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STABILITY OF THE SUPERMOLECULAR STRUCTURE OF GELS OF LITHIUM TETRAALKYLBORATES BY THE ACOUSTO-OPTICAL METHOD

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The destructive action of ultrasonic radiation on hydrocarbon gels of [B(OR)$_4$]Li complexes has been investigated. It has been established that the destruction and relaxation of the macrostructure of these gels under the action of acoustic radiation depend on the time of this action and the voltage applied to them. The kinetic dependences of the change in the refractive index and in the dynamic viscosity of the gels being investigated were determined as the response of structurized solutions of the indicated complexes to ultrasound action. Mathematical models are proposed for quantitative estimation of the kinetic parameters of the destruction–relaxation of the supermolecular structure of the gels of the complexes being considered.

Viscoelastic thixotropic liquids and gels are of great importance in the technology of hydraulic breakage of poorly penetrable gas- and oil-bearing stratums [1, 2]. For increasing the filterability of these stratums, a dispersion (wedging) material is transported into the channels formed in them with the use of structurized liquids. In [3–7] it was established by the methods of rheometry, NMR-spectroscopy, small-angle X-ray scattering, and mass spectrometry that complexes of lithium tetraalkylborates [B(OR)$_4$[Li (R = C_4H_9–$C_{16}H_{33}$) in hydrocarbonic liquids polyassociate intermolecularly along the coordination bonds Li ... O and, with the participation of the forces of dispersion interaction between the alkyl groups (R ... R), form spatial chelating structures (Fig. 1). In low-permittivity liquids, these complexes swell, similar to polymers, with the formation of thermodynamically stable structurized systems [8–10]. The supermolecular structure of the solutions and gels of the indicated complexes, subjected to mechanical destruction under the action of a shear stress in the deformation regime, is restored with no change in the rheological properties [5, 6, 11]. The thermodynamic parameters of the thermal desorption of these compounds point to a high affinity of the complex alkoxides of boron and lithium to hydrocarbons [12].

In the present work, the macromolecular instability of hydrocarbonic gels of the complexes [*tert*-C_4H_9OB (OR)$_3$]Li (R = C_4H_9, C_7H_{15}, $C_{10}H_{21}$) exposed to ultrasonic vibrations of frequencies 0.7, 6.0, and 7.0 MHz was investigated by the methods of correlated photon spectroscopy, interferometry, and rheometry.

Objects and Methods of Investigations. Complexes of lithium *tert*-butyltrialkylborates were obtained by mixing of *tert*-C_4H_9OLi with B(OR)$_3$ without a solvent. These complexes were synthesized in an argon atmosphere with the use of dehydrated reagents.

The sizes of the particles present in hydrocarbonic solutions of lithium tetraalkylborate complexes were determined by the method of correlation photon spectroscopy in the process of structurization of these solutions and after their exposure to ultrasonic radiation (USR). The measured responses of the structurized systems to the external ultrasound action were obtained in the form of photonograms of the size distribution of particles in them and of the change in their refractive index as well as in the form of rheologograms of the change in the shear stress and in the dynamic viscosity of the solutions and gels of the complexes. The photonograms of the solutions of the complexes with concentrations ranging from 0.002 to 0.05 mole/liter were measured at a temperature of 295 K on a computer-aided CULTER-4 apparatus. As a radiation source, a helium-neon laser (λ = 630 nm) was used.

The rheological characteristics of the solutions and gels of the complexes being investigated were measured at a temperature of 295 K in the range of deformation rates 0.003–1300 sec^{-1} on a REOTEST-2 elastoviscometer with a

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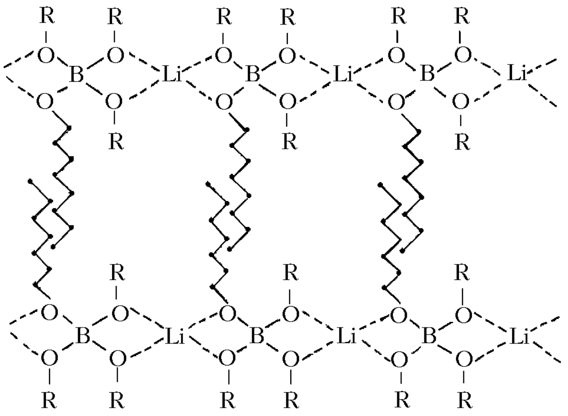


Fig. 1. Schematic diagram of the mechanism of intermolecular association of complexes of lithium tetraalkylborates.

