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PHYSICAL–CHEMICAL POLARIZATION NATURE OF LIVING GELS OF HEAVY METALS OXYHYDRATES

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Introduction

The term “liquid crystal” implies the aggregate state of a substance intermediate between the crystal body and amorphous liquid. The necessary condition for developing mesomorphism is the essential geometric anisotropy of molecules which are bound to be long and relatively narrow. Depending on the peculiarities of the molecule geometry the system may pass through one or more mesophases until it transfers into the isotropic liquid. We and other researchers found both experimentally and through calculations [1–4] that the geometry of yttrium and zirconium oxyhydrate macromolecules fits the above properties.

According to the Mayer–Saupe theory the criterion for the formation of the liquid–crystal ordering may be the polarization anisotropy of colloid gel particles. The calculations performed in the framework of the semiempirical quantum–chemical approximation ZINDO/1 show that polarizability along the main axis of zirconium oxide pentahydrate is $441,4 E^3$, perpendicularly to the main axis it is $302,7 E^3$. These values are quite comparable with polarizabilities of the myristic acid being a typical liquid crystal (along the main axis it is $410,7 E^3$, perpendicularly to the main axis it is $305,2 E^3$). It should be noted that similar liquid–crystal structural peculiarities with the addition of water to the hydrophilic part retain up to the high degrees of hydration of heavy metals oxyhydrate gels. Zirconium oxide dodecahydrate $ZrO_2(H_2O)_{12}$ (or $ZrO(OH)_2(H_2O)_{11}$) presented in [4] has the hydrophobic “head” part and the hydrophilic “tail” one consisting of bound water. Polarizability of such a particle along the main axis is $717,1 E^3$, perpendicularly to the main axis it is $459,5 E^3$.

2. Some Experimental Results Pertaining to the Polarization of Oxyhydrate Gel Systems

2.1. Experimental part

Freshly prepared gels of zirconium oxyhydrate (ZOHG) and yttrium oxyhydrate (YOHG) synthesized by the method of ammonia precipitation from solutions of zirconium oxychloride and yttrium nitrate were studied. Precipitation of ZO HGs was carried out by 10% ammonia solution at pH 9.0. This methodics was suggested in work [5]. To study rheology, freshly prepared ZO HGs were used, which were obtained from zirconium oxychloride solutions of variable concentrations: 65,77; 71,25; 108,82; 119,7; 131,54; 142,5; 150,88 mmol/l. After preparing the precipitates, gels were allowed to stand for 1 hour, then the mother liquor was decanted. The final volume of the sample was 10 ml. The content of zirconium in the gel was determined by the weight method. The solid/liquid ratio in the gel system was kept constant. Gels were obtained in the thermostat at the temperatures of $283\pm 0,5$; $293\pm 0,5$; $303\pm 0,5$; $323\pm 0,5$ K, viscosimetric characteristics being taken at the same temperatures.

YOHGs were synthesized from solutions with the concentration of 0,3 mol/l at pH 7,0 and pH 8,0. The precipitates were obtained in the thermostat at the temperatures of $293\pm 0,5$; $298\pm 0,5$; $303\pm 0,5$; $313\pm 0,5$ K, then rheological properties were studied at the same temperatures under isothermal conditions. Rheological studies were carried out on the “Rheotest–2” rotation viscosimeter in the system of coaxial cylinders.

Studies of oxyhydrate gels $ZrO_2 \cdot nH_2O$ and $Y_2O_3 \cdot nH_2O$ made it possible to construct complete rheological curves (CRC) at various temperatures. During the experiment a number of curves $\tau = f(t)$ for the “shift rate — shift speed” dependence for the interval of 20, 40, 60, 80, 100 and 120 minutes were taken. The total time of rheological measurements was 2 hours.

2.2. Experimental observation.

The dependences of optical density of air–dry gels on the wave length were obtained on the photocolorimeter in the automatic mode. Air–dry ZOHGs and YOHGs were synthesized from freshly–prepared precipitates by filtering off a gel on the “blue–paper” filter followed by slow isothermal drying of a cake for 6 months at the temperature of 298K. A part of the material was exposed to electromagnetic radiation in a special cell. A fraction of the gel with the granule size of 0.30—1.00mm was placed into the cell 1mm wide. The air–dry gel was moistened by distilled water. Measurements of optical density were carried out relative to distilled water.

In addition the macrotexture of gels was studied using the polarization microscope. For the analysis of thermotropic properties of gels the analytical (calculation) quantum–chemical methods were used.

The experimental results we achieved in studying the properties of heavy metals oxyhydrates confirm the critical role of the polarization phenomenon in such gel systems.

In colloid gel systems [6, 7, 12, 13] the spontaneous concentration differentiation of a substance in time and space is observed. It is of the autowave (pulsating) nature (periodic self — organization). The above phenomenon is most pronounced under the conditions of the sufficient saturation of the gel phase with water, since in this case the mobility of structuring fragments in a gel (air–dry gels) increases. The oscillation periodical profile of the density value for nematic liquid–crystal systems [14] is unlikely, though it may be supposed to occur in smectics.

Such periodicity of the mass has the form of helical whirls, e.g. yttrium oxyhydrate in fig. 1 (cholesteric or chiral–smectic type). The whirls are rather inertial in the gel system and retain for a long time due to the system being gel–like, i.e. “frozen”.



Fig. 1. Helical texture of yttrium oxyhydrate ($\times 150$)

Figure 2 shows a typical texture of yttrium oxyhydrate which is characteristic of a chiral–smectic liquid crystal. It is cholesteric that usually has the planar blue phase, which is clearly observed in the figure.

