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MESOPHASE–LIKE NATURE OF FORMING GEL YTTRIUM AND ZIRCONIUM OXYHYDRATES

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Introduction

The term “liquid crystal” implies the aggregate state of a substance (the intermediate state between the crystal body and amorphous liquid). The substantial geometric anisotropy of molecules, which are to be long and rather narrow, is the necessary condition for mesomorphism. Depending on the peculiarities of the molecules geometry the system may pass through one or more mesophases until it changes into the isotropic liquid. By means of both calculations [1, 2, 3] and experiments it was shown that the geometry of yttrium and zirconium oxyhydrates macromolecules meets the above mentioned properties.

Thermotropic mesomorphism and lyotropic one are distinguished which are due to the thermal processes or the influence of the dissolving phase [4, P. 8–18]. Lyotropic mesomorphism for oxyhydrate systems is practically evident due to the gels' synthesis as well as the conditions of their existence, but thermotropic mesomorphism is not so evident.

Mesophases' fluidity is due to the fact that some molecules easily slide relatively the others while retaining almost parallel orientation. This became the main reason for studying the rheological properties of oxyhydrate gel systems, namely, yttrium and zirconium oxyhydrates, since it is considered to be the straightforward and very informative method for the mesophases study.

1. Experimental Part

Freshly prepared gels of zirconium oxyhydrate (ZOHG) and yttrium oxyhydrate (YOHG) synthesized by ammonia precipitation from the solutions of zirconium oxyhydrate and yttrium nitrate were studied. The 10 % ammonia solution with pH 9.0 was used for ZOHG precipitation. The above technique is recommended in [3]. To study rheology, freshly prepared ZOHG obtained from the solutions of zirconium oxychloride with variable concentration of 65.77, 71.25, 108.82, 119.7, 131.54, 142.5, 150.88 mmol/l were used. Gels were allowed to stand for 1 hour. Then the mother solution was decanted. The final volume of a sample was 10 ml. The weight method was used to determine the content of zirconium in gel. The «solid–liquid» ratio in the gel system was maintained constant. Gels were prepared in a thermostat at the temperatures of 283 ± 0.5 , 293 ± 0.5 , 303 ± 0.5 , 323 ± 0.5 K, viscosimetric characteristics being taken at the same temperatures.

YOHGs were synthesized from the solutions with the concentration of 0.3 mol/l with pH 7.0, 8.0 and 9.7. Sediments were obtained in the thermostat at the temperatures of 293 ± 0.5 , 298 ± 0.5 , 303 ± 0.5 , 313 ± 0.5 K, their rheological properties were studied at the same temperatures with the proper isothermal condition. Rheological studies were carried out on the rotation viscosimeter «Rheotest–2» in the system of coaxial cylinders.

The studies of oxyhydrate gels $ZrO_2 \cdot nH_2O$ and $Y_2O_3 \cdot nH_2O$ made it possible to obtain complete rheological curves (CRC) at different temperatures. In the course of the experiment a number of curves $\tau = f(t)$ for the dependence “shift speed (γ) — shift stress (τ)” for the moments of time 20, 40, 60, 80, 100 and 120 min were studied. The total time of rheological measurements amounted 2 hours.

The dependencies of the optical density on the wavelength are obtained on the photocolourimeter. A gel fraction with the granule size of 0.3—1.0 mm was placed into the cell with the width of 1 mm. Gel was wetted with distilled water. Measurements of the optical density were carried out comparing with distilled water optical density.

2. Discussion of the Results

The main peculiarities of the mesophase formation of oxyhydrate system (quasi-liquid crystal systems) unlike classical liquid crystal ones may be formulated as follows:

1. As was shown before [5, 6, 7], spontaneous concentration differentiation of a substance in time and space is observed in colloid gel systems. The differentiation is of autowave (pulsating) nature (periodical selforganization). This phenomenon is mostly manifested in the conditions of sufficient saturation of the gel phase with water, since the fluidity of gel-structuring fragments increases. The oscillation profile of the density for nematic [4, P. 102] liquid crystal systems is unlikely, though it can be supposed to occur in smectics.

2. In particular, oscillations have the form of helical whirls, which are presented in fig. 1 (cholesteric or chiral-smectic type). They remain for quite a long period of time, since the gel system becomes so to say “frozen”. Fig. 2 presents the texture of yttrium oxyhydrate which is characteristic of chiral-smectic liquid crystals. Usually, the cholesteric possesses the planar blue phase. The plate texture usually characterizes the cholesteric blue phase which is observed in fig. 2.

