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Effect of Magnetic and Mechanical Fields on Phase Liquid Crystalline Transitions in Solutions of Cellulose Derivatives

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1. Introduction

Phase diagrams of multicomponent systems provide full information on the thermodynamic compatibility of components in wide concentration and temperature ranges. One of the first phase diagrams of polymer–solvent systems was published by Papkov et al., (1937), Rogovin et al. (1937), Kargin et al. (1939). In 1941, the works of Tager & Kargin (1941) devoted to the thermodynamics of polymer solutions were published. From the end of the 1940s, systematic research into the thermodynamic properties and construction of phase diagrams of polymer solutions have been performed at the Laboratory of Colloid Chemistry (at the Polymer Chair with 1958), Ural State University. Over the course of sixty years, phase diagrams have been constructed for hundreds of polymer systems with amorphous and crystalline phase separations. Many of these data were included in textbooks, monographs, and reviews: Tager (2007), Papkov (1981), Nesterov & Lipatov (1987), Vshivkov (1991), Chalykh et al. (1998), Malkin & Kulichikhin (1996), Vshivkov et al. (1998), Vshivkov & Rusinova (1998, 2001), Rusinova & Vshivkov (1997), Klenin (1995). The phase liquid crystalline transitions of the cellulose derivatives solutions are studied at the polymer chair of Ural State University last ten years.

Academician Kargin was the first who described the ability of polymers to produce mesophases. In 1941, he wrote "interactions between big molecules is rather strong even when the interaction between individual units is weak. As a result, this can lead to the orientation of big molecules in one common direction". In 1956 Robinson (1956, 1958) has discovered, that poly(γ-benzyl-L-glutamate) (PBG) can form the liquid crystals in concentrated solutions in chloroform, methylene chloride, trichlorethane, dioxane, *m*-cresol. Flory (1956) has suggested the phase diagram for a polymer – solvent system with the liquid crystalline transition. At a later date such diagrams were built for the systems: PBG – DMF (Wee & Miller, 1971), polycarbobenzoxyline – DMF (Miller et al., 1974, 1978), poly-*p*-benzamide – DMA (Papkov et al., 1974), poly-p-benzamide – DMA, LiCl (Iovleva et al., 1976), poly(*p*-phenyleneterephthalamide) – H_2SO_4 (Papkov & Kulichikhin, 1977, Andreeva et al., 1981), PBG – ethylene chloride, PBG – benzyl alcohol (Sasaki et al., 1983), poly(*p*-phenyleneterephthalamide) – H_2SO_4 – water (Nakajima et al., 1978), PBG – *m*-cresol (Kiss & Porter, 1977), copolymer on the bases of p-phenylenediamine + terephthalic acid and 4,4"-diphenyldicarboxylic acid) – H_2SO_4 Lukashova et al. , 1978), PBG – DMF and PBG –

dicloracetic acid (Konevets et al., 1985), poly(*p*-benzamide) – DMA – LiCl (Salaris et al., 1976), polyhexylisocyanate and poly(50 % butyl + 50 % p-anisole-3-propyl)isocyanat in tetrachlorethane (Aharoni & Walsh, 1979), copolymer on the bases of *p*-phenylenterephyhalaamide + benzimidazole) – H_2SO_4 (Iovleva & Banduryan, 2010).
The influence of a magnetic field on the liquid crystal structure was studied by Meuer (1968), de Gennes (1968). The authors have considered such a field distortion of the cholesteric structure and find that the transition to complete nematic order occurs at a critical field strength given by

$$Hc = \frac{\pi^2}{2}\left(\frac{K_{22}}{\Delta\chi_m}\right)^{1/2}\frac{1}{p_0} \quad (1)$$

Where p_0 is the zero field pitch, $\Delta\chi_m$, the diamagnetic anisotropy of the liquid crystal, K_{22} , the twist elastic constant. As the field increases the pitch is predicted to oncrease slowly at first and then diverge logarithmically as the critical field is approached. The theory has been verified for lyotropic liquid crystals of PBG in a number of different solvents (Chandrasekhar, 1977, Iizuka, 1973, DuPre & Duke, 1974, 1975, DuPre et al., 1976, 1977, Patel & DuPre, 1979). Molecules of liquid crystals orient themselves in the magnetic field so that their long chains are oriented parallel to the magnetic field lines (Miller, 1978). This orientation is associated with the molecular anisotropy of macromolecules rather than the existence of permanent magnetic moments.
The LC state in solutions and melts of cellulose derivatives was characterized later on 1970–1980s (Kulichikhin & Golova, 1985, Meeten & Navard, 1982, Bhadani & Gray, 1983, Navard & Haudin, 1981, Yunusov et al., 1982, Iovleva, 1989, Vshivkov et al., 2006, 2007, Vshivkov & Rusinova, 2007, 2008). Molecules of cellulose and cellulose derivatives are characterized by a rigid helical conformation and, hence, they are capable of ordering and formation of cholesteric liquid crystals in concentrated solutions. Investigation of the LC state in polymer solutions is of evident practical importance because, owing to the ability to orient under the action of external fields, such solutions are used for the preparation of high-modulus fibers. To control the above processes, the knowledge of phase diagrams for the systems under processing is crucial. However, data on the phase diagrams of such systems in the applied magnetic and mechanical fields are not numerous (Vshivkov & Rusinova, 2007, 2008). The goal of this work is to study phase liquid crystalline transitions of cellulose derivative solutions in magnetic and in a shear stress fields for the following systems: CEC – DMA, CEC – DMF, CEC – mixture of trifluoroacetic acid with methylene chloride, HPC – ethanol, HPC – acetic acid, HPC – DMA, HPC – DMF, HPC –water and poly(γ-benzyl-L-glutamate) (PBG) – DMF.