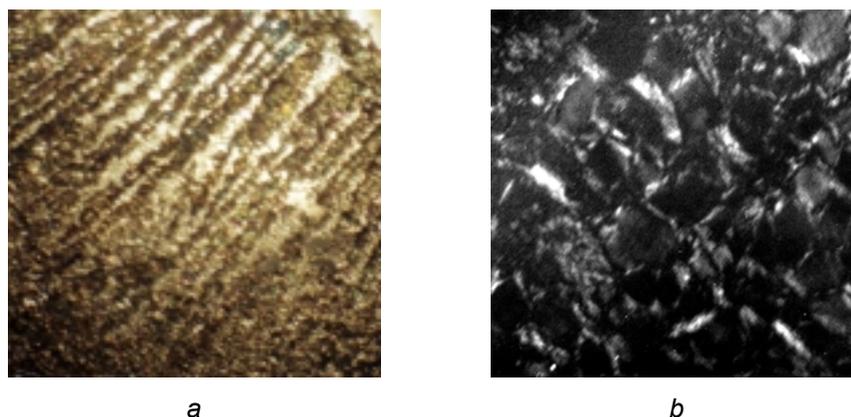


Fig. 2. Distinctive texture of yttrium oxyhydrate, which is characteristic of chiral smectic liquid crystals

With sufficiently large step of chiral smectic the peculiar periodic phenomena in time are also observed in optical characteristics of a liquid crystal. In particular, the functional dependence of the optical density of yttrium oxyhydrate gels under study on wave lengths of incident light (fig. 3) exhibits rather wide alternating regions with low optical density of gels, i. e. the samples became optically transparent in a particular discrete interval of wave lengths. The above phenomenon was observed on several hundreds of samples.

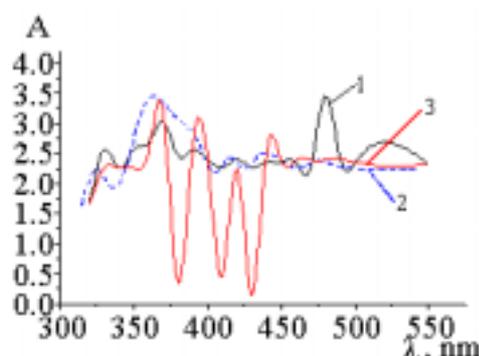


Fig. 3. Absorption spectra of the yttrium oxyhydrate

The sample synthesized at pH 9.27; amount of yttrium in the sample is 0.080 mol; the synthesis time is 2 hours; spectra 1, 2, 3 are obtained every 30 minutes

Consider the following problem: let the light be incident on the gel, in which the processes of self — organization proceed. The problem is to find the level of absorption in the gel and the effect of the light on it. Suppose the beam with the electric field to be incident on the gel $\vec{E} = \{E_0 \sin \omega t, -E_0 \cos \omega t\}$. Let there be the polarization \vec{P} in the gel. The equation of dynamic polarization in the absence of light is:

$$\frac{\partial \vec{P}}{\partial t} = \Delta \vec{P} + \Omega[\vec{P}] + L[n]\vec{P}, \quad (1)$$

where $L[n]$ — the Liesegang operator depending on the gel density, $\Omega[\vec{P}]$ — the rotation operator. Let us neglect the member with the Liesegang operator, since this expression contributes little as compared to the resonance of the outer electromagnetic field and the rotation of gel.

We will assume the residual effects (a kind of hysteresis) to be due to the Frederiks effect [12]. They may be described as Frederiks effects:

$$\frac{\partial u}{\partial t} = E_0^2 \left(1 - \frac{2u^2}{3} \right) u + K \Delta u,$$

where K — some constant value, E_0 — the outer field intensity.

We would like to consider the director as being the vector value. Let us suppose approximately the director to coincide with the vector field direction and $|u| = |\bar{P}|$. From the equation $\frac{\partial u}{\partial t} = E_0^2 (1 - 2u^2/3)u + K\Delta u$ let us take the vector relation for the polarization vector deformation in the outer field:

$$\frac{\partial \bar{P}}{\partial t} = E_0^2 \left(1 - \frac{2\bar{P}^2}{3} \right) + K\Delta \bar{P}$$

Having added the outer field and the rotation operator with frequency Ω to this relation, we will have the system of equations:

$$\begin{cases} \frac{\partial P_x}{\partial t} = E_0^2 \left(1 - \frac{2\bar{P}^2}{3} \right) P_x - P_y \Omega + D\Delta P_x + \omega E_0 \cos \omega t \\ \frac{\partial P_y}{\partial t} = E_0^2 \left(1 - \frac{2\bar{P}^2}{3} \right) P_y + P_x \Omega + D\Delta P_y - \omega E_0 \sin \omega t, \end{cases}$$

where $\omega = \pi/\lambda$ is a frequency of passing electromagnetic flow, λ is a wavelength. To solve the relation obtained let us consider the particular case, in which we neglect the values $E_0^2 P_x + D\Delta P_x$ and $E_0^2 P_y + D\Delta P_y$. We will find solutions as $P_x = A \cos \Omega t$, $P_y = A \sin \Omega t$. In case when the situation is far from being the resonance we may neglect the outer field. As a result, we have the equation for A : $A' = -2/3 E_0^2 A^3$. This equation is easily solved, its particular solution being $A = \frac{1}{E_0 \sqrt{t}}$.

Finally we have:

$$P_x = \frac{\cos(\Omega t)}{\sqrt{t}}, \quad P_y = \frac{\sin(\Omega t)}{\sqrt{t}}.$$

Adding amplitudes and calculating the spectral transformation: $I = \frac{1}{E_0} \int_0^T \frac{\cos \omega t}{\sqrt{t}}$, we obtain:

$$I = C_s \frac{\text{FresC} \left(\sqrt{\frac{\omega T}{2}} \right)}{\sqrt{\omega}},$$

where $\text{FresC}(x)$ — Fresnel cosine integral. Actually, there are quite a lot of periods in the vicinity of the resonance $I = \frac{1}{\sqrt{\omega - \Omega}}$. This case of the periodical variation of the optical density in passing the light through the gel layer is shown in fig. 4.