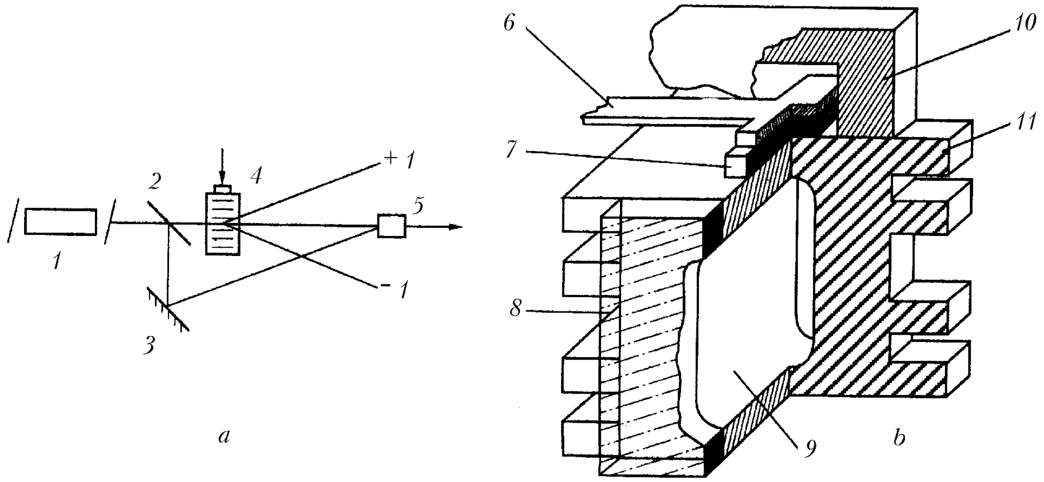


Fig. 2. Block diagram of an acousto-optical setup (a) and design of a cell (b): 1) helium-neon laser; 2) semireflecting mirror; 3) nontransmitting mirror; 4) photodetector; 5) acousto-optical cell; 6) electrode; 7) piezoelectric crystal; 8) glass windows of the cell; 9) space of the cell; 10) upper cover; 11) metallic body of the cell.

coaxial cylinder–cylinder working unit and on a PIRSP-03 shear rheogoniometer. The measurement error was ±3%. The dynamic viscosity of the solutions and gels of the complexes was determined by the formula

$$\eta = \tau/\gamma .$$

The change in the refractive index of the structurized solutions of the complexes, caused by the action of an ultrasonic radiation, was determined, with an accuracy of ±2%, with the use of an interferometric setup (Fig. 2a) consisting of a helium-neon laser 1 generating a coherent radiation of wavelength 630 nm and power of 3 mW, a semireflecting mirror 2, a nontransmitting mirror 3, a photodetector 4, and an acousto-optical cell 5 with an investigated structurized solution (gel) of a complex at a temperature of 293 K. The cell (Fig. 2b) had dimensions 50 × 40 × 30 mm and consisted of a ribbed metallic body 11 and an upper cover 10 hermetically closing electrode 6 and a piezoelectric plate 7 of dimension 3 × 4 mm. An investigated gel of a complex was placed in the space of cell 9 closed on two sides by transparent glass plates 8. A light beam penetrated to the space of the cell through the glass plates. The thermostating of the cell was performed with the use of an air thermostat.

TABLE 1. Distribution of Particles of Associates [*tert*-$C_4H_9OB(OC_7H_{15})_3$]Li in a Heptane Solution at 295 K

c_c = 0.002 mole/liter		c_c = 0.004 mole/liter		
d, nm	*N*, %	*d*, nm	*N*, %	
			before USR action	after action of USR of frequency 0.7 MHz
3.0	0.5	10.0	—	4
4.4	5	21.5	—	4
6.5	16	46.4	—	4
9.5	15	100	—	4
13.9	4	215	8	31
20.4	0.3	464	8	8
56.2	1	2150	72	31
1300	56	2500	—	8
4700	2.2	4640	12	6

For the purpose of determining the change in the intensity of the light passing through the gel deformed by the ultrasonic radiation, two coherent light beams were formed and directed to one and the same point on photodetector 4 (Fig. 2a) with the use of mirrors 2 and 3. In this case, the period of the optical interference was determined by the angle of intersection of the light beams, and the spatial positions of the light-intensity maxima were determined by the phase difference of the interfering beams. The angle of intersection of the beams remained unchanged in the process of measurements and was equal to 1^o. One of the beams passed through the cell and the other propagated in the air. The change in the density of the gel under the action of acoustic vibrations led to a change in its refractive index and, in accordance with Snell's law, to a change in the velocity (intensity) of the light wave.