3. Periodical peculiarities are observed with rather large step of the chiral smectic in optical studies. In particular, the functional dependence of the optical density of YO HGs on the light wave length (fig. 3) reveals rather wide alternating areas with the low optical density of gels, i. e. the samples became optically transparent in a certain discrete interval of wave lengths. This phenomenon was observed on several hundreds of samples. The similar phenomenon is observed on rather movable organic liquid crystals. In this case, the confocal texture in the electric field perpendicular to the base surface changes into the texture of “finger prints”. The direct transition from this texture into the homeotropic one is known to be the usual transition of Frederics [8, P. 213]. In case of oxyhydrate systems the same effect is achieved through the spontaneous structuring in the conditions of the “slowing down” of the gel system, i.e. the electromagnetic field’s action is replaced by the similar action of the flexoelectric effect (extended in time).



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

Mesophase-like cholesteric gel loses its whirled helical texture and slowly changes into the homeotropic one [8, P. 213], i. e. ordered-stripped. This is observed experimentally, — gel is transformed from the selectively dissipating into the transparent one. The destruction of the original chiral-smectic texture may be clearly observed in case when gel is irradiated by the electromagnetic radiation (i. e., by the non-hard ultraviolet). The samples obtain high sorption capacity connected with the unwinding (or the destruction) of chiral-smectic formations as well as with the gel’s transition into some homeotropic-like state. Before this procedure gels were sorptionally inactive. These states after the irradiation are optically transparent as well.

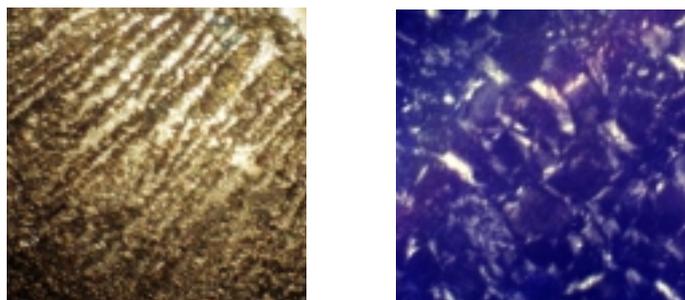


Fig. 2. Distinctive texture of yttrium oxyhydrate, which is characteristic of chiral smectic liquid crystals

Such a transition of the gel phase is reversible and periodical with the variation of the light wavelength. This phenomenon is specially noted to point out the specific role of the substance' texture differentiation in the gel phase

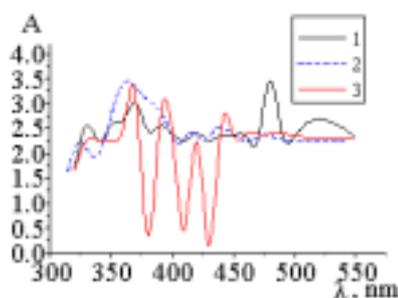


Fig. 3. Absorption spectra of the yttrium oxyhydrate

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

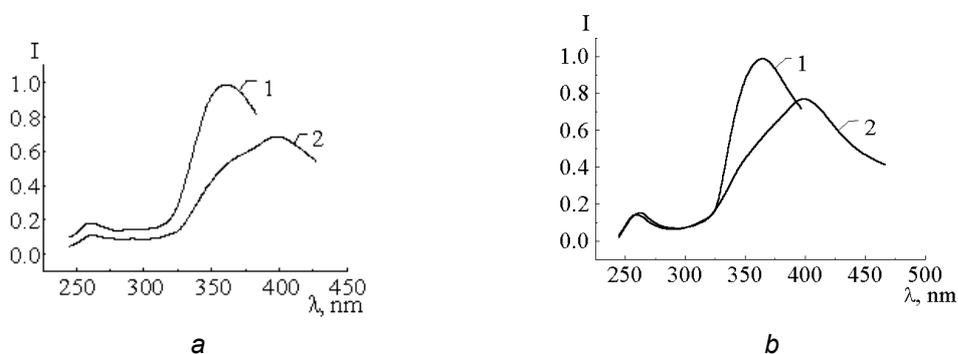


Fig. 4. Spectra of excitation for lines 1 — $\lambda = 420$ nm; 2 — $\lambda = 504$ nm

a — sample 1 synthesized with pH = 7,00, n = 0,08 mol; b — sample 2 synthesized with pH = 9,45, n = 0,09 mol

4. The effect of forming the whirled smectic type structures explains the colouring of yttrium oxyhydrate gels as well [9]. In this case the optical effect [10] is manifested in the shift of the selective deflection (diffraction) wave length to the wave of large length (the so-called red shift). The decrease in the helix step in its turn, is accompanied (selforganization) by the shift of colouring to the smaller wave lengths (blue shift). These are extreme cases for our system as well. As [9, 10] we show, in this case some oxo-hydroxial reactions take place, which may form either stable or unstable molecular formations in oxyhydrate (which are coloured as well). It is rather difficult to distinguish the colouring the reason of which is the gels' liquid-crystallinity (selective deflection) i. e. electron transitions.