The mesophase-like cholesteric gel (samples after prolonged isothermal drying) loses its helical whirl texture and transforms slowly into the homeotropic texture, i. e. ordered-stripped one [8, P. 213] under the influence of electromagnetic radiation. That the gel transforms from the selectively scattering into the transparent one was found experimentally. The destruction of the initial chiral-smectic texture may be observed, if a gel is exposed to electromagnetic radiation (near soft ultra-violet radiation). Samples gain the high sorption capacity related to the untwisting (or destruction) of chiral-smectic formations and to the transition of a gel into a homeotropic-like state. Before this procedure gels were sorptionally inactive. After radiation these states become optically transparent.

The effect of forming the helical structures of a smectic type accounts for the colouring of yttrium oxyhydrate gels, which was considered in work [7]. As shown in [9, 3], the optical effect in such a case is manifested in shifting the wave length of selective diffraction reflection towards long wave lengths (the so-called red shift). The decrease in a helix step is accompanied (self-organization) by the shift of colouring.

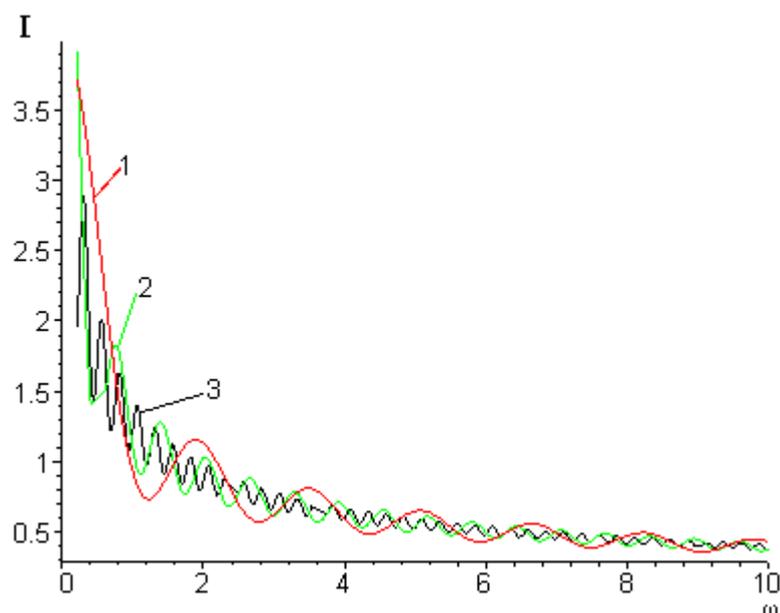


Fig. 4. Graph of the spectrum in the vicinity of resonance

The 1 line — $T=1.0$; the 2 line — 5; the 3 line — 25; all the other constants are taken as 1.0. $\omega = 2\pi/\lambda$, where λ is a wave length

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As shown in [6, 7], in this case particular oxoolic reactions proceed, which may give rise to either stable or metastable molecular formations in oxyhydrate, which are coloured as well. It is rather difficult to distinguish colouring due to gels crystallinity (diffraction scattering) or quantum reasons, i. e. electron transition. Work [7] presents electron reasons for yttrium oxyhydrate samples colouring due to the formation of some unstable transition states whose absorption spectra are also found in the visible region.

2.3. Introduction of the Liesegang operator, i.e. the polarization operator.

Based on the above experimental data determining the liquid–crystallinity of gel systems as well as taking into account the mass differentiation of a substance we introduced the Liesegang operator [10], responsible for the process of structuring in gels. We suppose a gel to structure randomly under the influence of thermal motion of water molecules. On the other hand, a part of gel molecules is self–organized in the most optimal way. The layer of randomly structured molecules is unstable and breaks down into the components on exceeding some critical value. Optimally structured molecule associates are more stable. From the above reasoning, we introduce a Liesegang operator for describing the above mentioned processes of self–organization in a gel.

The physical significance of the operator is that it describes the spontaneous destruction of the structure formed exactly at the moment when the concentration of gel fragments at some point

approaches the maximum critical value, the further destruction proceeding up to some final value. On reaching the low critical value the self-organization of a gel commences, and the process proceeds over and over again. The physical-chemical description of periodic processes data is given in detail in [1]. The diffusion causes the continuous recurrence of the process up to the completion of oxolation with subsequent gel crystallization (after prolonged aging).

At the same time, the following questions require elucidation: What is the random process? How much is it random? To this purpose let us consider long gel molecules to be dipoles (such, indeed, is the case). Of special interest is the interaction of these gel dipoles with the electromagnetic field, i. e. with visible and ultraviolet radiation.

It should be noted that, in this case, the adsorption of some substances by a gel is very important. This results in the change in gel macromolecule parameters, in other words the shape and conformation of molecules vary.

To describe the self-organizing processes in a gel, we restrict ourselves to the simplest one-dimensional model which would make it possible to illustrate the behaviour of the Liesegang operator and, hence, that of gel concentration. To describe the behaviour of the latter we will use the diffusion equation, the Liesegang operator being included:

$$\left\{ \begin{array}{l} \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + L[u] \\ u|_{x=0} = u_0, \quad u|_{t=0} = u_0 = \text{const} \\ u|_{x=l} = u_0 \end{array} \right.$$

where the following notations are used: D — the diffusion coefficient; l — the length of the line where the equation is considered; $L[u]$ — the Liesegang operator; u , u_0 — some current and initial values of the structuring fragments concentration.

