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THE OPTICAL PROPERTIES OF OXYHYDRATES GELS OF SOME HIGH-DENSITY METALS

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Introduction

As we demonstrated earlier [1, 2, 3], gel oxyhydrate systems of high-density metals (titanium, zirconium, rare earth elements, and others) are living systems, meaning in the process of holding, for example, granulated or make up gels under a layer of water, processes develop in polymer matrices that result in a certain directed morphogenesis of the matrices. Chiefly, these are the effects of cross-linking which occur through the intermicellar molten phase by: the link destruction of gel fragments (gel protonation), the transfer of light (monomolecular) fragments in solution and their subsequent diffusion to the active gel center of polymerization (the formation of an active complex), and the secondary directed copolymerization with the matrix's gel. The above mentioned processes develop in conditions far from equilibrium [4, 5].

Experimental Observations of the Distinctive Features of Oxyhydrates of Yttrium

Experimental physicochemical research on gel systems, for instance, on the basis of oxyhydrate of yttrium and gadolinium, have shown regular periodic changes in the material properties, such as the sorption properties. In [6] it has been established that in these gels: the thermogravimetric characteristics (the temperatures of dehydration effects, the amount of hydrate moisture, etc.), reflected in the structure of the material, change periodically, the isotherms of sorption have a wave-like oscillation nature, and the morphogenesis of the gels is of a spiral-like shape, etc.

Some specimens of oxyhydrate of yttrium and gadolinium possess a very unusual property: their coloring. For nearly all colored oxyhydrates of yttrium and gadolinium, the gel color can change from a yellow-green or yellow to red, blue, or blue-green. However, this does not mean that every gel synthesis yields colored material. The reproducibility of the synthesis of colored gels is fairly low. For the most part, colorless semi-transparent or white gels of oxyhydrates of yttrium or gadolinium result. Gel synthesis in the sensing unit of Reotest 2's viscosity gage (in the gap of the coaxially revolving cylinders) makes the fairly stable formation of pink tinted oxyhydrate of yttrium gels possible.

Air-dried red-colored gel of oxyhydrate of yttrium was successfully obtained which, when placed in distilled water, underwent periodic changes in the intensity of its coloring over time and subsequent damping (fig. 1). It is important to note that the ability of this gel to change the intensity of its coloring over time, by the natural law of periodic damping, was maintained for at least three years if the gel was kept in an air dried state. Placing gel in water, after storing it for a few months, showed that the

frequency of change in the intensity of its coloring was much higher than what is indicated in fig. 1 (results obtained after holding the specimen for three years).

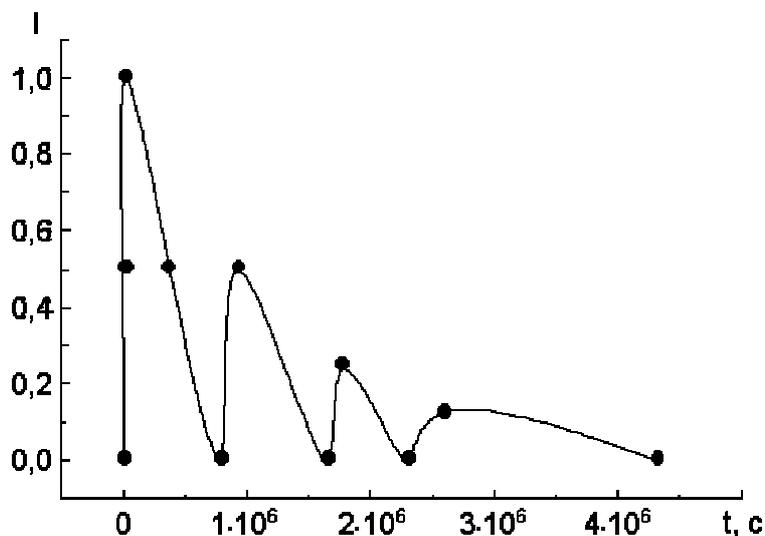


Fig. 1. The periodic change in the intensity of the coloring of a gel of oxyhydrate of yttrium over time where I — is the intensity in relative units