Work [10] presents the electron reasons for the colouring of yttrium oxyhydrate samples due to the formation of some unstable transition states whose absorption spectra are seen in the observable region.

At the same time yttrium oxyhydrate samples manifest periodic in time red colouring [11], which is quite spontaneous and should be interpreted by the liquid-crystal properties of gels. However, the above effects of colouring are interconnected, since due to the effect of mass differentiation (con-

centration) there may appear structural instabilities, which are the reason for colouring (electron interactions) (these may be the transitional $\sigma - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ and possible $d - d^*$ transitions).

5. The effects of luminescence are characteristic of mesophase-like systems. This effect appears to characterize the electronic-structural activity of gel, which initiates the above mentioned electronic transitions. While yttrium oxides samples themselves do not possess the property of luminescence, yttrium oxyhydrate gels, i.e. the systems containing bound water, do possess. This is illustrated in fig. 4, 5. Though this peculiarity may not be common but it may be considered to be the specific case. The chiral groups of yttrium oxyhydrate molecules may be the luminescence centers.

Let us consider the rheological properties of yttrium oxyhydrate gels in detail. Fig. 6 presents the typical dependencies of dynamic viscosity (η) of yttrium oxyhydrate gels on the shift speed (γ). About 5–6 peak-like “ejections” of dynamic viscosity are clearly observed in the figures. These maxima may shift along the ordinate axis depending on the environment, pH and temperature. Fig. 7 presents complete rheological curves, e. g. at pH 7.0 and $T = 313$ K drawn in the coordinates “shift speed–shift stress”. It should be noted that starting with some boundary value of the shift stress there appears the plateau-region due to the deep polymerization of gel and subsequent separation of the substance. As a result, the adjacent gel gel regions mechanically slide relatively each other without interacting.

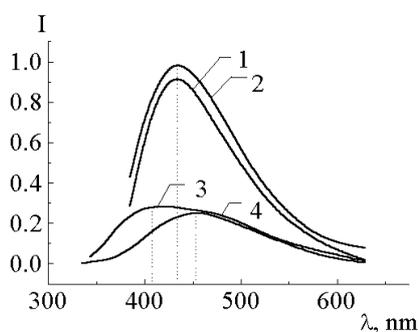


Fig. 5. Spectra of YOH gels fluorescence:

1 — sample 2, $\lambda_{exc} = 352$ nm; 2 — sample 1, $\lambda_{exc} = 352$ nm;
3 — sample 2, $\lambda_{exc} = 259$ nm; 4 — sample 1, $\lambda_{exc} = 259$ nm
(see fig. 4)

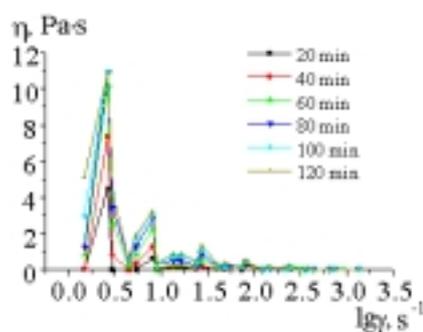


Fig. 6. Dependencies of dynamic viscosity (η) of yttrium oxyhydrate gels on the speed-shift (γ)

What is the reason for the appearance of the discrete regions on the complete rheological curve? These effects may be explained in two ways. On the one hand, they are due to successive polymerization and subsequent serious destruction of gel components, which, in its turn, develop as a result of some threshold shift stress. On the other hand, it should be taken into consideration that in the system there is some original concentration differentiation of the substance, which is the reason for developing subsequent polymerization (with the shift along the abscissa axis). The latter explanation appears to be the most logical one.