Further, it is necessary to derive at least the approximate formula for the Liesegang operator. Remind that the Liesegang operator $L[u]$ equals $+\alpha u$ when the concentration has not reached the upper critical value u_{\max} yet; and it equals $-\alpha u$ when the concentration has exceeded u_{\max} and started falling, but has not fallen to u_{\min} yet, i.e. to the low critical value. To have a definite idea of all possible formulae of the Liesegang operator let us consider some simplest cases. So, let us neglect the diffusion in (1) and simplify the Liesegang operator itself as much as possible: take it as: $L[u] = \alpha \text{Sg}[u]$. Here, α — a numerical coefficient, where the operator $\text{Sg}[u]$ is determined as follows: let there be two values, i. e. u_{\max} and u_{\min} , $u_{\min} < u_{\max}$. When u increases and reaches u_{\max} , $\text{Sgn}[u] = -1$, when it decreases and reaches u_{\min} , $\text{Sg}[u] = +1$. The equation takes the following form: $\frac{du}{dt} = \alpha \text{Sg}[u]$. At the beginning we consider $\text{Sg}[u] = +1$ at any point.

In the simple case, if we can assume $D \approx 0$, $L[u] = \alpha \text{Sg}[u]$. And equation is $\frac{du}{dt} = \alpha \text{Sg}[u]$. Let us

calculate the module of both parts: $\left| \frac{du}{dt} \right| = \alpha u$. As a result, we have that the rate module equals α ,

i. e. the rate of concentration variation is constant in such a model. Hence, since in our case the upper critical value u_{\max} and the low critical u_{\min} value remain unchanged, the Liesegang operator may be written as:

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

Then, the concentration of the self-organized gel is:

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

The graph of this expression with $u_{\max} = 3$, $u_{\min} = 1$ is given in figure 5 (the coefficient $\alpha = 0.1$). The same parameters are used for the rest graphs.

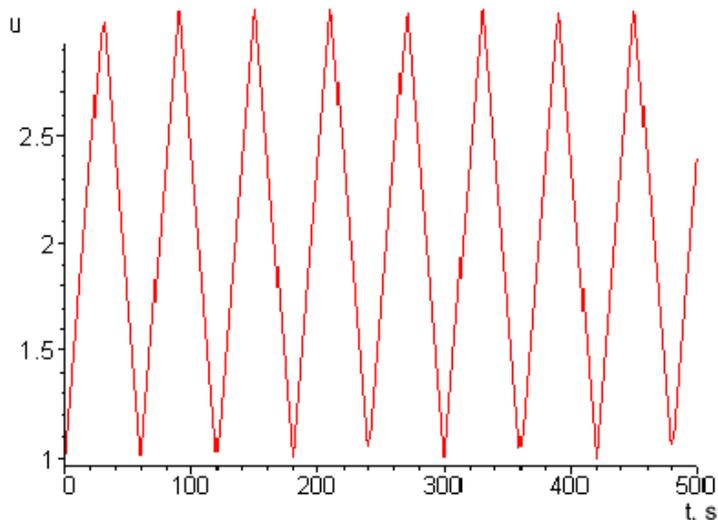


Fig. 5. Graphic notation of the expression $u(t) = u_{\min} + \frac{u_{\max} - u_{\min}}{\pi} \arccos\left(\sin\left(\frac{\pi\alpha t}{u_{\max} - u_{\min}}\right)\right)$, solution of the equation $\frac{du}{dt} = \alpha Sg[u]$, where $u_{\max} = 3$, $u_{\min} = 1$, coefficient $\alpha = 0.1$

The next form of the Liesegang operator is written as: $L[u] = \alpha Sg[u]$. Having calculated the module of both parts of the equation, we have that the rate of self-organization is determined by the current concentration, which is quite obvious. In this case the Liesegang operator may be written as follows: $L[u] = \alpha \text{sign}\left(\sin\left(\frac{\pi\alpha}{u_{\max} - u_{\min}} \int_0^t u(\tau) d\tau\right)\right)$. Having solved the equation with the Liesegang operator as written above, we will get the following simplified graph of the dependence $u = f(t)$, fig. 6.

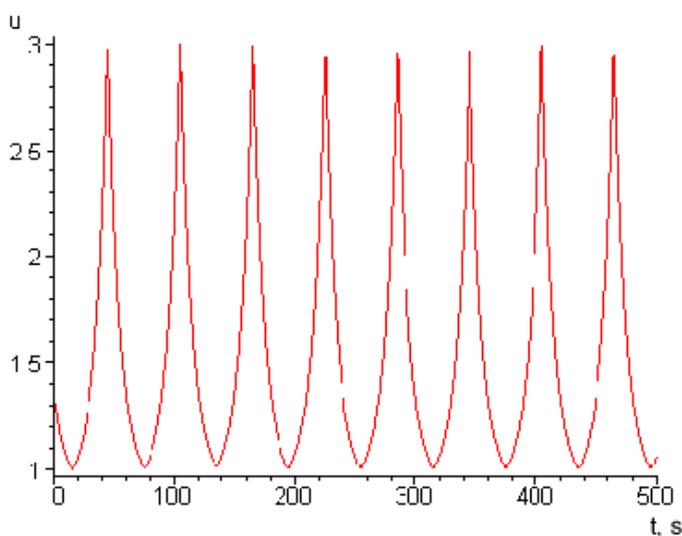


Fig. 6. Dependencies $u = f(t)$, where $L[u] = \alpha \text{sign}\left(\sin\left(\frac{\pi\alpha}{u_{\max} - u_{\min}} \int_0^t u(\tau) d\tau\right)\right)$, u is a solution of equation

$$\frac{du}{dt} = \alpha u Sg[u] \quad (\text{The parameters are the same as in the fig. 5})$$

Let us consider more complex Liesegang operator as:

$$L[u] = \alpha u \operatorname{sign} \left(\sin \left(\frac{1}{T} \int_0^t \left| \frac{\partial u}{\partial t} \right| dt \right) \right),$$

where T — the period of the decay self-organization process replication.