2. Results and discussion

2.1 Experimental

Cyanoethyl cellulose (CEC) sample with a degree of substitution of 2.6 and M_w= 1.9x105 and hydroxypropyl cellulose (HPC) samples with a degree of substitution of 3.4 and M_w=9.5x10^4 (HCP-1), 1.4x10^5 (HPC-2), and 1.15x10^6 (HPC-3) were used. According to X-ray studies, degree of crystallinity of HPC samples did not exceed 15%. The degree of crystallinity for the CEC samples was 35%. All X-ray measurements were performed on a DRON-13

diffractometer (Cu Kα-irradiation). The CEC and PBG sample with M_η = 2.4× 10^5 were synthesized at the laboratory of the Institute of Macromolecular Compounds, Russian Academy of Sciences.

Dimethylformamide (DMF), dimethylacetamide (DMA), acetic acid (reagent grade), twice-distilled water, ethanol and a 1 : 1 (by mass) mixture of trifluoroacetic acid with methylene chloride were used as solvents. The polymer solutions were prepared in sealed ampoules for several weeks at 298 (water), 340 (in ethanol), 350 K (DMF, DMAA, and TFAA–methylene chloride mixed solvent).

Phase-transition temperatures T_{ph} were estimated by the cloud-point method. The solution temperatures were varied at a rate of 12 K/min. The structure of solutions was examined with the help of an "Olympus BX-51" polarization microscope. A polarization photoelectric setup was used to determine the type of phase transition in solutions: a sealed ampoule containing the transparent polymer solution was placed in the gap between the crossed polaroids and the temperature of the ampoule was decreased. The polarized light of an LGN-015 He–Ne laser was transmitted through the polaroids in the direction normal to the ampoule containing the solution. When the solution was transparent (isotropic) the intensity of the transmitted light was zero. As the system became turbid upon variation in temperature or increase in the concentration of solution, the transmitted light intensity increased. This indicated formation of the anisotropic phase, that is, the LC phase transition. Experiments in the magnetic field were performed using a setup generating a constant magnetic field with an intensity of up to 15 000 Oe (Fig. 1).

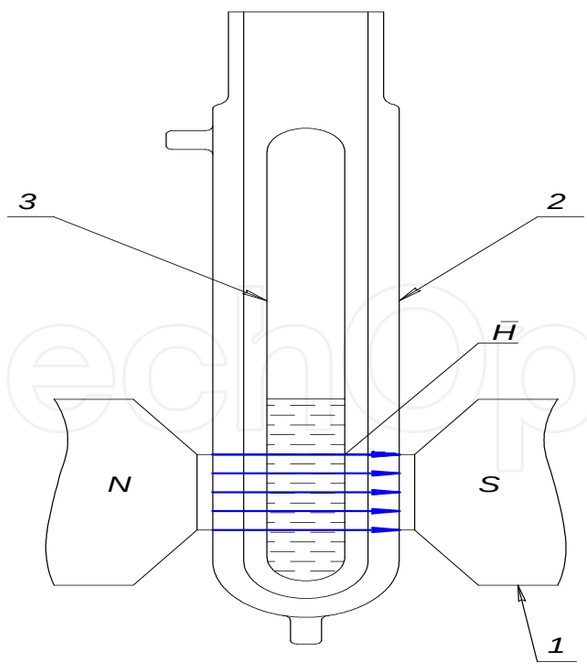

Fig. 1. Schematic presentation of the magnetic facility: (1) electromagnet tips, (2) the thermostating jacket and (3) the ampoule with the test solution. H is the magnetic field vector.

The sealed ampoule containing a transparent polymer solution was placed between the magnet poles. The magnetic field vector was directed normal to the solution layer (~5 mm thick) in the sealed ampoule. The temperature of solution was varied with the thermostating jacket, and the onset temperature of opalescence development was measured. This temperature was related to the appearance of the LC state. The coefficients of magnetic susceptibility χ were determined by means of a vibration magnetometer. The values of χ are presented in the table 1. The energy of the magnetic field E stored by the solution volume unit was calculated via equation $E=\chi H^2$, where H is the magnetic intensity.