Theoretical Analysis of the Color Effect of Oxyhydrate Gels

It is known that the presence of coloring in compounds is determined by the possibility of flows of electron transition between the pairs of levels i and j , so that a change in the energy ($\Delta E = E_j - E_i$), during the transition, will lead to radiation absorption with the frequency ($\nu = \Delta E / h$) in the visible zone. Usually, the $\sigma - \sigma^*$, $\pi - \pi^*$ and $n - \pi^*$ junctions pertain to these types of transitions. In inorganic systems, that contain high-density metals, $d - d^*$ junctions and a line of charge transfer in the visible region are also possible. A reason for the appearance of color in polymer gel oxyhydrates, containing uncolored compounds in individual forms, could be the result of energy orbital change (in particular the removal of the degeneration of d -levels) under the effect of a hydrate casing and neighboring monomolecular links in the structural link of the polymer chain $(\text{MeO}_2 \cdot n\text{H}_2\text{O})_m$. Furthermore, the emergence of the absorption band in the visible region might be due to a different structural cause: the formation of a system analogous to an organic aromatic compound. This leads to the appearance of conjugate π -electron links, a reduction in the ΔE junction, bathochromic displacement of the frequency, and the appearance of the possibility of $\pi - \pi^*$ and $n - \pi^*$ junctions which are not usually characteristic of inorganic compounds.

These hypotheses can be checked by a quantum-chemical examination of structural units of oxides and hydroxides of uncolored individual compounds and their polymer hydrate-like systems. To make spectral quantum-chemical calculations of oxyhydrate systems of transition metals, precise knowledge of the structure of such systems in the gel phase is necessary; however, experimental structural data for these gel oxyhydrate compounds in the gel phase are missing. Additionally, we need to take into consideration that gels are living systems (are metastable) within which it is possible to find several types of order. Therefore, in order to effectively simulate the possible structures of hydrate-like systems, it is logical to use combining strategy, consisting firstly of the probable simulation of the structure, and then the subsequent optimization of the geometry of the system within known quantum-chemical methods, such as those shown in [7].

In the beginning, an appropriate monomolecular link of an oxyhydrate of metal is chosen that has a molar ratio of 1:1 with water or with another similar monomolecular link within the limits of the DENSON/MERA model (modifications for solutions) [8]. By using this model without explicitly examining the structure of the possible associate, it is possible to establish the most probable location of atoms of monomolecular links and water molecules or of atoms of dimeric links that take part in the

structure forming contact. Then, within the bounds of semi-empirical quantum-chemical approximation ZINDO/1 the structure of the associate is suggested in an obvious form and its geometry is optimized.

To eliminate the possibility of a fall in the local energy minimum at the end of the optimization, the system is brought out of the minimum by using the Monte-Carlo method in to force field MM+. After which, the structure again optimizes within the limits of the semi-empirical quantum-chemical approximation ZINDO/1. These types of procedures are carried out until a stable level of total system energy is reached. When optimization has ended, the spectral characteristics of the anticipated associates are calculated within the bounds of the same approximation.

Discussion

The produced calculation for the molecular forms of oxides and hydroxides of rare earth elements in an individual form, such as Y_2O_3 , $YO(OH)$, $Y(OH)_3$, in the limits of the semiempirical quantum-chemical approximation ZINDO/1 indicated the presence of spectral lines only in the ultraviolet region, which sufficiently explains the absence of coloring in these individual compounds.

After simulating the aqua-systems and calculating their spectral characteristics, it was ascertained that hydrate systems of individual compounds are also without absorption bands in the visible region of the spectrum. Thus, in terms of the spectrum of the $YO(OH) \cdot H_2O$ system, represented in fig. 2, it is apparent that the maximum effective length of the wave of absorption is 217 nm. In this way, the effect of the solvent (water) does not result in the removal of degeneration from d-orbitals of these compounds, which does not contradict the experiment (the absence of coloring of soluble saline of yttrium in water).

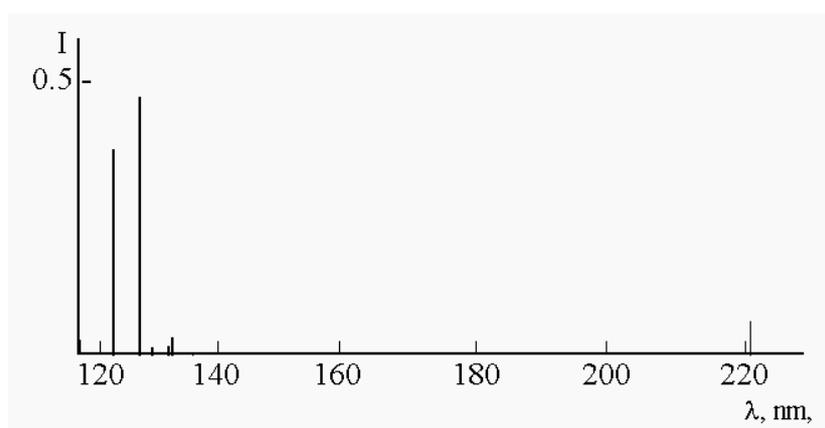


Fig. 2. The calculated spectrum of the absorption of a hydrated monomer $YO(OH) \cdot H_2O$

Where I — is the intensity in relative units, and λ — the wave length in nm.