Let us return to problem (1). Regarding the form for the Liesegang operator

$$L[u] = \alpha u \operatorname{sign} \left[\sin \left(\int_0^t \left| \frac{\partial u}{\partial t} \right| dt \right) \right] \text{ let us rewrite problem (1) as:}$$

$$\begin{cases} \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + \alpha u \operatorname{sign} \sin \left(\int_0^t \left| \frac{\partial u}{\partial \tau} \right| d\tau \right) \\ u|_{x=0} = u_0, \quad u|_{t=0} = u_0 = \text{const} \\ u|_{x=l} = u_0 \end{cases}$$

We will find the solution as a series by eigenfunction of the one — dimensional Liesegang operator on the line $[0; L]$, i. e. as $u = \sum_{n=1}^{\infty} u_n(t) \sin \left(\frac{\pi n x}{L} \right)$. For each coefficient $u_n(t)$ we have the following equation:

$$\frac{du_n}{dt} = -D \frac{\pi^2 n^2}{l^2} u_n + \alpha \sum_{m=1}^{\infty} u_m \int_0^l \sin \frac{\pi n x}{l} \sin \frac{\pi m x}{l} \operatorname{sign} \left(\sin \left(\frac{\alpha}{u_{\max} - u_{\min}} \int_0^t \sum_{k=1}^{\infty} u'_k \sin \left(\frac{\pi k x}{l} \right) \left| d\tau \right| \right) \right).$$

To obtain (even if approximately) the graphs constructed numerically, it is necessary to take at least several tens of harmonics. However, we need to construct the illustration of the Liesegang operator function, hence, we will restrict ourselves to the first harmonic only. As a result we have:

$$\frac{du_1}{dt} = -D \frac{\pi^2}{l^2} u_1 + \alpha u_1 \int_0^l \sin \frac{\pi x}{l} \sin \frac{\pi x}{l} \operatorname{sign} \left(\sin \left(\left| \sin \left(\frac{\pi x}{l} \right) \right| \frac{\pi \alpha}{u_{\max} - u_{\min}} \int_0^t |u'_1| d\tau \right) \right) dx.$$

According to the known theorem of analysis the integral in the right part of the equation equals the value of the subintegral function at some point $x = \xi$. Introducing the notation $\sin \pi \xi / l = \beta$, we have the equation:

$$\frac{du_1}{dt} = -D \frac{\pi^2}{l^2} u_1 + \alpha \beta^2 u_1 \operatorname{sign} \left(\sin \left(\beta \frac{\pi \alpha}{u_{\max} - u_{\min}} \int_0^t |u'_1| d\tau \right) \right).$$

From the point of view of illustration, the particular value α does not matter, $0 = \alpha = 1$. The approximate solution with $\alpha = 0.7$ and 0.3 is given in fig. 7.

The figure 8 shows the wave with markedly increased diffusion coefficient to illustrate its effect on the wave shape (on the previous graph the diffusion coefficient was 0.0001).

The figure shows that the wave is non-symmetrical, the diffusion prolongs the time rate growth and decreases time of self-organization period. The set of harmonics, then starting with some harmonics the diffusion will exert the significant effect and the structure will stop growing. (Periods and the scale do not correlate with previous figures 5—7).

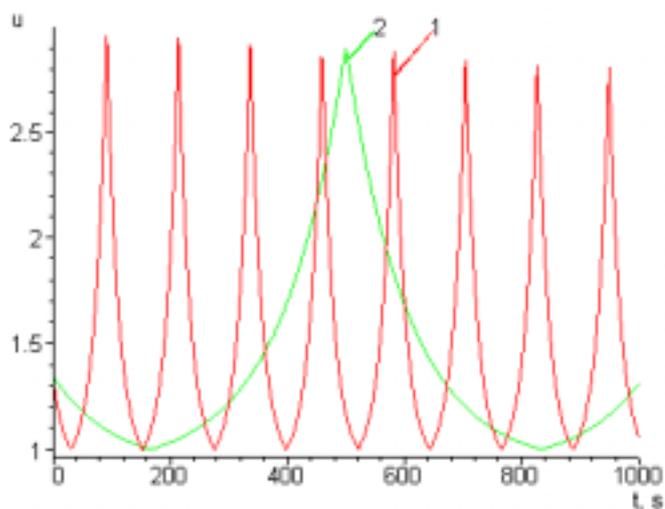


Fig. 7. Graphic dependence of the kind: $\frac{du_1}{dt} = -D \frac{\pi^2}{l^2} u_1 + \alpha \beta^2 u_1 \operatorname{sign} \left(\sin \left(\beta \frac{\pi \alpha}{u_{\max} - u_{\min}} \int_0^t |u_1'| d\tau \right) \right)$, where the approximate solution at $\beta = 0.7$ and $\beta = 0.3$ is given in the figure (the 1 graph — 0.7, the 2 one — 0.3, the graph is constructed approximately).

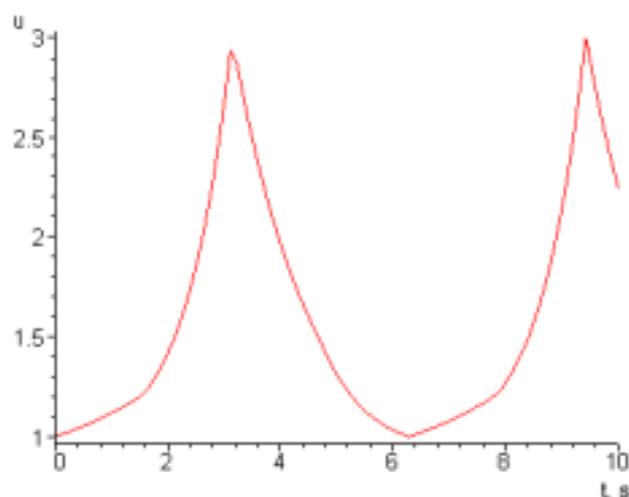


Fig. 8. Representation of a separate wave with markedly increased diffusion coefficient

In case of the three–dimensional solution corresponding to the first harmonic only, we have fig. 9.