An acoustic vibration was excited and transported to the gel in the following way. An a.c. voltage was applied to electrode 6 and the metallic body of cell 11 used as the second electrode (Fig. 2b). Under the plate of the piezoelectric element 7, on the surface of the body of the cell 11 there arised a piezoelectric effect that gave rise to an ultrasound beam. This beam was directed to the space of cell 9 and acted on the gel of the complex. The power of the acoustic vibration excited in this way was 100 mW. It was estimated by the first maxima of the Raman–Nath light diffraction (orders +1, −1) relative to the standard liquid (water, methanol). The resonance acoustic effects (standing waves) were excluded due to the design of the cell containing convexities at its bottom. The acoustic power was low and, therefore, cavitation effects were absent. The gel in the cell was subjected uninterruptedly to harmonic and impulse actions during periods of time lasting from 15 min to 2–3 h. In the case where the gel was acted upon by ultrasonic-radiation pulses of different durations in the form of a meander, we considered only pulses with t_p = 100 and 300 μsec, causing a pronounced destruction of the gel.

Results and Discussion. *Character of the change in the photonograms depending on the concentration of the complexe.* The photon correlation spectrum of a solution or a gel of a complex is defined by the function of the size distribution of particles

$$K = \frac{D3\pi\eta d}{T},$$

obtained from the formula

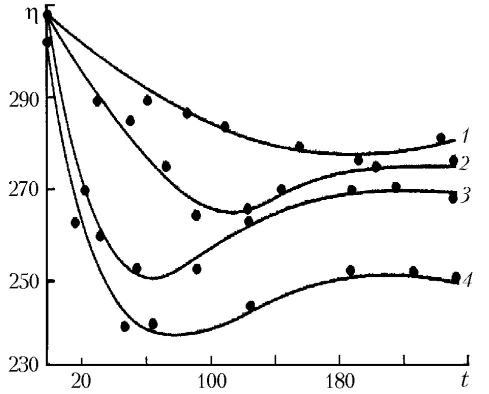
$$D = \frac{KT}{3\pi\eta d}.$$

The kinetic curves of the distribution $K(t)$ contain rapidly and slowly decaying portions corresponding to the particles with sizes from several tens of angstroms to several hundreds of nanometers. The dependence of the size distribution of particles (associates) on their concentration in a complex is presented in Table 1. The photonograms of the solutions of the complexes point to the polydispersity of their particles. When the concentration of lithium *tert*-butyltriheptylbo-

TABLE 2. Dependence of the Time Parameters (min) of the Transformation of Gels of Complexes into Liquids on the Modulation, Power, and Pulse Duration of USR of Frequency 7.0 MHz for 25 min

System	c_c, wt. %	Harmonic USR		Impulse USR	
		U_{in} = 15 V	U_{in} = 30 V	U_{in} = 30 V, t_p = 100 μsec	U_{in} = 30 V, t_p = 300 μsec
[ROB($OC_{10}H_{21})_3$]Li-decane	5	—	35	35	28
[ROB($OC_{10}H_{21})_3$]Li-heptane	3	15	12	13	10
[ROB($OC_7H_{15})_3$]Li-heptane	5	30	26	27	20
[ROB($OC_7H_{15})_3$]Li-decane	3	25	20	17	15

Note. R = *tert*-C_4H_9.



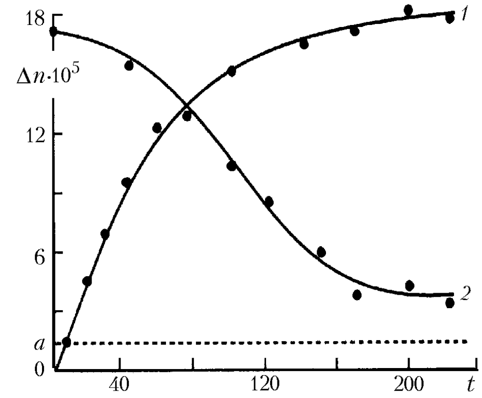


Fig. 3. Change in the viscosity of the gel [*tert*-$C_4H_9OB(OC_7H_{15})_3$]Li (5 wt. %) in heptane as a function of the time of action of an ultrasonic radiation with a frequency 650 kHz at different values of the applied voltage: U = 30 (1), 60 (2), 120 (3), and 600 V (4). t, min; η, Pa·sec.