Viscosity, stress and shift speed for a certain temperature were calculated for each discrete stripe on the complete rheological curve. Then functional dependencies $\eta = f(T)$, $\tau = f(T)$, $\gamma = f(T)$, were constructed and analyzed (fig. 8, 9, 10). The decrease in viscosity on the dependence curves $\eta = f(T)$ is known to correspond to the phase transition in the system «liquid crystal — gel phase». The figures show at least several temperatures of such transitions for yttrium oxyhydrate gel: 292.5 K, 302.5 K, 312.5 K (19.5, 29.5, 39.5 °C). It is at these points where viscosity is minimal for all the six separated differentiation stripes. It should be noted that pH value of the gel phase influences gel polymerization as well and, consequently, the viscosity. With pH 7.0, the above temperature intervals of transitions are manifested less clearly than with pH 9.7. The increase in pH solution contributes to the OH-groups' bound of the matrix, since there are more free OH-groups in the system.

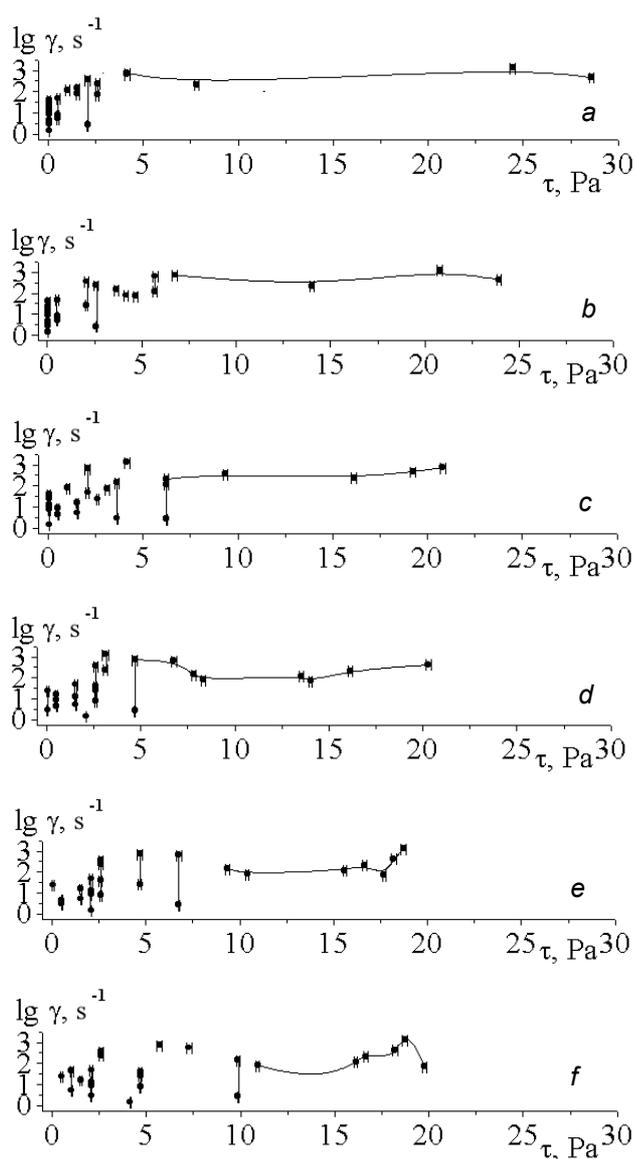


Fig. 7. Complete rheological curve of yttrium oxyhydrate gels synthesized at pH = 7,0; $T = 293$ K for the moments of time a, b, c, d, e, f — 20, 40, 60, 80, 100 and 120 min

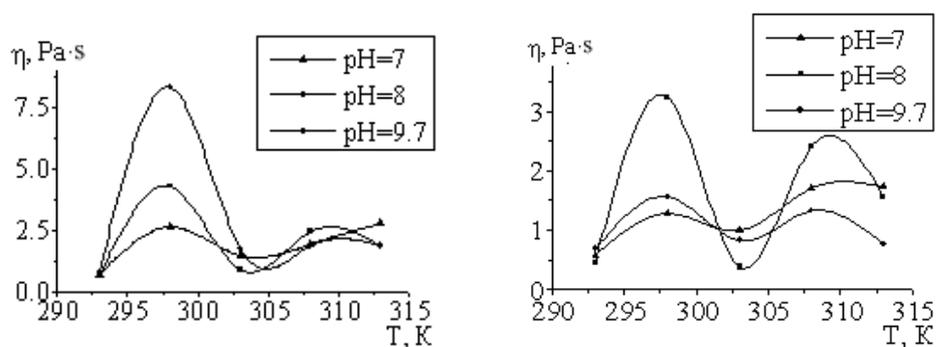


Fig. 8. Dynamic viscosity for a certain temperature, where c, d (from fig. 7) — for each discrete strip on the complete rheological curve