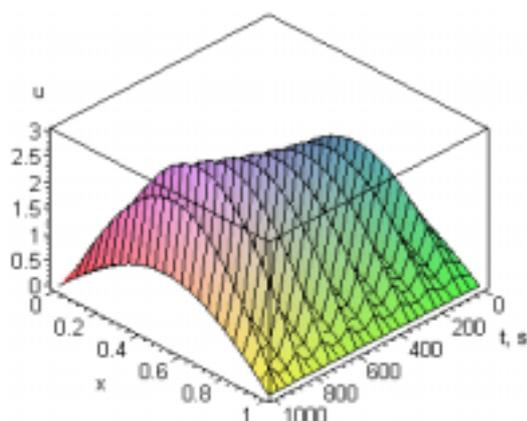


Fig. 9. Three–dimensional representation of the function $U = f(t)$ corresponding to the first harmonic

Note, that approximate analytical calculations do not give those qualitative results as the numerical ones. Experimentally analyzed graphs of dependence are presented in the works and theoretical similar [10, 1].

2.4. Polarization of the gel system

The concentration periodicity of the oxyhydrate gel system analyzed by means of introducing a Liesegang function causes us to consider the given function as being some periodic invariant of the gel oxyhydrate system vibration in general. For unbalanced gel systems the Liesegang function is a peculiar kind of the isotherm of gel system concentration variation in time.

The equation of gel system self-organization used to study the processes in a gel has form (1). What is the critical value of the concentration in a gel system and how does it vary in time, in particular, if some concentration centers are developed (self-organizing) in a gel. It is not a simple matter to give an answer on the basis of the concentration value variation alone. Therefore, let us use the expression for polarization known from the dynamics of continuous media [15], for it is polarization which is the macroscopic characteristic (actually the cause) giving rise to the concentration differentiation of a gel: $u = n = \text{div } P$, where P — the polarization vector. Substituting this expression into equation (1) containing the simplest Liesegang operator we have:

$$\frac{\partial}{\partial t} \bar{P} = D\Delta\bar{P} + \bar{P}Sg[n] + \delta\bar{P},$$

where the component δP is stipulated by the “joints” of the regions where the Liesegang operator has different signs.