Fig. 4. Kinetics of the ultrasonic destruction (1) — relaxation (2) of the structure of the gel [*tert*-$C_4H_9OB(OC_7H_{15})_3$]Li (5 wt. %) in heptane. t, sec.

rate in a solution increases, the sizes of the polyassociates increase sharply and the molecular-mass distribution becomes narrower. In the case of action of an ultrasonic radiation on a more concentrated solution of a complex, the largest particles of the polyassociates are destroyed; their sizes and polydispersity change as in the case where the solution is diluted (Table 1) or the supermolecular structure of the gels of the complexes is subjected to a mechanical deformation [5, 6, 11]. After the ultrasonic-radiation action is terminated, the sizes of the particles and the molecular-mass distribution of polyassociates in a slightly viscous solution are restored for 25–30 min, and they are not restored in gels.

Influence of the character of ultrasonic-radiation action on the stability of gels of the complexes. Since the destructive of the macrostructure of the gels being investigated is followed by its relaxation, the destructive action of an ultrasound radiation on these gels depends on their molecular weight, the concentration of the complexes, the voltage applied to them, the modulation of the ultrasonic radiation, and the duration of the radiation pulses (Table 2). It was established that the time of transformation of the gels of the complexes into the liquid state is also determined by the type of modulation of the ultrasonic radiation. For example, the macrostructure of gels of the complexes (Fig. 1) is less stable in the case where they are acted upon by an ultrasonic radiation with a pulse modulation than in the case of their exposure to harmonic vibrations (Table 2). However, the stability of the structurized hydrocarbonic solutions of lithium *tert*-butyltrialkylborates depends to a greater extent on the concentration, the structure parameters of a complex (the length of the alkyl fragment), the voltage applied, and the duration of action of ultrasonic radiation than on

TABLE 3. Kinetic Parameters of Destruction–Relaxation of the Macrostructure of Hydrocarbon Gels [*tert*-$C_4H_9OB(OR)_3$]Li

c_c, wt. %	By the destruction model		By the relaxation model		
	$\Delta n_0 \cdot 10^5$	k_d, sec^{-1}	$\Delta n_0 \cdot 10^5$	k_r, sec^{-1}	$a \cdot 10^5$
			C_7H_{15}-*heptane*		
5	19.3	0.015	16.9	0.009	1.4
7	20.3	0.0088	17.5	0.0055	2.7
10	19.8	0.0061	17.6	0.0044	4.1
			C_7H_{15}-*decane*		
3	14.2	0.0058	14.7	0.0081	4.1
5	17.4	0.0055	14.8	0.0048	2.7
7	18.7	0.0046	11.1	0.0041	0
10	14.6	0.0043	14.0	0.0037	0
			$C_{10}H_{21}$-*decane*		
3	24.8	0.0071	18.4	0.0053	0
7	22.1	0.0055	16.8	0.0048	0

the type of modulation. The destructive action of this radiation on the macrostructure of gels of the complexes manifests itself directly as a change in the dynamic viscosity and in the refractive index of the gels depending on the voltage applied and the duration of the ultrasound action (Figs. 3 and 4). The kinetic dependence of a viscous gel flow in the field of ultrasonic vibrations of frequency 0.65 MHz is extremum in character. A sharp decrease in the viscosity of the gel [*tert*-$C_4H_9OB(OC_7H_{15})_3$]Li in heptane at the initial period (20–80 min) of its interaction with the ultrasonic radiation points to the fact that the intermolecular bonds (Li ... O and R ... R) relax slowly in a solution of a polyassociated complex (Fig. 1). In this period, the equilibrium destruction–relaxation process is characterized by a maximum rate of rupture (weakening) of the associative bonds. Once elastic energy is accumulated in the structurized system, its spatial macrostructure begins to relax with increasing rate. This additive effect manifests itself as an increase in the structural viscosity (Fig. 3) and in the refractive index of the gel (Fig. 4).

