ХИМИЯ И БИОЭКОЛОГИЯ

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LAG EFFECT CAUSED BY MAGNETIC FIELD ACTING ON YTTRIUM AND FERRUM OXYHYDRATE GELS

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Introduction

The effect of weak magnetic and electric fields on sorption [1, 2], rheological [1] and optical properties of oxyhydrate gels was found in our previous works. Therefore, there is firm evidence to the fact that weak magnetic fields have effects on the colloid–chemical gel states.

The lag effect of the magnetic field on gel structure and gel properties, detected on the yttrium and ferrum oxyhydrates, is discussed in this paper as well as the possible way of its action.

1. Experimental

Yttrium oxyhydrate gel (YOG) was synthesized using the method [2] where pH =9,75, n=0,09 mole, t of synthesis is equal to 20°C, with the time of pattern aging equal to 1 year. Ferrum oxyhydrate gel (FOG) was synthesized using the method [1] where Cr/Fe = 0,15; nitriletrimethylphosphonic acid/Fe = 0,1; t of synthesis is equal to 20°C, with the time of pattern aging equal to 10 years.

The processes taking place in hard dry gel–like patterns of yttrium oxyhydrate under the static magnetic field 980 Oe (77986 A/m) have been studied. The exposure time of the magnetic field was 24 hours.

To study the sorption properties of the FOG pattern portion, it was put in contact with the potassium bichromate solutions for 24 hours. Then the sorbate was decanted and the quasi–equilibrium value of the sorption G, mmol/g was calculated using the concentration difference before and after the patterns contact with the sorbate. The relationship of “hard to fluidal” masses was 0,01 g/ml. The bichromate–ions concentration was determined by iodometric titration and the errors were calculated for three dimensions with 95% acceptance probability.

The structure and properties of oxyhydrate gels are mainly determined by the quantity of water contained in them and its degree of connectivity [4]. To evaluate the different form of structured water contained in the xerogel the yttrium oxyhydrate gel pattern was studied by thermogravimetric and differential thermal analyses using the derivatograph Paulik–Paulik–Erdey 3434–C with the heating rate equal to 10 °C/min. For different temperature intervals where the endoenergic effects (curves DTA) and the mass losses (curves TG) were observed the following values were calculated: the gross–composition of gel, the quantity of water, splitting out at different stages of dehydration (k_i), relative enthalpy (ΔH_i), equal to the relationship of corresponding areas under DTA curves. Since the value of the calibration factor for the T_i as well as the law of heat–absorption capacity in the given interval are unknown, it’s impossible to calculate the absolute value of the enthalpy [5].

The process of yttrium oxyhydrate gel dehydration consists of three stages. During the first stage with the temperature under 150°C one endoenergic maximum of dehydratation is observed, with the splitting out of adsorbed and pore water. During the second stage of dehydration with the temperature between 200 and 500°C the structured water, appearing as the result of splitting out of aqua–groups

and terminal hydroxo–groups oxolation, is splitting out. During the third stage of dehydration with the temperature interval equal to 530…750°C the strongly connected structured water appearing as the result of oxolation of ol–groups is splitting.

As a rule, each of these stages consists of some periods of dehydratation, i.e. the main dehydratational peak is divided into several ones. The presence of multiple–periods in each dehydratation stage can be explained by the existence of some pacemakers, which differ from each other by the conformational structure [6]. Depending on the conformation the structured water of one type will split out under different temperatures.

The thermograms of yttrium oxyhydrate gel pattern are given in Figs. 1, 2, 3. The values of dehydratation temperatures and the quantities of split water are given in Tables 1, 2.

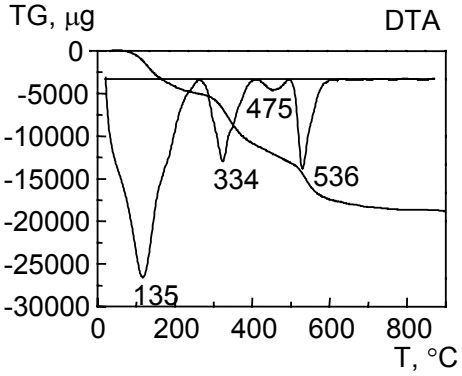


Fig. 1. The differential thermal analysis curves
of the yttrium oxyhydrate gel pattern before the magnetic field action