The simulation of dimer compound structures indicated that in the gel phase two structures, similar in energy, could form (structures A and B — represented respectively in figs. 3a and b). Structure B is more stable of the two (its enthalpy of formation is 616.6 kJ/mole). In this case, structure A is metastable (its enthalpy of formation is 499.5 kJ/mole). However, the difference in the energy of the two structures is not great, and under the influence of negligible stresses (changes in pH, ionic force, saline composition, mechanical stress, etc.,) conditions could arise that would support the preferential formation of structure A. These structures very probably form in meta-stable phases, to which the gels pertain.

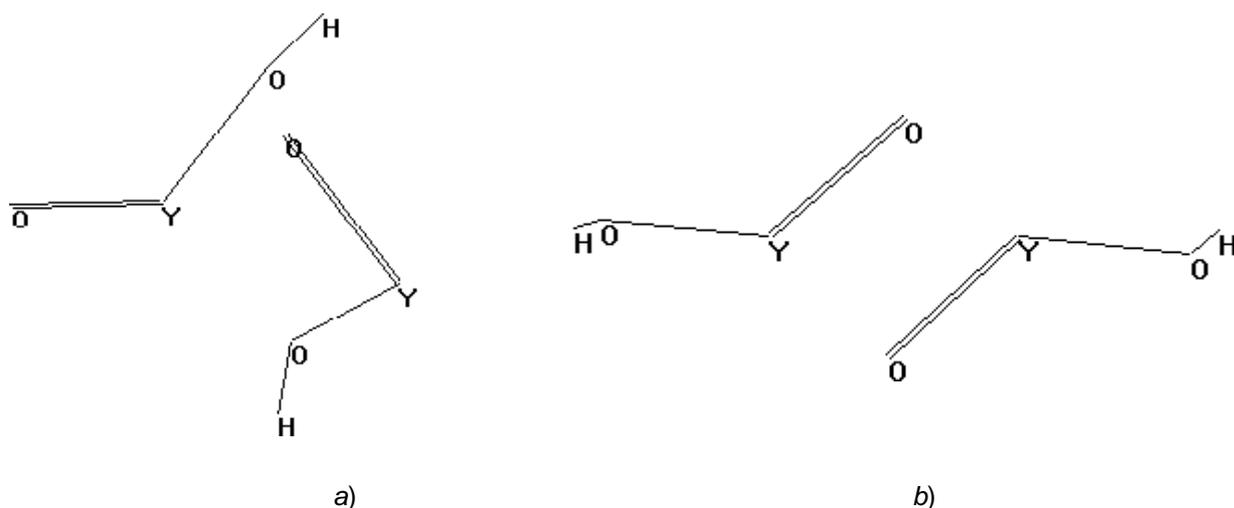


Fig. 3. The structures of two types of dimers of oxyhydrate of yttrium, that have the minimum total energy: a) the local minimum (the metastable structure A); b) the global minimum (the stable structure B).

A bathochromic shift of the absorption band is observed in the calculated spectrums of both structures (figs. 4a and b). However, the maximum absorption wave length of structure B lies in the ultraviolet region ($\lambda_{max} = 305$ nm), whereas for structure A, the maximum absorption wave length is located in the visible region ($\lambda_{max} = 449$ nm). The significant bathochromic shift of the absorption band in structure B can be explained by the formation of a cyclical dimer with the conjugate π -electron system, which is similar to an organic aromatic compound. However, in contrast to organic aromatic compounds, lower energy of electron transitions of elements of the highest cycles provide for a more substantial band shift. In structure B, attention is drawn to the order of dipole links $Y=O$, characteristic of the crystal structure Y_2O_3 , that forms after the loss of a water molecule. Since the crystal oxide of yttrium is uncolored, it is logical that the structure, containing a crystal prototype, is also uncolored.