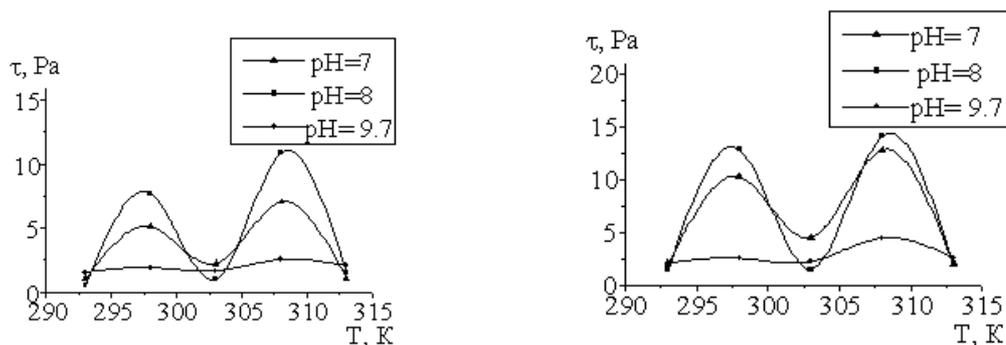


Fig. 9. Shift stress for a certain temperature, where c , d , e (from fig. 7) — for each discrete strip on the complete rheological curve

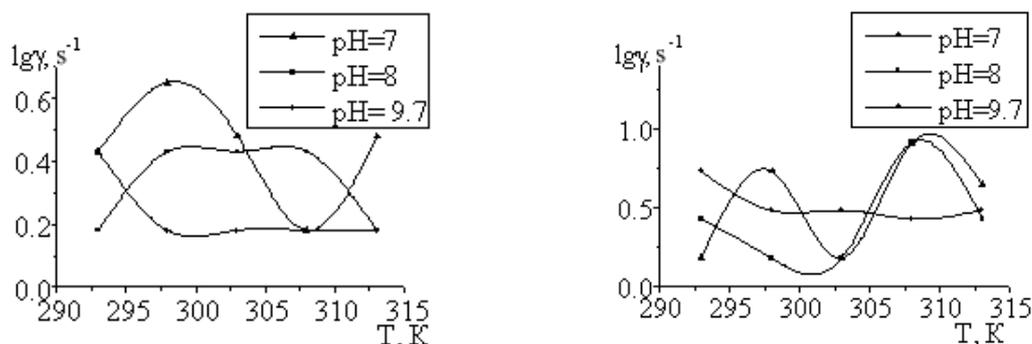


Fig. 10. Shift speed for a certain temperature, where a , b — for each discrete strip on the complete rheological curve

The difference in absolute viscosity values corresponding to different stripes of differentiation depending on the shift speed in the region of 0.0 – 3.5 s^{-1} is found. Maximum viscosity is found for maxima 1, 2, 3 (fig. 6). For the rest stripes the viscosity values are much lower. This fact causes us to suppose that the structure of differentiation stripes is different. At least, substance densities in these formations are different. One should probably suppose the varying value of polymer fragments (mass or volume) constituting oxyhydrate gel, which are relatively independent in the polymer sinter. The curves of the shift stress variation (τ) depending on the temperature are of the same nature as those of the viscosity variation.

Lytropic mesophase of yttrium oxyhydrate manifests thermotropic properties as well. Separation and differentiation of the above thermotropic mesophases is even performed at the stage of the gel formation, while the formation of a certain thermotropic structure capable of linear bound (mesophase property) takes place at a certain temperature. Possible components of such mesophases calculated quanta–mechanically are presented in fig. 11 (a , b , c).

Quanto–chemical calculations for the structures of polymer oxyhydrate yttrium complexes showed that gels are metastable systems where some types of ordering are observed. For the effective modelling of possible structures it is reasonable to use the combined methodology including the probabilistic modelling of the structure with the subsequent optimization of the complex geometry in the context of quanta–chemical methods similar to those in [1]. To this end, it is supposed to combine the monomeric unit of yttrium oxyhydrate with the similar one in the ratio of $1:1$ in the context of the model DENSON/MERA (the modification for the solutions) [12].