System	$-\chi \cdot 10^7$
HPC-1	18,1
CEC	5,3
HPC-1 – ДМА (ω_2=0.5)	6,9
CEC - ДМА (ω_2=0.5)	6,7
HPC-1 – Water (ω_2=0.5)	3,4
HPC-1 – CH_3COOH (ω_2=0.3)	71,3
PBG	78,8
PBG – DMF (ω_2=0.4)	2,3

Table 1. The value of χ for the studied systems.

The phase transition temperature under dynamic conditions was measured using two methods: (1) a polymer solution that occurred in the isotropic state at elevated temperatures was placed in a gap between a glass rotor and a stator of the plastoviscometer. The shear rate was set constant, and the working unit was cooled at a rate of 12 K/h. A temperature corresponding to the onset of solution opalescence was taken as the phase transition temperature. (2) a polymer solution was placed in a metallic working unit of the rheometer HAAKE MARS. The shear stress was measured as a function of temperature, and viscosity η was calculated. The temperature corresponding to a sharp change in the run of the η – T curve was taken as the phase transition temperature T_{ph}.

2.2 The HPC, CEC and PBG solutions in organic solvents

2.2.1 Influence of the molecular weight of polymers on the phase liquid crystalline transitions

The boundary curves delimiting transparent isotropic and opalescent anisotropic solutions for HPC-1–DMA, HPC-2–DMAA, HPC-1–ethanol, HPC – acetic acid, HPC-2–ethanol, CEC–DMA, CEC–DMF, CEC–(methylene chloride/TFAA) and PBG – DMF systems are determined. Under conventional light, the concentrated solutions of HPC and CEC are opalescent. This is suggests formation of cholesteric liquid crystals.

Figures 2 a – c show boundary curves delimiting transparent isotropic and opalescent anisotropic solutions for solutions of the polymers with the different molecular weights.

It is seen, that as the molecular mass of the polymer increases, the boundary curve corresponding to the development of anisotropic LC phase in solutions is shifted to lower concentrations. This behavior agrees with the existing theoretical concepts (Flory, 1956). According to Flory, the critical concentration of a polymer, φ_2^*, above which the LC order arises, is related to the asymmetry of macromolecules x (the length-to-diameter aspect ratio) through the following relationship: $\varphi_2^* = \frac{8}{x}(1-\frac{2}{x})$. As the molecular mass of the polymer increases, the degree of anisometry of macromolecules x increases; as a result, φ_2^*

decreases. The boundary curves of the HPC-1 and HPC-2 in acetic acid coincide practically, because the molecular weights of these samples are not too different.

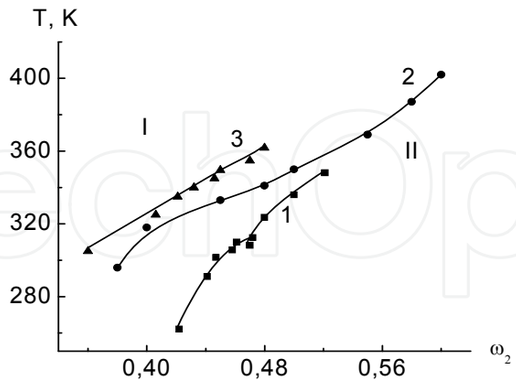

Fig. 2 a. Boundary curves for the systems: (1) HPC-1 – ethanol, (2) HPC-2 – ethanol, (3) HPC-3 – ethanol. I – isotropic solutions, II – anisotropic solutions.

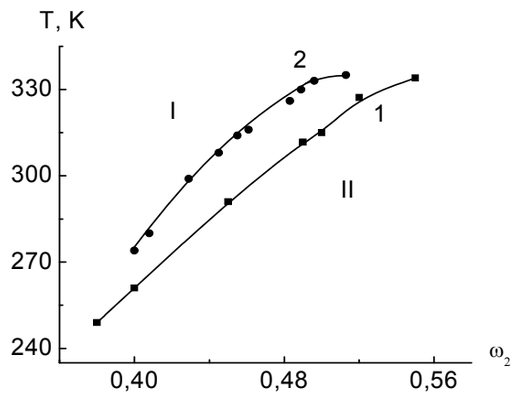

Fig. 2 b. Boundary curves for the systems: (1) HPC-1 – DMA, (2) HPC-3 – DMA. I – isotropic solutions, II – anisotropic solutions.

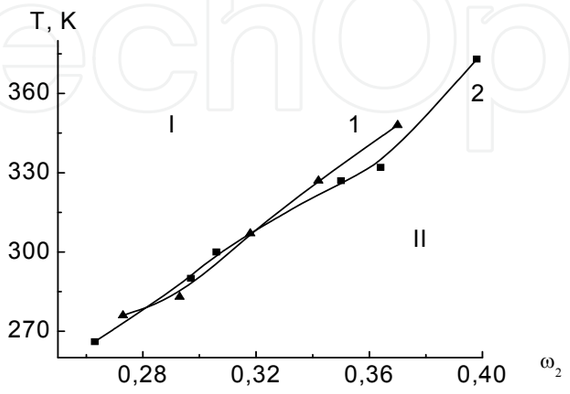

Fig. 2 c. Boundary curves for the systems: (1) HPC-1 – acetic acid, (2) HPC-2 – acetic acid. I – isotropic solutions, II – anisotropic solutions.