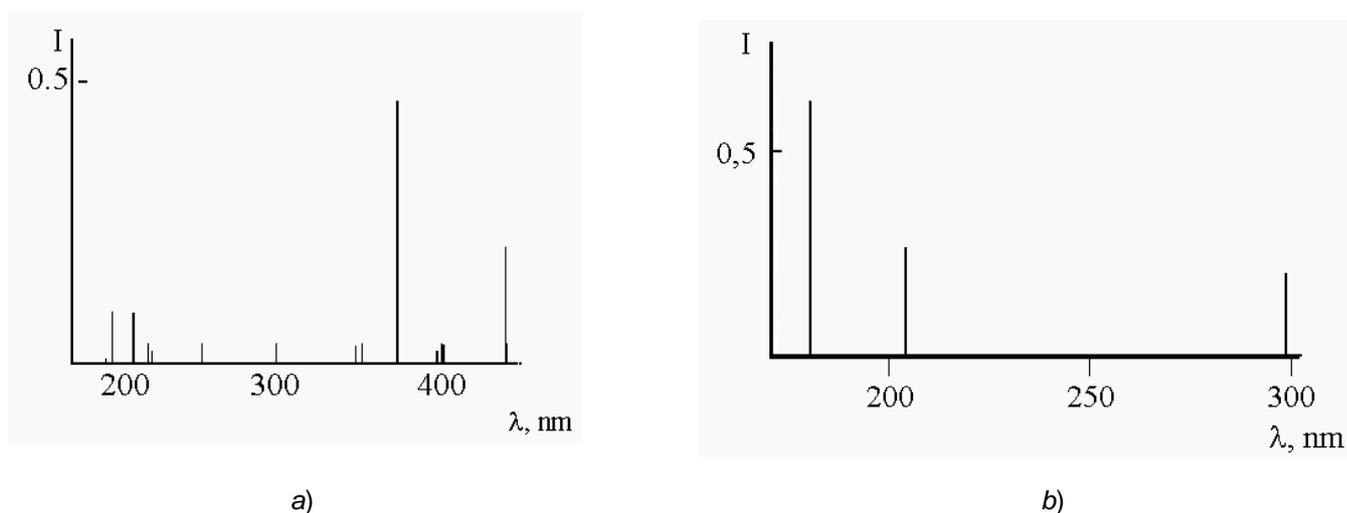


Fig. 4. The calculated spectrums of the absorption of dimers $(YO(OH))_2$: a) for structure A; b) for structure B.

By adding a water molecule to each dimer, an even greater shift of the absorption band in the long wavelength region of the spectrum occurs (for structure A the value $\lambda_{max} = 453$ nm; for structure B $\lambda_{max} = 314$ nm). The calculated spectrums of hydrated dimers $(YO(OH))_2 \cdot H_2O$ are represented in figs. 5a and b. This may be caused by the removal of degeneration from the electron levels under the

influence of the solution, and/or by the participation of water, in the additional linking of a dimer on account of hydrogen links, which increases the charge level in the system. The addition of yet another water molecule to each dimer results in an even greater bathochromic shift (for structure A value $\lambda_{max} = 570$ nm; for structure B $\lambda_{max} = 292$ nm). The calculated spectrums of the hydrated dimers ($YO(OH) \cdot H_2O)_2$ are represented in figs. 6a and b. With subsequent increases in the hydration level, a substantial shift of the absorption band is not observed. By increasing the polymerization level (a trimer), only a small bathochromic shift is observed. With continued increases in the level of polymerization the shift is practically absent. The position of the maximum of absorption in relation to the number of water molecules for dimers with A and B structures is illustrated in fig. 7. The position of the maximum of absorption in relation to the level of polymerization (structure A) is demonstrated in fig. 8. Similar results are obtained when examining oxyhydrates of zirconium.