In this case, without considering the structure of the possible associate the atom coordinates for the two monomeric units taking part in the more probable contact may be determined. Then, the probable associate structure is assumed in an explicit form, its geometry being optimized in the context of the semiempirical quanta–chemical approximation ZINDO/1. To avoid the possibility of entering the local energetic minimum on completing the optimization the system is removed from the minimum by the Monte Karlo method in the field of forces MM^+ . Then, the structure is optimized again in the context of the semiempirical quanta–chemical approximation ZINDO/1. Such operations are performed until the stable constant value of the system's complete energy is achieved.

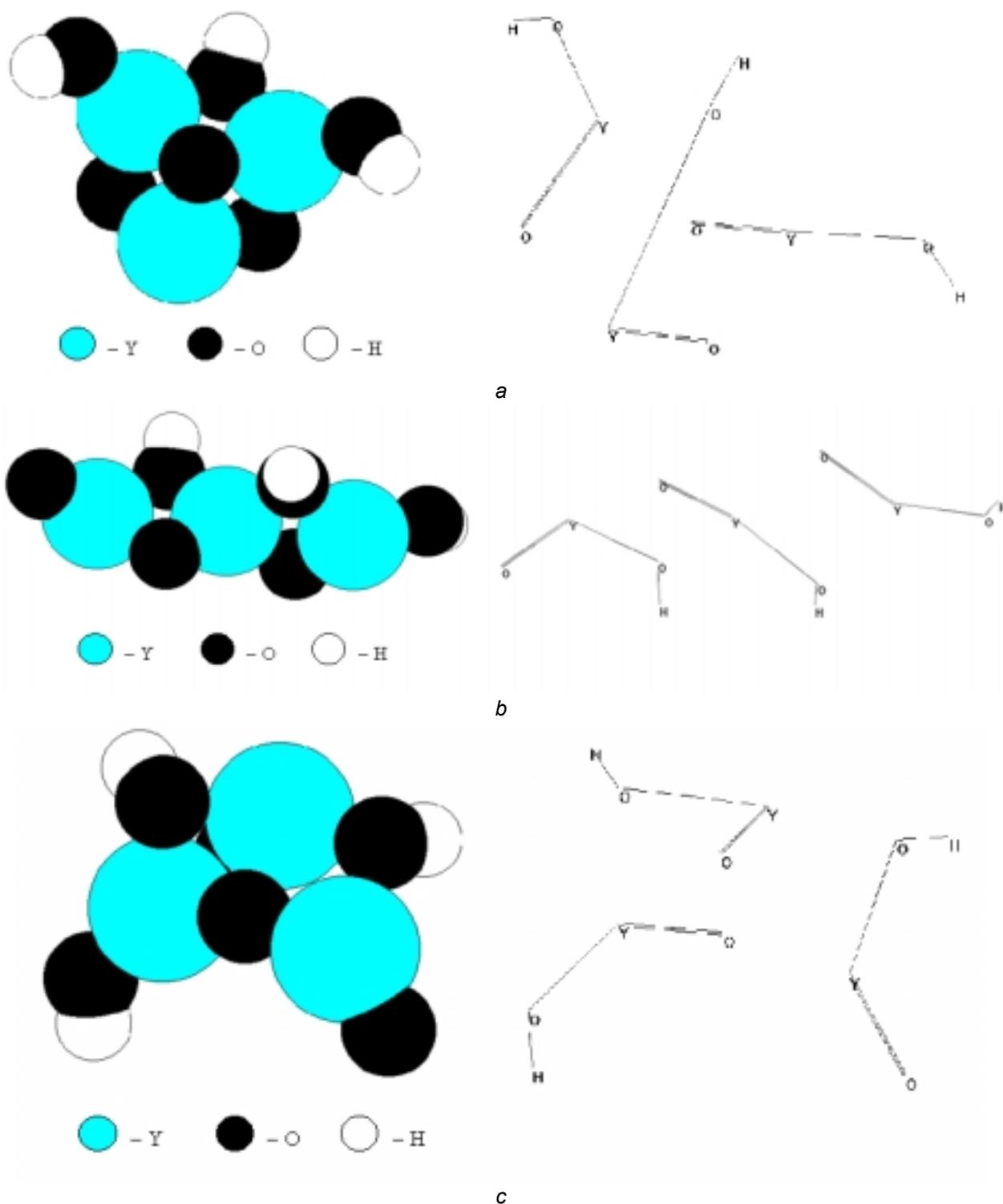


Fig. 11(a, b, c). Possible components of polymer oxyhydrate yttrium mesophases calculated quanto-mechanically

Modelling the structures of polymer compounds showed the presence of several close-in-energy structures in the gel phase. The gain in energy in adding the monomeric unit is presented in fig. 12. As shown in [12, 13], the dependences of the mean structural-sensitive frequency (ν'_m) (MSSF) calculated in the context of the model DENSON upon the temperature possess some peculiarities at the points of phase transitions. For mesogenetic substances there are maxima on the temperature dependence of MSSF near the phase transition “crystal — liquid crystal” and “liquid crystal — isotropic gel”.