2.2.2 Influence of the solvent nature on the phase liquid crystalline transitions

Figures 2 d – 2 g show the boundary curves for the polymer solutions in the different solvents. It is seen from these figures and from the table 2, that as the solvent polarity is increased (solvent dipole moment μ is increased), the LC phase appears at higher concentrations and lower temperatures since with an increase in polarity, a solvent ruptures bonds between macromolecules to a higher extent. It is seen, that DMA and DMF are the best solvents of the cellulose derivatives. The cellulose and cellulose derivative molecules may form the hydrogen bonds between the chains. So the good solvent has to be also an electron donor. This ability is determined by the ionization potential φ. As φ is decreased, ω_2^* is increased, that is such solvent is better.

Solvent	μ dipole moment, D [61]	φ-ionization potential, eV [62]	ω_2^* (mass fraction) T=298 K			
			HPC-1	HPC-2	HPC-3	CEC
DMA	3,86	≤9,65	0,45		0,43	0,42
DMF	3,81	≤10,16				0,42
ethanol	1,69	10,25	0,44	0,38	<0,36	
acetic acid	1,74	10,35	0,3	0,305		
water	1,84	12,59	0,25	0,25	0,195	

Table 2. Physical parameters of the solvents and critical polymer concentration ω_2^*, above which the LC order arises. T = 298 K.

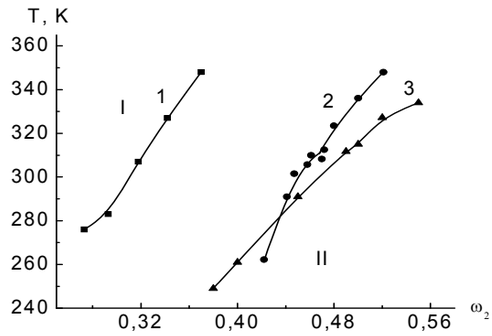

Fig. 2 d. Boundary curves for the HPC-1 solutions in (1) acetic acid, (2) ethanol, (3) DMA. I – isotropic solutions, II – anisotropic solutions.

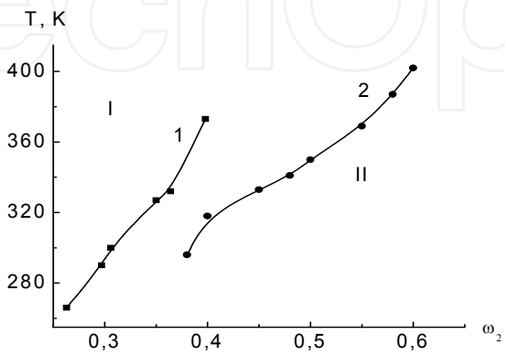

Fig. 2 e. Boundary curves for the HPC-2 solutions in (1) acetic acid, (2) ethanol. I – isotropic solutions, II – anisotropic solutions.

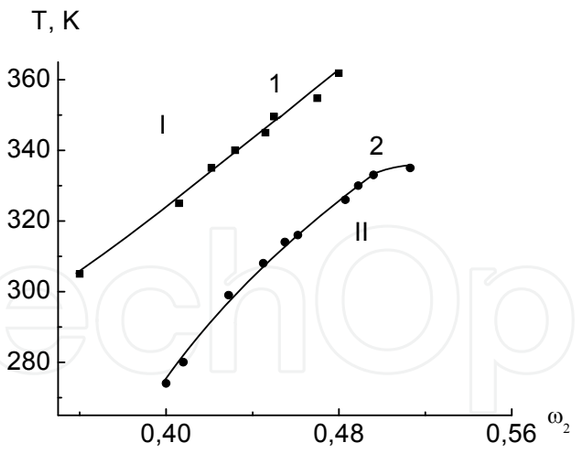

Fig. 2 f. Boundary curves for the HPC-3 solutions in: (1) ethanol, (2) DMA. I – isotropic solutions, II – anisotropic solutions.

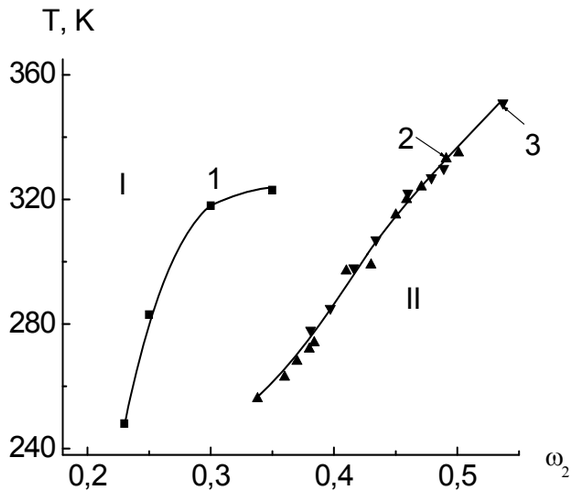

Fig. 2 g. Boundary curves for the CEC solutions in: (1) mixture of trifluoroacetic acid with methylene chloride (1 : 1), (2 ▲) DMF, (3 ▼) DMA. I – isotropic solutions, II – anisotropic solutions.