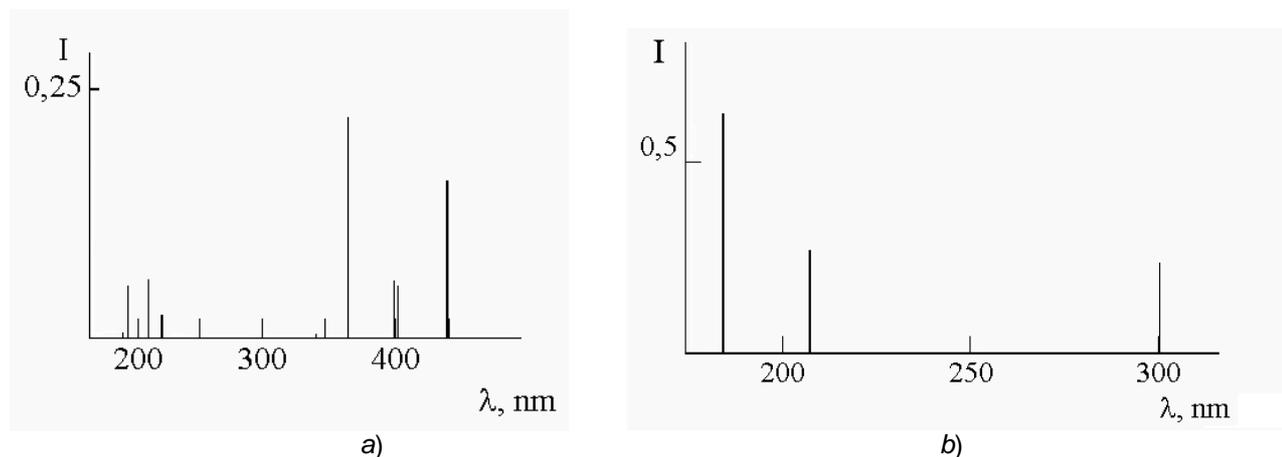


Fig. 5 The calculated spectrums of the absorption of hydrated dimers $(YO(OH))_2 \cdot H_2O$:

a) for structure A; b) for structure B. Where I — is the relative intensity, and λ — the wave length in nm.

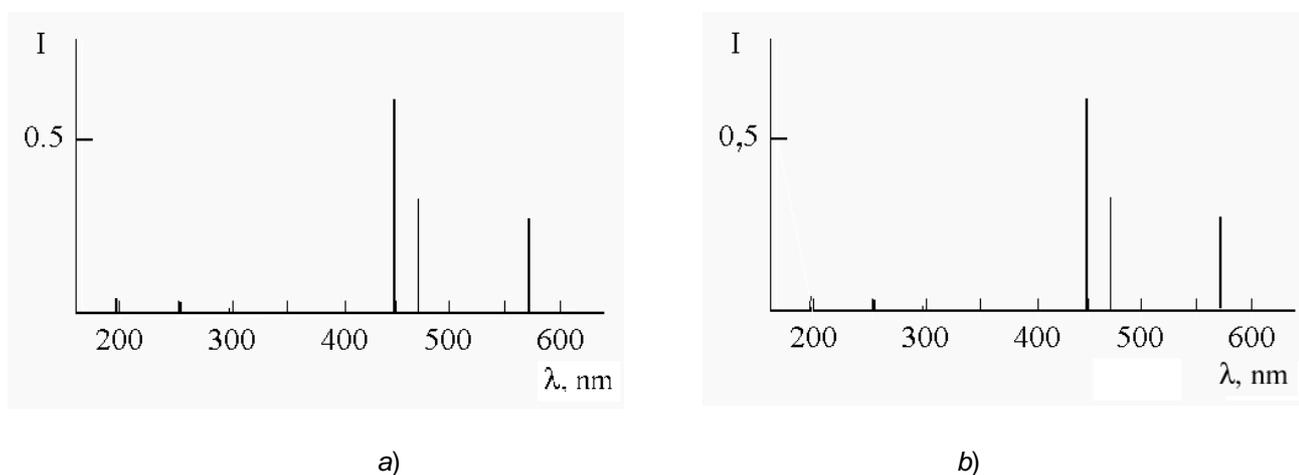


Fig. 6. The calculated spectrums of the absorption of hydrated dimers $(YO(OH) \cdot H_2O)_2$:

a) for structure A; b) for structure B. Where I — is the relative intensity, and λ — the wave length in nm.

In this way, it is theoretically possible to distinguish minimally structured units of gel phases of the structure $(YO(OH))_2 \cdot (H_2O)_N$ ($N = 1 \dots 3$), which, under certain conditions (for example, the formation of metastable A phases) will be colored. It is also important to note that the gel structures A and B are probably reciprocal. In [3, 5] we demonstrated the formation of supramolecular gel organizations of oxyhydrates of yttrium, gadolinium, lanthanum, and zirconium in the form of, for example, spiral-like twists. We discovered these swirl-like states experimentally. The hydrogen link in similar types of morphogenesis of polymer oxyhydrates plays the determining role [9].