Fig. 13 shows that the most energetically useful formation is that of a single structural unit-trimer for which the MSSF values were calculated at different temperatures. Fig.13 shows that maximum is observed at the temperatures of 13, 17, 26, i.e. at these temperatures the phase transitions with the formation of the mesogenetic phase may occur. The above temperatures were found to be close to the experimental ones: (13, 17) °C → 19.5 °C, 26 °C → 29.5 °C. The phase transition temperature 39.5 °C isn't confirmed by the calculations. We think that this temperature corresponds to the liquid crystal phase in which a more complex particle (not trimer, but a less stable one) is the single structure part.

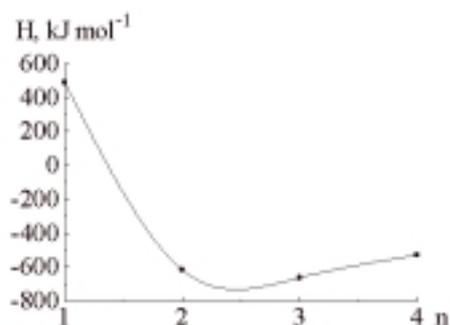


Fig. 12. Dependence of enthalpy of the monomer addition reaction on the degree of polymerization

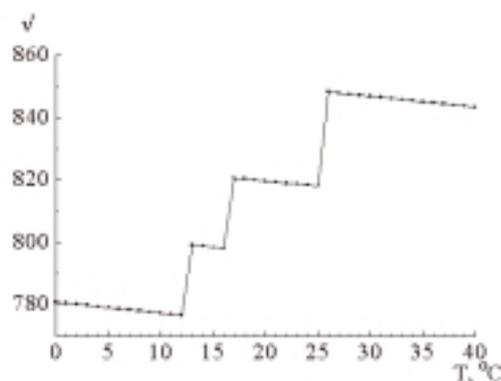


Fig. 13. Dependence of the structural-sensitive frequency (ν_m'') (MSSF) of trimer on the temperature

Heptamer $[\text{ZrO}(\text{OH})_2]_7$ is an energetically useful single structuring fragment of gel for zirconium oxyhydrate (fig. 14). The MSSF of this formation has the point of bend at the temperature of -4 °C (269K) (fig. 15), i. e. the mesophase formation takes place at very low temperatures, which were not considered in our experiments. Structural elements of such a mesophase may be presented as follows (fig. 16).

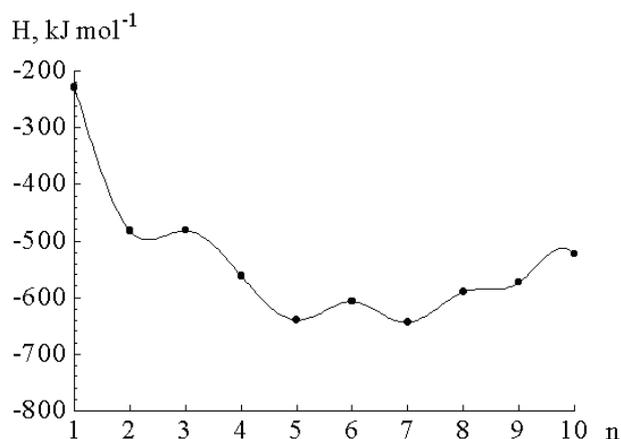


Fig. 14. Dependence of enthalpy of the monomer addition reaction on the degree of polymerization for $[\text{ZrO}(\text{OH})_2]_n$