2.2.3 Influence of the shear stress field on the liquid crystalline phase transitions

Figures 3 a, b, c show the temperature dependences of viscosity for the solutions under study. The above dependences are described by curves with well-pronounced sharp maxima. This behavior is typical of the solutions with LC transitions (Kulichikhin & Golova, 1985, Vshivkov & Rusinova, 2008, Gray, 1962). According to Gray (1962), this profile of the temperature dependences of viscosity corresponds to the (isotropic liquid)–(nematic liquid crystal) phase transition. Therefore, upon cooling of HPC, CEC and PBG solutions under deformation conditions, no cholesteric crystals are formed: in other words, under dynamic conditions, a liquid crystal changes its type from cholesteric to nematic. The results obtained are in good agreement with the data of other authors (Volkova et al., 1986), who showed that the shear deformation of CEC solutions (c= 30%) in trifluoroacetic acid and a 2 : 1

TFAA–methylene chloride mixture results in the formation of similar textures that indicated the formation of an XRD-detectable nematic liquid crystal. Thus, the deformation of CES solutions leads to the change of an LC type from cholesteric to nematic. When the deformed solutions were studied by the method of polarization microscopy, the development of striped textures was observed (fig. 4). This fact is indicative of the formation of the domain supramolecular structure (Papkov & Kulichikhin, 1977, Aharoni & Walsh, 1979). Since, compared to cholesteric liquid crystals, nematic liquid crystals exist at higher temperatures, the temperature–concentration region corresponding to the existence of anisotropic solutions under the mechanical field should change.

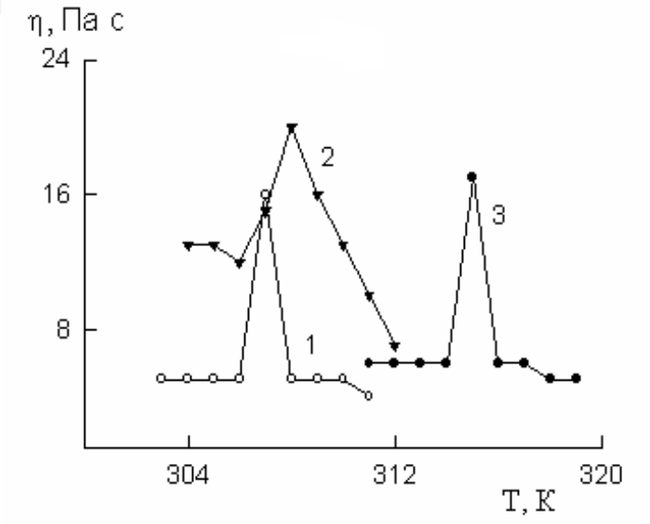

Fig. 3 a. Temperature dependences of viscosity for solutions (1, 3) HPC-3–DMA and (2) PBG–DMF (2); C = 42.9 (1), 19.4 (2), 44.5 % (3). Shear rate $\gamma = 8\ s^{-1}$.

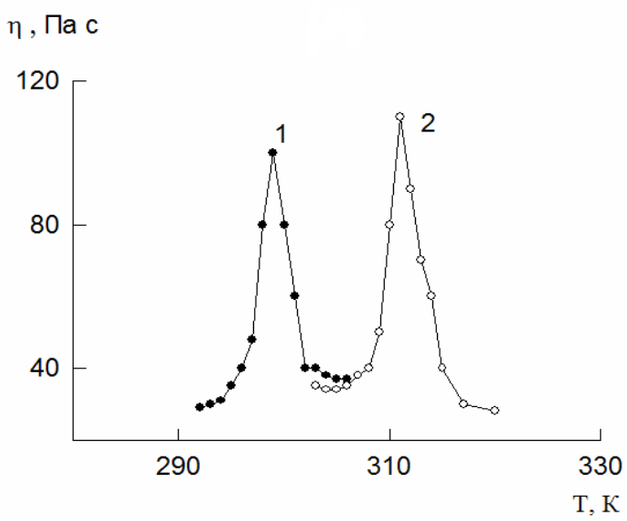

Fig. 3 b. Temperature dependences of viscosity for solutions: HPC-3– ethanol; c = (1) 36 and (2) 42.1%; Shear rate $\gamma = 8\ s^{-1}$.