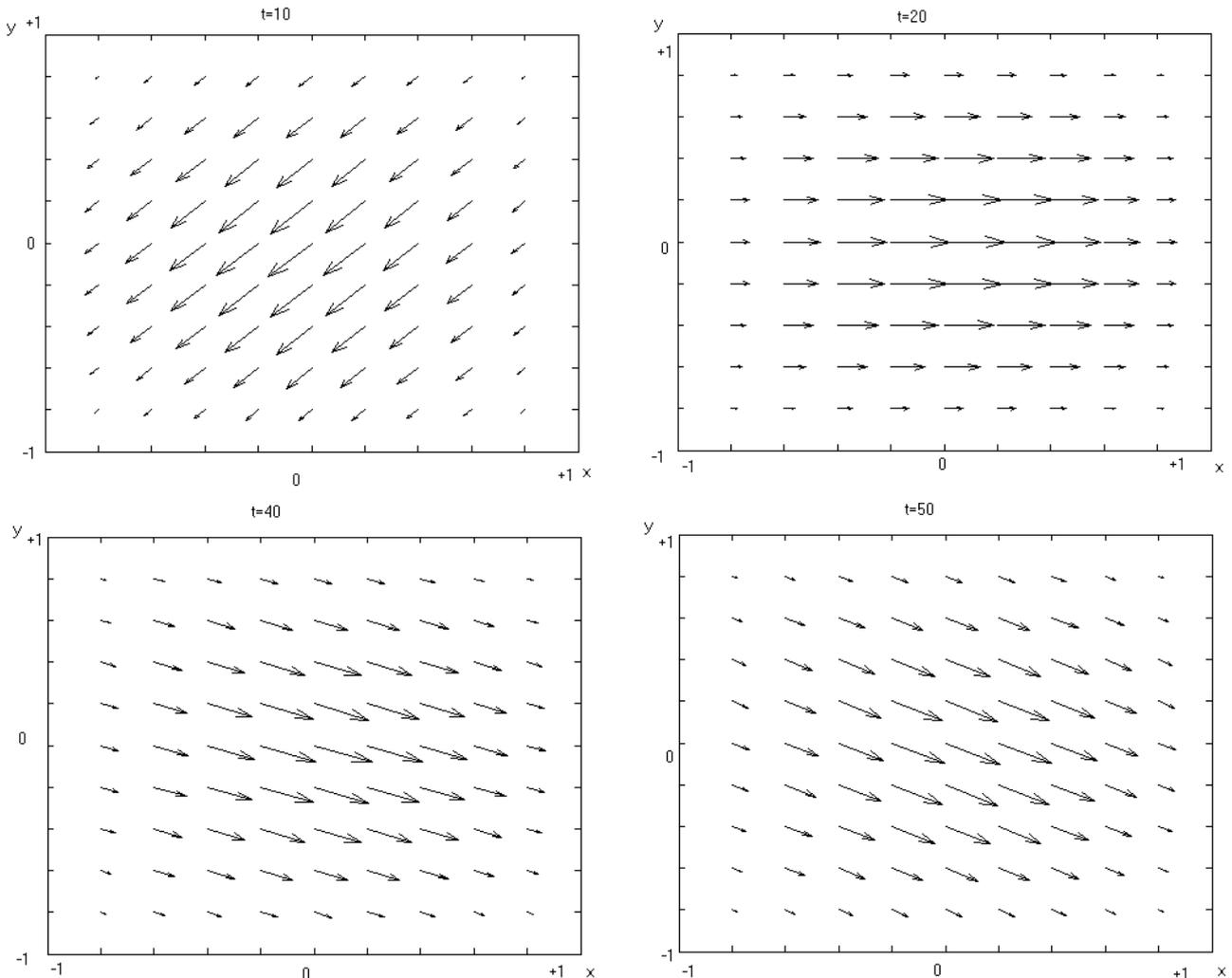


Fig. 10. Polarization vectors of a gel for different moments of time

What physical–chemical processes proceed in a gel? In this connection it is interesting to consider in this connection the interaction of attractors (a similitude of autosolitons) which are formed in the gel system of oxides–hydroxydes of such heavy metals as Nb, Zr, Ti, Y, Ga and others. An attractor is formed by walls possessing some thickness and made up of molecules of the structured oxyhydrate gel. Earlier in [10, 11] it was shown that attractor walls are formed only by macromolecules–dipoles, i.e. gel fragments. The process is as follows: at the initial moment of time some inhomogeneity of the gel concentration with non–zero dipole moment forms at some point of gel space. Under the influence of the double electric layer field of this inhomogeneity other oxyhydrate macromolecules having the dipole moments are concentrated in the given volume of space as well, which increases the total density of dipoles at the points of concentration fluctuation. On the other hand, dipoles attach to a gel wall in a particular way; walls similar to the Archimedean spiral detach from the initial concentration maximum (peak). Helical whirls are formed whose model of formation was studied in [2]. At the same time, if the gel concentration density exceeds some critical value at a given place, density vibrations start developing under the influence of chemical reactions of different gel fragments with intermicellar liquid [10, 11, 16]. What interactions occur in this case?

First, under the influence of the electric dipole moment of the double electric layer macromolecules of moving gel fragments are ordered in a particular way, which make it possible to strengthen the concentration peak. Second, a part of molecules interacts randomly with the gel surface, which screens and decreases the dipole potential of the peak. Third, molecules of intermicellar liquid encourage peptization and loosing of the concentration peak, i. e. destroy it. Fourth, gel macromolecule fragments present in the solution interact chemically (co–polymerization), which decreases their concentration. These reactions were considered in detail in [1].

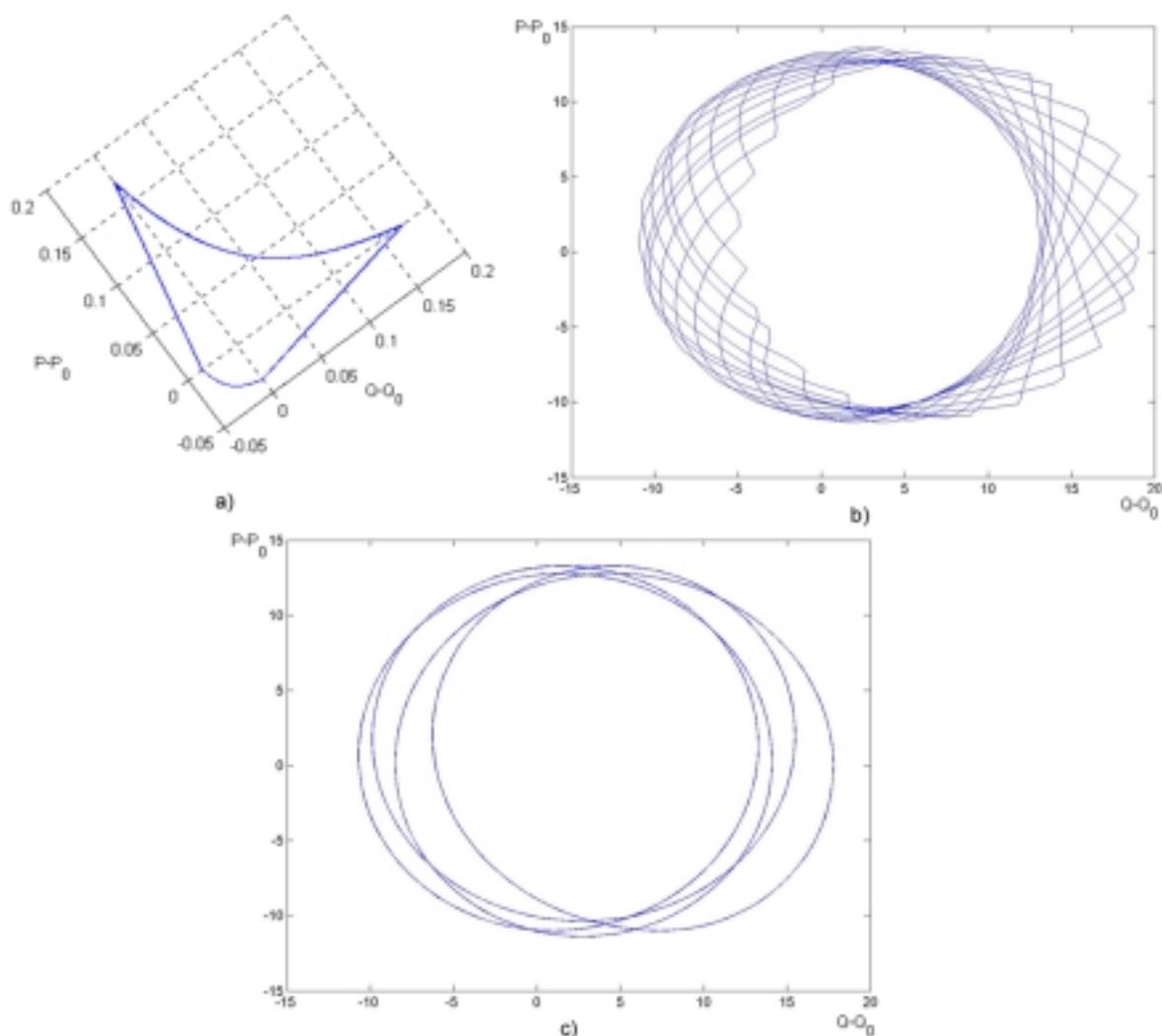


Fig. 11.