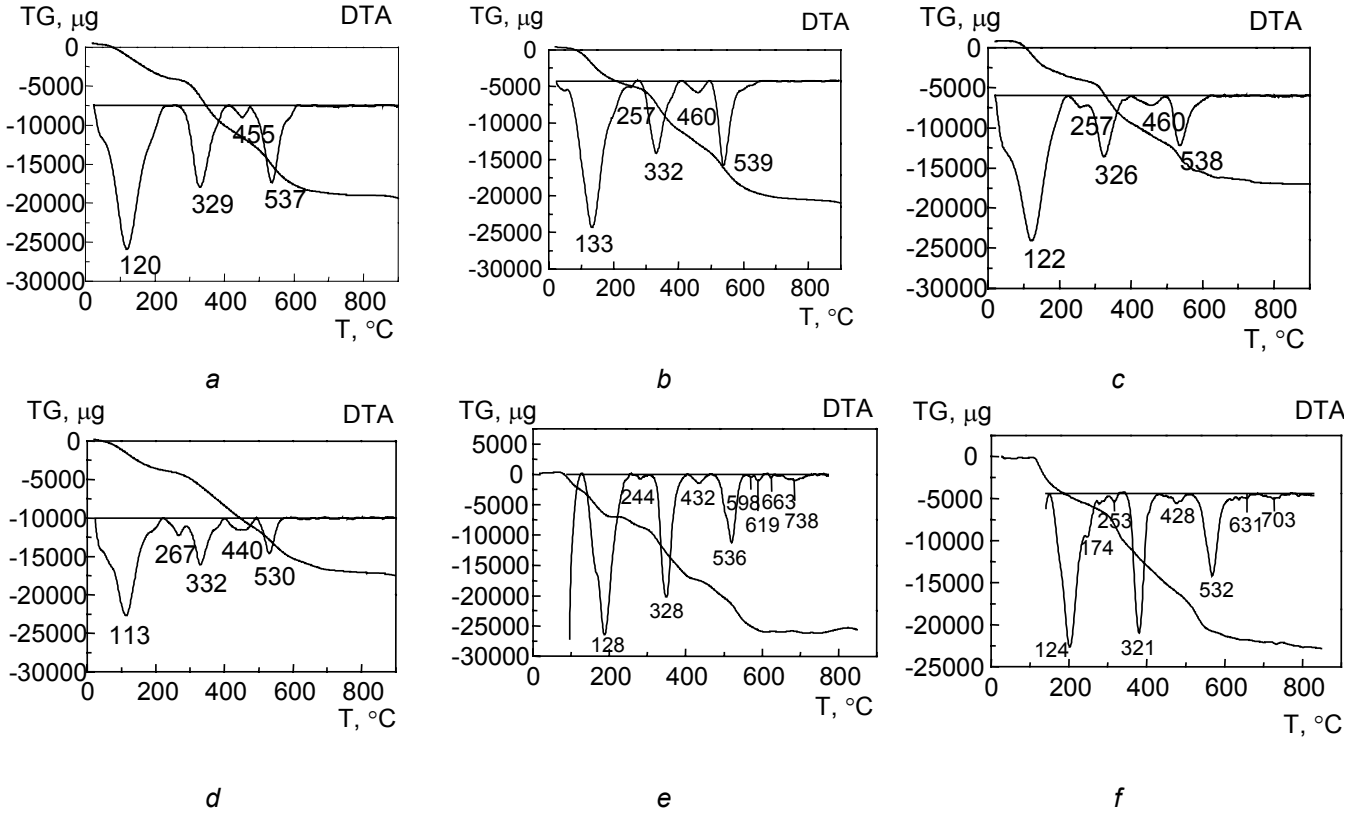
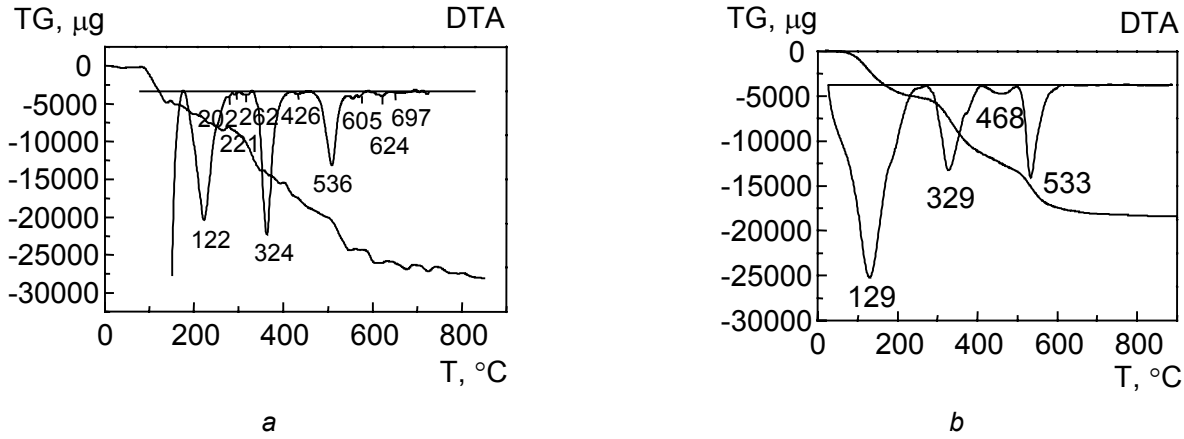