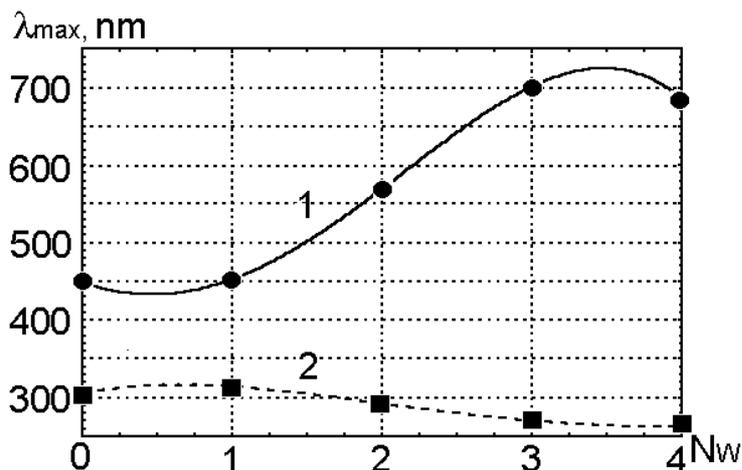


Fig. 7. The dependence of the position of the maximum of the absorption band (λ_{max}) on the number of water molecules (N_w):

1 — the metastable phase of A; 2 — the stable phase of B.

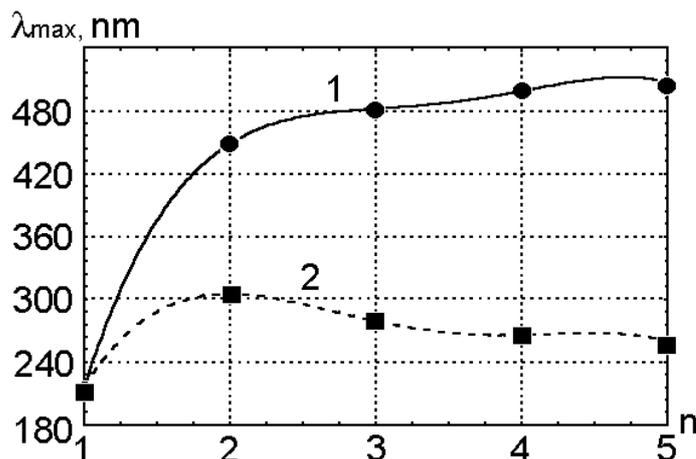


Fig.8 The dependence of the position of the maximum of the absorption band (λ_{max}) on the polymerization level (n):

1 — the metastable phase of A; 2 — the stable phase of B.

At the moment of synthesis of an oxyhydrate gel in a system, structures like A and B, for instance, of the dimer composition $(YO(OH))_2 \cdot (H_2O)_N$, are objectively absent. Their formation begins under several mechanical stresses, such as shift stresses during the study of the rheology of gels. Additionally, similar structures can emerge as the results of the natural flow of gels or the drying process.

It is also evident that the pH level of intermicellar liquid effects the formation of structures like A and B. The mixing of gels in turbulent conditions with reduced pH levels should further the formation of dimers like A. In fact, in the subacid region of pH, as it appears in fig. 3 (in which the structures of two types of dimers (A and B) are represented), the formation of structure A is more likely due to the maintenance of a link in a dimer matrix of gel. The preservation of complex water is advantageous namely for the formation of the A dimer (fig. 7). In very acidic medium, the effect of gel coloring should disappear due to the condensation of the ol-group and the formation of oxy-polymers.

During a lengthy unidirectional mechanical stress (centrifugal), in alkaline medium, a B-structure dimer should form. The pink coloring of oxyhydrate of yttrium, detected during rheology investigation, was probably triggered by the B structure.

Conclusions

1. The coloring effect of oxyhydrate gels of some high-density metals was found experimentally, in particular for the rare earth elements of yttrium, gadolinium, lanthanum, and others. The periodic oscillating nature of the change in the intensity of the gel color of oxyhydrate of yttrium over time was demonstrated.
2. Theoretical and calculation methods were developed to explain the effect of coloring (the chromatic effect) of the oxyhydrate gels of high-density metals.
3. Through calculations, metastable and stable dimer phases A and B of oxyhydrates of yttrium were found which have absorption spectrums that show the presence or absence of the chromatic effect. This was confirmed experimentally.

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