \arcsin(\sin(5.50000*t - 3.900000)) - 0.000480 * \arcsin(\sin(6.30000*t - 6.000000)) + 0.000240 * \arcsin(\sin(17.50000*t + 1.900000)) - 0.000360 * \arcsin(\sin(3.00000*t + 2.600000));$$