Fig. 2. The differential thermal analysis curves of the yttrium oxyhydrate gel pattern:

a — right after the magnetic field action;
b, *c*, *d*, *e*, *f* — in 2, 4, 24, 168, 336 hours after the magnetic field action correspondingly



a *b*

Fig. 3.The differential thermal analysis curves of the yttrium oxyhydrate gel pattern:
a, *b* — in 504, 720 hours after the magnetic field action correspondingly

Table 1

Temperatures of the stepwise yttrium oxyhydrate gel pattern dehydratation

№	*T*										
	I stage	II stage					III stage				
	1	2	3	4	5	6	7	8	9	10	11
1	135	—	—	—	334	475	536	—	—	—	—
2	120	—	—	—	329	455	537	—	—	—	—
3	133	—	—	257	332	460	539	—	—	—	—
4	122	—	—	257	326	460	538	—	—	—	—
5	113	—	—	267	332	440	530	—	—	—	—
6	128,6	—	—	245,2	327,6	432,3	535,6	597,5	619	662,9	738,2
7	125	209,4	—	251,6	322,4	428,6	532,5	588,9	608	631,2	—
8	120	201,8	220	262	323,6	424,8	535	—	604,6	623,7	692,4
9	129	—	—	—	329	468	533	—	—	—	—

1 — before the magnetic field action; 2 — right after the magnetic field action, 3,4,5,6,7,8,9 — in 2, 4, 24, 168, 336, 504, 720 hours after the magnetic field action correspondingly.

Table 2

The quantity of water (mol) split out during the process of yttrium oxyhydrate gel pattern dehydratation

№	*k*													
	I stage	II stage						III stage						sum
	1	2	3	4	5	6	sum	7	8	9	10	11	sum	
1	3,06	—	—	—	3,68	1,09	4,77	2,55	—	—	—	—	2,55	7,32
2	2,40	—	—	—	3,95	1,07	5,02	2,25	—	—	—	—	2,25	7,27
3	3,23	—	—	0,18	3,86	1,84	5,88	1,89	—	—	—	—	1,89	7,77
4	1,97	—	—	0,31	3,84	1,66	5,81	1,36	—	—	—	—	1,36	7,17
5	2,19	—	—	0,20	3,51	1,40	5,11	2,16	—	—	—	—	2,16	7,27
6	1,70	—	—	0,35	2,16	1,16	3,67	2,01	0,20	0,05	0,18	0,03	2,47	6,14
7	1,09	0,15	—	0,17	1,51	1,02	2,85	1,73	0,09	0,08	0,10		2	4,85
8	1,50	0,06	0,22	0,10	2,04	1,06	3,48	2,14		0,44	0,06	0,45	3,09	6,57
9	3,04	—	—	—	3,57	1,12	4,69	2,50	—	—	—	—	2,5	7,19

1 — before the magnetic field action; 2 — right after the magnetic field action; 3, 4, 5, 6, 7, 8, 9 — in 2, 4, 24, 168, 336, 504, 720 hours after the magnetic field action correspondingly.

2. Results and discussion

The effect of magnetic field on the oxyhydrate gels is a specific one. It could be quite natural to suppose that after a short–time increase the effect of the magnetic field must spontaneously and gradually decrease and disappear. But if we take into consideration the gel oxyhydrate system we can observe that right after action of the magnetic field on the system it does not change. The magnetic field effect manifests itself after some lag time.

For example in Fig. 4 the sorption isoterms of ion bichromate on ferrum oxyhydrate gel patterns are shown. In paper [1] it was observed that under the action of the constant magnetic field the sorption activity of oxyhydrate gels increases. For the pattern mentioned the influence of the magnetic field shows itself only after the week magnetic field action.

Similar lag effect can be seen in figs. 1, 2, 3 where the thermograms of yttrium oxyhydrate gel patterns are shown.

