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THE PERIODIC ISOTHERMS OF SORPTION STATE

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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 a periodic curve describes the state of the far-from-equilibrium sorption system (fig. 1). 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” (fig. 1).

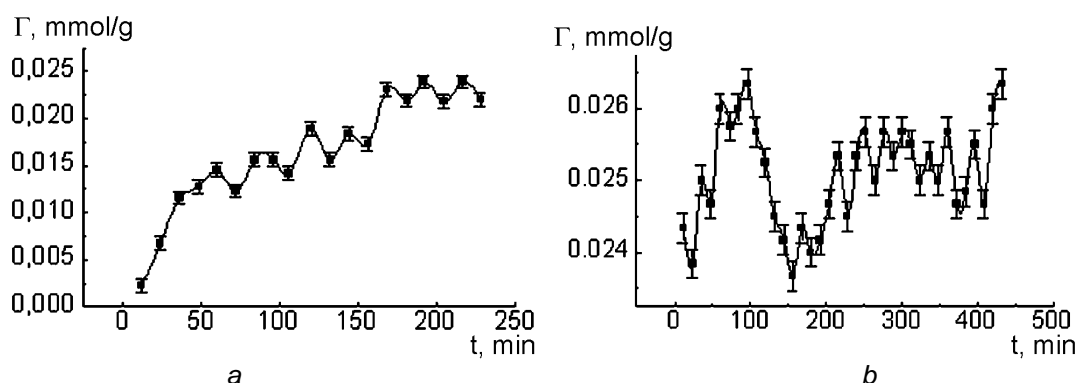


Fig. 1. Sections of functions' surfaces $\Gamma = f(C_p, t)$ in the “sorption–time” plane immediately after the contact of gel with sorbate:

a — $t = 0$ hours; *b* — after the gel standing in sorbate for 24 hours

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 third time coordinate since classical sorption isotherms don't give us such a possibility. In our previous works we introduced the so-called process evolution operator, the Liesegang operator [1, 2] to describe the periodic self-organizing systems. To describe 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:

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

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 has not been found yet for a general case 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:

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

The value u can be described as $u = A \sin(\omega t)$, $u = A \arcsin(\sin(\omega t))$, where t is the time, ω is the frequency of given oscillations, A is the amplitude (fig. 2). For a more complex case we may write:

$$\frac{\partial u}{\partial t} = auL[u],$$

if the solution of equation takes the form $u = A \exp(\arcsin(\sin(\omega t)))$. The graphs of the function is presented in fig. 3.

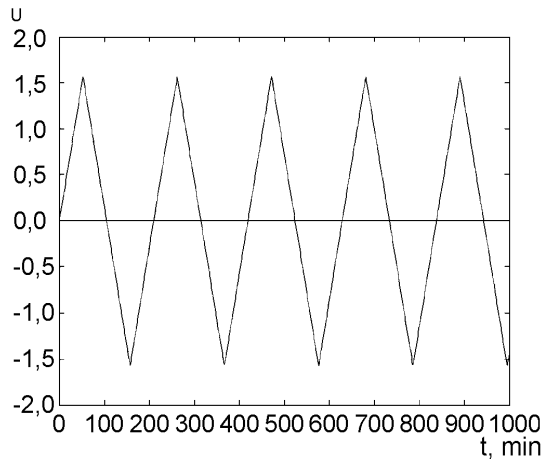


Fig. 2. Function $u=f(t)$ written by the equation $u = A \arcsin(\sin(\omega t))$

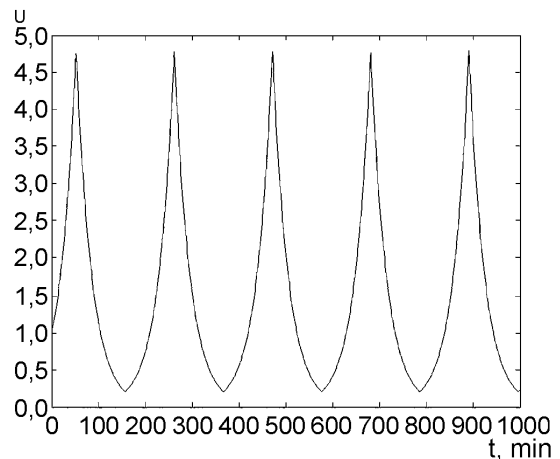


Fig. 3. Function $u=f(t)$ written by the equation $u = A \exp(\arcsin(\sin(\omega t)))$