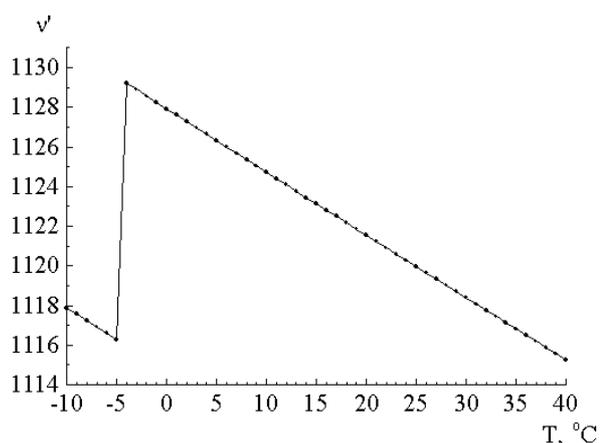


Fig. 15. Dependence of the structural-sensitive frequency (ν_m'') (MSSF) on the temperature for heptamer $[\text{ZrO}(\text{OH})_2]_7$

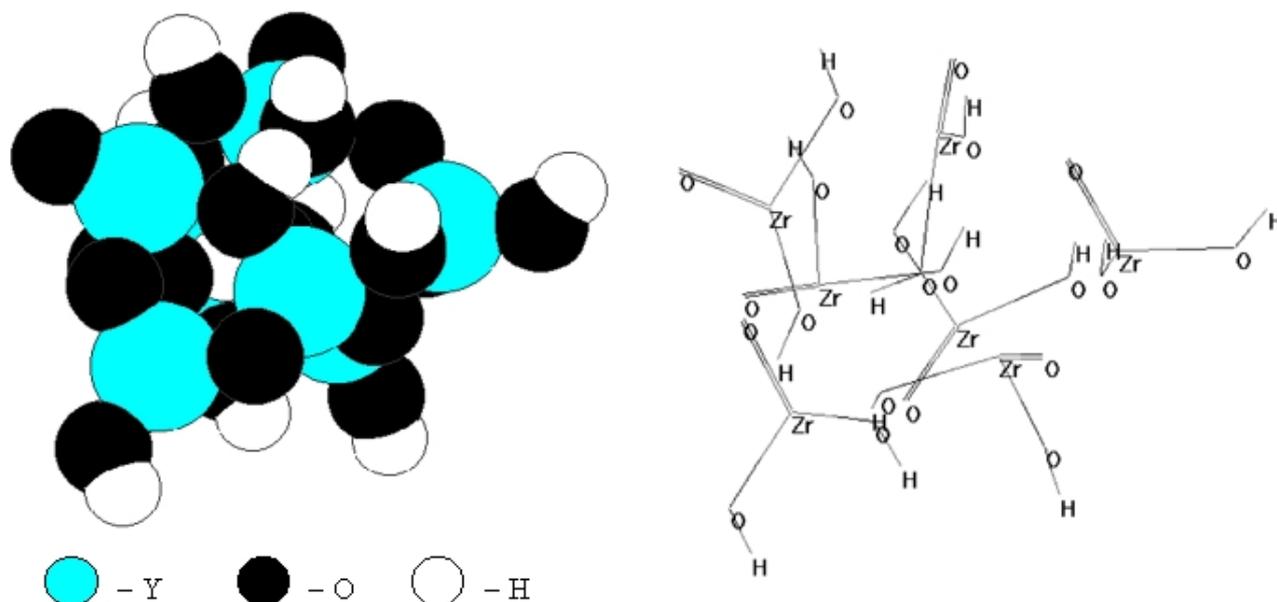


Fig. 16. The structure $[\text{ZrO}(\text{OH})_2]_7$

Conclusions

1. The chiral–smectic type of the planar texture of yttrium oxyhydrate gels is found. The spontaneous concentration differentiation of a substance in time and space is observed in colloid gel systems. The differentiation is of autowave (pulsating) nature (periodical selforganization), which takes the form of the so–called «frozen» helical whirls.
2. The optical density of YO HGs depending on the light wavelength reveals rather wide areas with the low optical density of gels (the formation of homeotropic–like structures with the reformation of helical whirls), i. e. the samples became optically transparent in a certain discrete interval of wavelengths. The effect of forming the chiral–smectic type structures explains the colouring of yttrium oxyhydrate gels.
3. Lyotropic mesophases of yttrium oxyhydrate manifest the thermotropic properties. Separation and differentiation of the above thermotropic mesophases is performed at the stage of the gel formation. The phase transitions with the formation of the mesogenetic phases take place at the temperatures of 13, 17, 26 °C. The above temperatures were found to be close to the experimental ones: (13, 17) °C → 19.5 °C, 26 °C → 29.5 °C. The mesophase of zirconium oxyhydrate forming at the temperature of –4 °C (269K) is found. The possible structures of the mesophase’s elementary units are proposed.

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