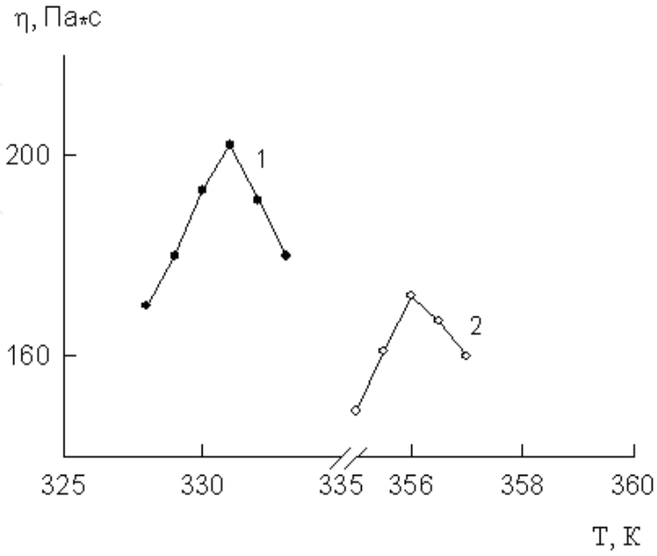

Fig. 3 c. Temperature dependences of viscosity for solutions: HPC-1–DMF: c = (1) 50 and (2) 54.9%. Shear rate γ = 8 s–1.

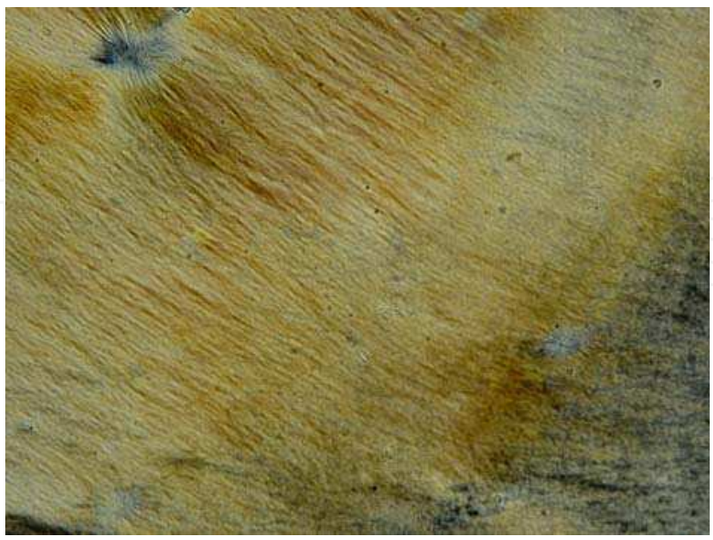

Fig. 4. Mocrograph of the CEC solution in DMA c=51.2 % after deformation. γ=60 s^{-1}. x120.

The phase transitions in the CEC–DMF and CEC–DMAA systems under static conditions and in a shear field are studied. The mechanical field leads to an extension of the temperature – concentration region of the existence of the LC phase (fig. 5), a phenomenon that is due to the change of orientation of CEC macromolecules in solutions.

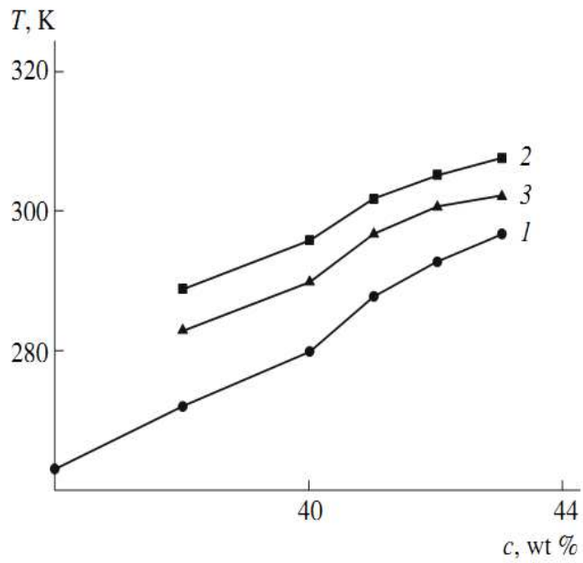

Fig. 5 a. Boundary curves of CEC – DMF system. γ: (1) 0, (2) 12 and (3) 60 s^{-1}.

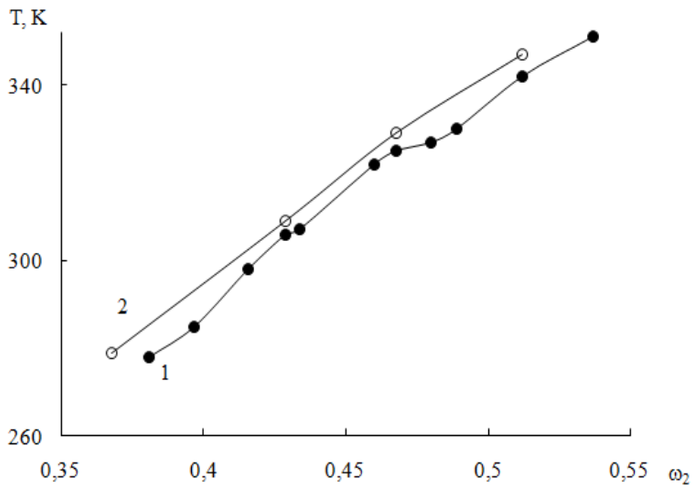

Fig. 5 b. Boundary curves of CEC – DMA system . γ=0 (1) и 12 s^{-1} (2).