Thus, we neglect the diffusion in (1), simplify the Liesegang operator and write it as $L[u] = \alpha \text{Sgn}[u]$, where α is some constant coefficient. The operator $\text{Sgn}[u]$ 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} , $\text{Sgn}[u] = -1$, when u reaches u_{\min} , $-\text{Sgn}[u] = +1$.

Equation (1) takes the following form: $\frac{du}{dt} = \alpha \text{Sgn}[u]$. 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:

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

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

$$u = u_{\min} + \frac{u_{\max} - u_{\min}}{\pi} \arccos \left(\sin \left(\frac{\pi \alpha t}{u_{\max} - u_{\min}} \right) \right). \quad (2)$$

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

The vibrations of a simple harmonic oscillator may be an actual analogue of periodic sorption. 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 [3] Hamiltonian systems 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” will increase 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:

$$p = \frac{\partial}{\partial q} S(q, I), \quad \theta = \frac{\partial}{\partial I} S(q, I).$$

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:

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

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

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

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

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:

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

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:

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

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 sorption with time. In this case we don't need to find the analytical form of the complex sorption 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. works on the principle "all at once" [4, 5]. Therefore describing the isotherms of sorption 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 sorption with time ($u = f(t)$) often has a not-simple vibration nature (fig. 1), 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 $u = A \sin(\omega t)$, $u = A \arcsin(\omega t)$, $u = A \exp(\arcsin(\sin(\omega t)))$ it follows that the experimental data (e.g., fig 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 [6], there is a certain number of pacemakers 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 sorption. In case of zirconium oxyhydrate gels the number of pacemakers is 3—5 [6]. Large diameter pacemakers are little different from the amorphous non-structured phase of gel.

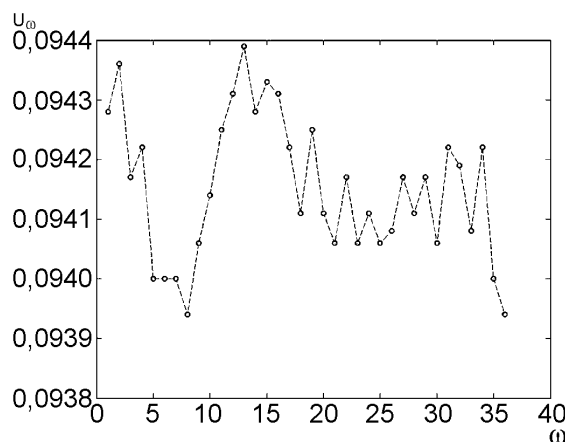


Fig. 4. Experimental data of the function $u = f(t)$

In this connection a supposition arises: if autowave vibrations 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

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

Note, that in the left equations (3 (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 (3, 1b). The spectrum of solutions is determined by:

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

The spectrum of frequencies, for the experimental data presented in fig. 4, is diagramed in fig.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 (3, 2b) and (3, 3b). This problem is incorrect, so the regularization is needed. We used the Fridman's method of iterative regularization [7].

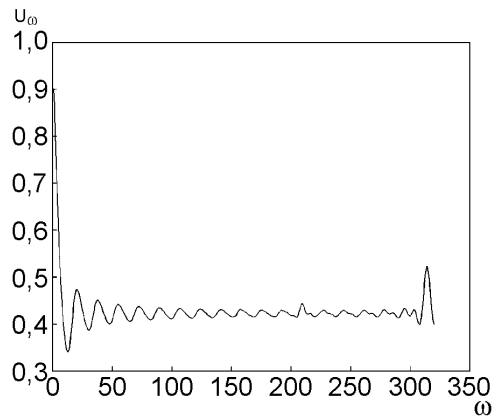


Fig. 5. The spectrum of frequencies for the data of fig. 4 in case of equation (3, 1b) solution