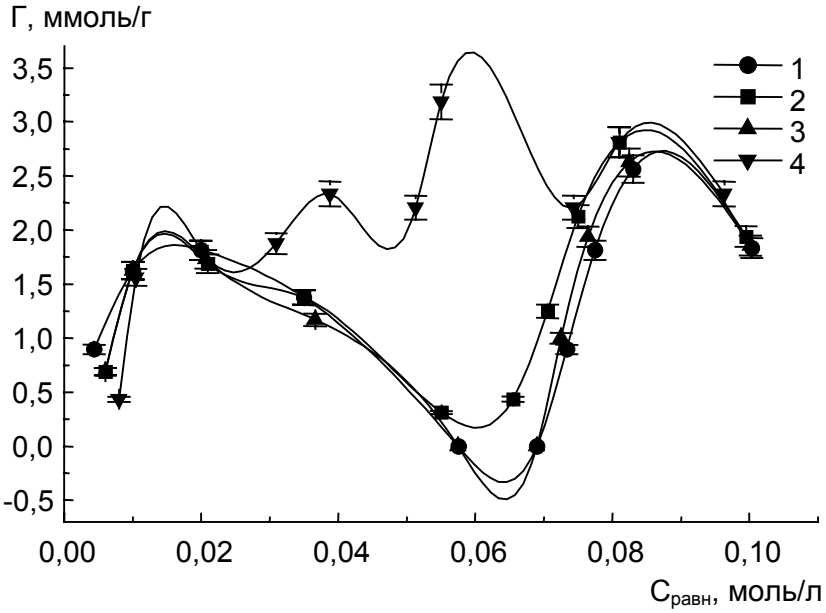


Fig. 4. Sorption isoterms of $Cr_2O_7^{2}$ ions on ferrum oxyhydrate gel patterns. The pattern is modified by nitriletrimethylphosphonic acid and ions bihromate; molar relationships Cr/Fe = 0,15; nitriletrimethylphosphonic acid/Fe = 0,1; the temperature of synthesis is equal to 20ºC; the time of exposure to constant magnetic field effect is 2 hours: 1 — before the exposure to constant magnetic field; 2,3,4 — right after the exposure to the constant magnetic field, in 24 hours, in 148 hours

The changes in the pattern are minimum right after the magnetic field action. Then the disproportionation of the water structure starts in yttrium oxyhydrate gel. It causes the dehydratation temperature and the quantity of water splitting out at each stage to change. The new stages of dehydratation appear. It is experimentally proved that the most noticeable differences in derivatograms before and after the magnetic field effect can be observed after the pattern treated by the magnetic field stays under ambient temperature for 7 days.

The lag effect can be explained as follows. The oxyhydrate molecules having energetically close conformations are combined into pacemakers. Thus, the synchronized polymer chain is formed. According to this conformational structure a double electrical layer (DEL) appears around the oxyhydrate fragments during gel phase. Some domain pattern is formed which possesses minimum surface energy.

Since gel system is a living one the self–organization processes are taking place in it. The spontaneous change of the conformational structure of gel fragments causes the change of DEL configuration. Constant magnetic field acts on the moving charged particles (aquated ions of DEL) when the gel is put into the special device. Pulsating movements of ions in gel phase or, in other words, the observation of the electric current into the second–class conductors was proved experimentally for the first time (Fig. 4).

Primarily, magnetic field alters the diffusive DEL and after that it changes the DEL structure organization. Then, the conformation of polymer oxyhydrate gel dipoles changes with some time lag as the DEL structure is the derivative of the oxyhydrate matrix structure, while the surface energy of pacemakers is minimum. After the action of the magnetic field is over the diffusive DEL acquires quasi–stability. The polymer oxyhydrate fragment changes its conformational structure very slowly as the restructuring is detained by the van der Waals intermolecular forces acting between the conformer elements. As a result the gel structure becomes different from the initial one only in a week or longer time period. In this regard the differentiation of the structured water in accordance with the new macromolecule configuration of polymer base strucure is observed (see Fig. 1, 2, 3).

In gel system under consideration the macromolecule practically does not break up but it changes its configuration, which can be proved by the balance of strucutred water in the yttrium oxyhydrate gel (Table 2). The van der Waals forces of elastic interaction act in the same directions and after a period of time the polymer macromolecules start their restructuring striving to the initial structure. In the process some bonds may break, which leads to the balance upset of structured water. The change in the oxyhydrate macromolecule structure is followed by the DEL change. In a month the yttrium oxyhydrate molecule acquires the conformational structure close to the initial one, which may be proved by the derivatograms of yttrium oxyhydrate gel obtained in 2, 3, 4 weeks after the magnetic field action.

Conclusion

The lag effect of the magnetic field on the gel properties of yttrium and ferrum oxyhydrate gels is discovered.

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