The dependence of ΔT (ΔT is the difference of phase transition temperatures under dynamic and static conditions) on the shear rate is described by a curve with a maximum (fig. 6). The same behavior was reported for some polymer–solvent and polymer–polymer systems with crystalline phase separation (Vshivkov et al., 1998, Vshivkov & Rusinova, 2001).

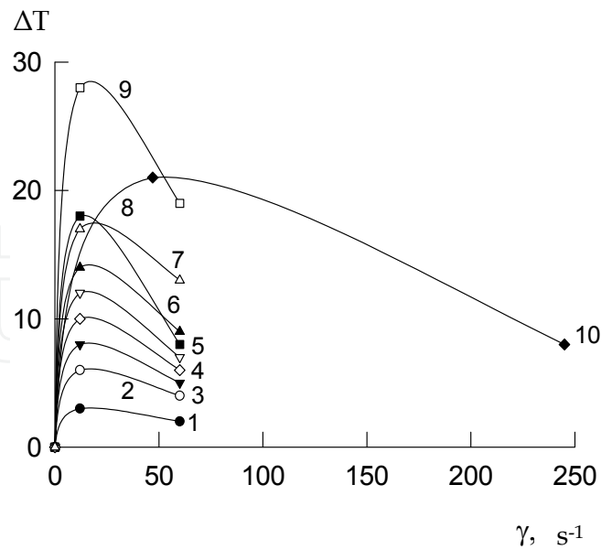

Fig. 6 a. ΔT vs. shear rate for the following solutions: HPC-2 – DMA (1 – 3), CEC – DMF (4, 6, 7), HPC-1 – DMA (5, 8, 9), PE (M=2.3x10^5) – p-xylene (10). c = 48.9 (1), 44.6 (2), 40.8 (3), 43.0 (4), 50.0 (5), 41.0 (6), 38.0 (7), 45.0 (8) and 40.0 % (9, 10).

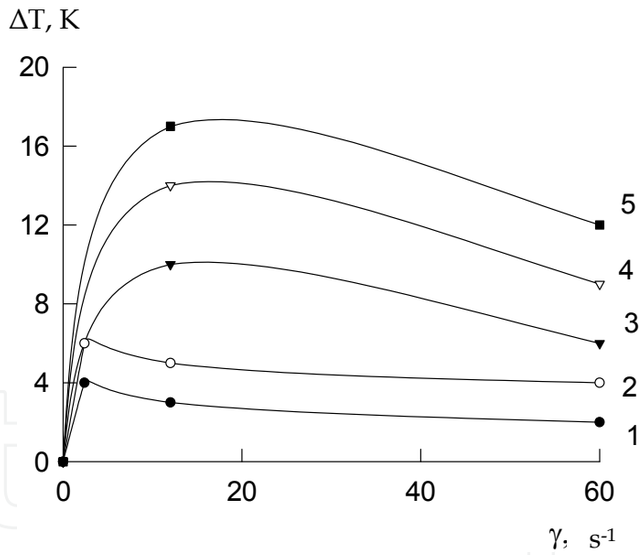

Fig. 6 b. ΔT vs. shear rate for the following solutions: (1, 2) CEC in DMA and (3–5) DMF; c = (1) 42.9, (2) 51.2, (3) 43.0, (4) 41.0, and (5) 38.0%.

This pattern of the curve was associated with two opposite processes in the system, namely, the orientation of macromolecules along the flow direction, which is favorable for phase transition, and the destruction of nuclei of the new phase by a mechanical field, a process that retards the formation of the LC phase. In the examined range of shear rates, the orientation processes dominate, thereby resulting in the elevation of the formation temperature (relative to static conditions) of the LC phase. as manifested in the elevation of the LC phase transition temperature. For comparison, Fig. 6 a shows the data for the PE – *p*-

xylene system with crystalline phase separation (Vshivkov et al., 1998). As follows from fig. 6 a , the orientational processes (increase in ΔT) during the LC transition are observed at lower shear rate (by approximately an order of magnitude).

2.2.4 Influence of the magnetic field on the liquid crystalline phase transitions

Application of the magnetic field raises the temperature of LC phase formation T_{ph} in HPC, CEC and PBG solutions; that is, it widens the temperature–concentration region of the existence of anisotropic solutions. Molecules of liquid crystals orient themselves in the magnetic field so that their long chains are oriented parallel to the magnetic field lines [46]. According to published data (Meuer (1968), de Gennes (1968), Chandrasekhar, 1977, DuPre & Duke, 1974, 1975, DuPre et al., 1976, 1977, Patel & DuPre, 1979), the cholesteric liquid crystal–nematic liquid crystal phase transition occurs in magnetic field. From a certain critical intensity, magnetic field causes untwisting of the cholesteric helix. Eventually, nematic liquid crystals are formed which occur at higher temperatures than cholesteric liquid crystals.