On the basis of an analysis of the experimental data on the change in the refractive index of the gels of the complexes being investigated, we constructed one-factor mathematical models for determining the kinetic parameters of destruction of the supermolecular structure of these gels under the action of an ultrasonic radiation

$$\Delta n = \Delta n_0 \,(1 - \exp\,(-\,k_d t)) \tag{1}$$

and the parameters of reduction (relaxation) of their macrostructure after termination of the ultrasound action

$$\Delta n = \frac{\Delta n_0}{1 + (k_r t)^4} + a\,. \tag{2}$$

The adequacy of models (1) and (2) in an actual situation, determined by the Pearson criterion, was 95%. The mathematical-model parameters Δn_0, k_d, k_r, and a, characterizing the kinetics of destruction–relaxation of the supermolecular structure of gels of the complexes, were determined in our experiment with the use of a computational program and are presented in Table 3. These data show that the values of Δn_0 for the stages of destruction and relaxation differ, on the average, by 10%. This points to the fact that the rates of destruction and restoration of the structures of the gels are not equal: the first rate is as a rule higher than the second one, and the difference between them is especially large in the case where there is no structural correspondence between the complex and hydrocarbon and the molecular mass of the complex–hydrocarbon system is increased (Table 3).

Complex–hydrocarbon systems with a small molecular mass are most sensitive to the action of an ultrasonic radiation. This sensitivity decreases with increase in the concentration of the complex in a solution (Table 3). As judged from the values of the coefficient a, the parameters of the structurized systems, which are most sensitive to the

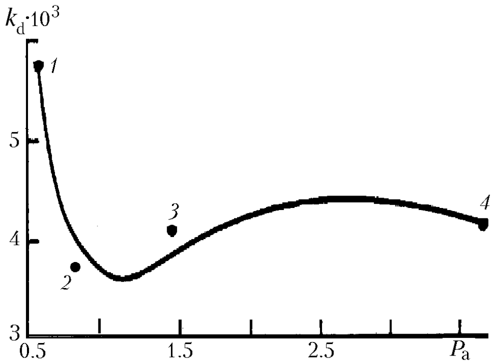


Fig. 5. Dependence of the rate of destruction of the structure of the gel [*tert*-$C_4H_9OB(OC_7H_{15})_3$]Li (3 wt. %) in decane on the power of acoustic vibrations and the multiplicity of the action: 1–4) multiplicity of ultrasound action on the gel. P_a, W; k_d, sec^{-1}.

vibrations caused by an acoustic radiation, are not restored to the initial values corresponding to the state preceding the ultrasound action. This is supported by the results of many experiments on the destruction–relaxation of a gel of a complex. "The sensitivity" of the structure of a gel to ultrasonic radiation increases markedly only after the first act of radiation action; in the next destruction–relaxation cycles, the rate of destruction of the gel remains practically unchanged even when the acoustic power and the multiplicity increase (Fig. 5). Analysis of the data on the change in the refractive index (Fig. 4) and in the dynamic viscosity (Fig. 3) of the gels being investigated shows that the changes in the macrostructure of these gels, caused by the action of ultrasonic radiation, are irreversible. Unlike the mechanical deformation, arising under the action of a shear stress [5, 6, 12], the action of an ultrasonic radiation on these gals, evidently, leads to the appearance of larger molecular destructions in them, and these destructions are not restored with time.

NOTATION

a, coefficient of change in the refractive index of structurized solutions caused by their partial destruction; c_c, concentration of a complex in hydrocarbon, wt. %; D, coefficient of selfdiffussion; d, diameter of particles, nm; Δn_0, maximum change in the refractive index; Δn, change in the absolute index of refraction of a light beam for the time t; K, coefficient of size distribution of particles; k_d, k_r, coefficients characterizing the rate of change in the refractive index of a structurized solution of a complex under the action of an ultrasonic radiation and after the termination of this action, sec^{-1}; N, number of particles, %; P_a, power of an acoustic vibration, W; T, absolute temperature, K; t, time of destruction–relaxation of the macrostructure of a gel, sec; t_p, duration of a pulse, μsec; U_{in}, power of an ultrasound action, V; γ, rate of a deformation shift, sec^{-1}; η, dynamic viscosity, Pa·sec; λ, wavelength of a coherent radiation, nm; τ, shear stress, Pa. Subscripts: a, acoustic vibration; r, restoration of the gel macrostructure; in, power of the ultrasound action at the input; c, complex; d, destruction of the gel macrostructure; p, pulse.

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