a) The rotation of the gel polarization vector in the plan XY for a very long interval of time (1000 unit). Axes are: P and Q components of polarization vector. Only Liesegang operator is taken.

b) Rough approximation of the rotation of the gel polarization vector in the plan XY for a very long interval of time (1000 unit). Axes are: P and Q components of polarization vector. Liesegang operator and reactions in gel are taken.

$$\text{Equation is: } \begin{cases} \frac{\partial P}{\partial t} = \omega Q + \alpha PL[u], \\ \frac{\partial Q}{\partial t} = -\omega P + \alpha QL[u], \end{cases} \quad \omega \ll \alpha$$

c) Rough approximation of the rotation of the gel polarization vector in the plan XY for a very long interval of time (1000 unit). Axes are: P and Q components of polarization vector. Liesegang operator and reactions in gel are taken.

$$\text{Equation is: } \begin{cases} \frac{\partial P}{\partial t} = \omega Q + \alpha PL[u], \\ \frac{\partial Q}{\partial t} = -\omega P + \alpha QL[u], \end{cases} \quad \alpha \ll \omega$$

The rotation of the polarization vector is quite complicated, the process proceeding continuously. Let us try to model rotation of the polarization vector. To this purpose, let us consider a pair of polarization vectors $\{P_x; P_y\}$ in space $D = \{0 \leq x \leq 1, 0 \leq y \leq 1\}$. Let us repeat the above presented procedure for deriving the solutions of the one-dimensional problem and solve this problem as Fourier series expansion:

$$P_x = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} P_{nm}(t) \sin(\pi nx) \sin(\pi my),$$

$$P_y = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} Q_{nm}(t) \sin(\pi nx) \sin(\pi my).$$

Substituting these expressions into equations for polarization vector, regarding that $n = \frac{\partial P_x}{\partial x} + \frac{\partial P_y}{\partial y}$,

and expanding all the expressions into the Fourier series, we will get the system of equations similar to those for the one-dimensional problem. Since we need the illustrative qualitative result, we will restrict ourselves to the first harmonic. The following approximation is performed for the first harmonics:

$$P_{1,1} \approx \sin(\pi x) \sin(\pi y) \frac{u_{\min} + \frac{u_{\max} - u_{\min}}{\pi} \left(\exp \left(\arccos \cos(\beta t) - \frac{\pi}{2} \right) - 1 \right)}{e^{\pi} - 1},$$

$$Q_{1,1} \approx \sin(\pi x) \sin(\pi y) \frac{u_{\min} + \frac{u_{\max} - u_{\min}}{\pi} (\exp(\arcsin \sin(\beta t)) - 1)}{e^{\pi} - 1}.$$

The figure 10, a,b,c,d shows vectors $\vec{P} = \{P_{1,1}; Q_{1,1}\}$ for different moments of time corresponding to these harmonics.

If we fix polarization vector at some point $(x_0; y_0)$ and study the diagram plotted by the polarization vector, we will have figures of this kind (figure 11) for the following conditions: very long interval of time (1000 units), the polarization vector is considered with the Liesegang function applicability as well as with the colloid-chemical reactions of structuring and peptization in a gel in a gel according to the equations:

$$\left\{ \begin{array}{l} \frac{\partial P}{\partial t} = \omega Q + \alpha PL[u] \\ \frac{\partial Q}{\partial t} = -\omega P + \alpha QL[u] \end{array} \right. \quad \omega \ll \alpha \text{ and:} \quad \left\{ \begin{array}{l} \frac{\partial P}{\partial t} = \omega Q + \alpha PL[u] \\ \frac{\partial Q}{\partial t} = -\omega P + \alpha QL[u] \end{array} \right. , \quad \alpha \ll \omega.$$

In the phase space (phase plane) being considered the intersecting orbits of the polarization vector are rather complex. Colloid chemical reactions result in the shifts of the polarization vector within the limited part of the phase plane, the shape of orbits being determined by the relationship of the processes of diffusion and speeds, destructions and polarizations.

Conclusion

1. In colloid gel systems the spontaneous concentration differentiation of a substance in time and space is observed. This differentiation is of the autowave (pulsating) nature (periodic self-organization) and takes the form of “frozen” helical whirls.

2. The optical density of YOYGs depending on the wave length of the incident light exhibits rather wide regions with the low optical density of gels (the formation of homeotropic-like structures with the transformation of helical whirls), i.e. the samples became optically transparent over a definite discrete interval of wave lengths. The effect of forming the structures of the chiral-smectic type accounts for the colouring of yttrium oxyhydrate gel due to the selective diffraction reflection.

3. The concentration periodicity of the oxyhydrate gels system is analyzed by introducing a Liesegang function. For unbalanced gel systems the Liesegang function is a peculiar kind of the isotherm of the concentration variation of the gel system in time.

4. The rotation of the polarization vector in the gel space is shown. This rotation is quite complicated, the process proceeding continuously. These phenomena are caused by physical–chemical processes of destruction — polymerization, which are responsible for the formation of the gel matrix. The mathematical model of the polarization vector rotation is considered.

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