The calculations of the isotherms of sorption of yttrium (2) ions by the zirconium oxyhydrate gels under conditions of saturation of gel phase by the yttrium (2) ions were performed on the assumption that the maximum number of pacemakers is 5 and the Liesegang operator (3, 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:

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

where u_0 is some average value of the sorption, mmol/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 sorption state in terms of a non-linear dynamic sorption system far from equilibrium as some section surfaces in coordinates $u=f(t)$ and $u=f(C_p)$. This approach was developed by Poincare and Birkhoff [3]. The isotherm states of the type $u=f(C_p)$ are written as:

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

For the comparison purposes the nature of experimental and calculated isotherms is given in fig. 6. We observe the satisfactory agreement between the experimental and calculated isotherms of sorption.

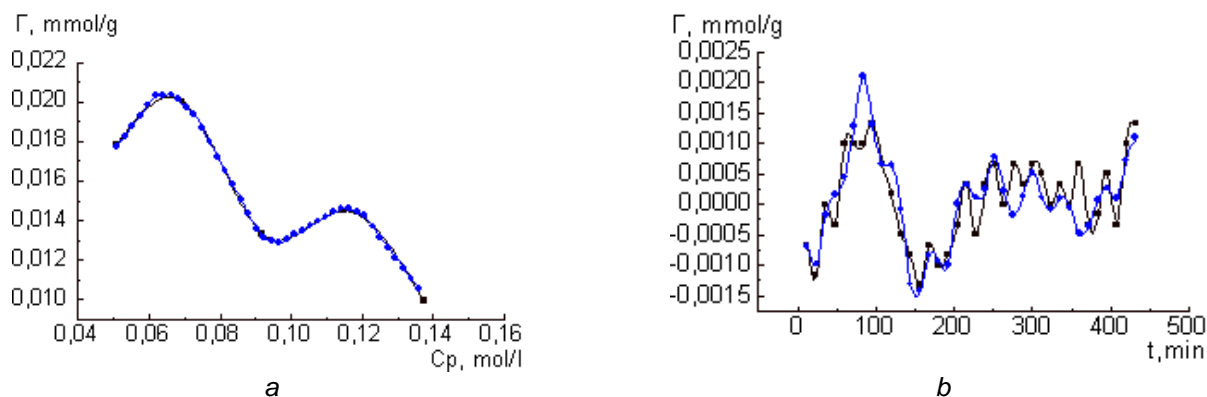


Fig. 6. Calculated isotherm of the sorption of the yttrium ions

$$\begin{aligned}
 a - \Gamma &= 9,7 \cdot 10^{-3} - 9,5 \cdot 10^{-4} \cdot \arcsin(\sin(2,58 \cdot C_p + 2,00)) + 9,9 \cdot 10^{-4} \cdot \arcsin(\sin(2,55 \cdot C_p - 0,07)) + \\
 &\quad + 2,7 \cdot 10^{-3} \cdot \arcsin(\sin(0,77 \cdot C_p + 0,88)) + 7,3 \cdot 10^{-4} \cdot \arcsin(\sin(1,30 \cdot C_p + 1,90)); \\
 b - \Gamma &= u = 5 \cdot 10^{-5} - 4 \cdot 10^{-5} \cdot \arcsin(\sin(4,10 \cdot t - 3,80)) + 3 \cdot 10^{-5} \cdot \arcsin(\sin(5,50 \cdot t - 3,90)) - \\
 &\quad - 4 \cdot 10^{-5} \cdot \arcsin(\sin(6,30 \cdot t - 6,00)) + 2 \cdot 10^{-5} \cdot \arcsin(\sin(17,5 \cdot t + 1,90)) - 3 \cdot 10^{-5} \cdot \arcsin(\sin(3,00 \cdot t + 2,60))
 \end{aligned}$$

Conclusion

The analytical equation for the Liesegang operator as well as the genetic relation between the empirically introduced Liesegang operator describing the behavior of the non-equilibrium oxyhydrate gel and the energy Hamiltonian of the vibrating sorption system are shown. We used the principle of separability to analytically describe the sorption state of gel systems by the Poincare—Birkhoff method of section surface in coordinates $u=f(t)$ and $u=f(C_p)$, where u is the value of sorption.

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