Polarization microscopy studies revealed a striped texture of HPC and CEC solutions treated in magnetic field (fig. 7), thus suggesting formation of large supramolecular structures—domains. A similar phenomenon was reported for other polymer–solvent systems (Papkov & Kulichikhin, 1977).

Fig. 7. Micrograph of the HPC-1 solution in DMA. c=52.0 %. x120. H=9 kOe.

It was discovered that after the magnetic field was switched off, an increased Tph was preserved in solutions for many hours. This is clearly seen from fig. 8, which demonstrates the time dependence of the time dependences of ΔT (ΔT is the difference in LC phase transition temperatures in the presence and absence of magnetic field) are determined. This fact provides evidence that structures induced by the magnetic field are preserved in solutions. Thus, the systems under study possess memory.

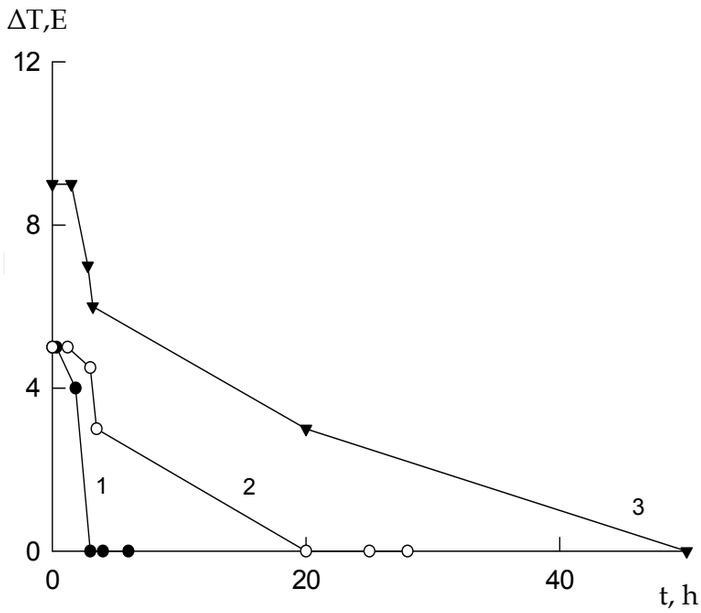

Fig. 8 a. Time dependence of ΔT for solutions: HCP-3 in DMAA (c = 51.3%) at (1) 370, (2) CEC in DMAA (c = 48.3%) at (2) 370 and (3) 298 K treated with magnetic field with intensity H = 7 kOe.

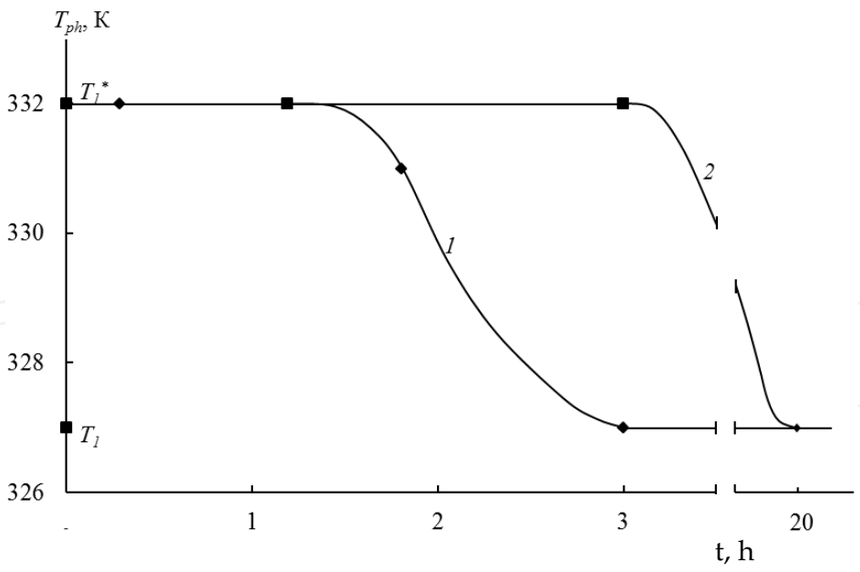

Fig. 8 b. Time dependence of T_{ph} for solution CEC in DMF (c = 48.3 %) at (1) 370 and (2) 298 K treated with magnetic field with intensity H = 7 kOe.

On the basis of the above data, the times of relaxation τ were calculated for the nematic liquid crystal – cholesteric liquid crystal reverse transition in solutions after switching off

the magnetic field. Calculations were performed according to the common exponential equation. The values of τ were found to be 18 h (HPC-3–DMAA); τ_1= 11 h at 298 K and τ_2= 8 h at 370 K (CEC–DMAA). The calculation results made it possible to estimate the order of the enthalpy of activation ΔH* for the nematic liquid crystal–cholesteric liquid crystal transition in solutions after switching off the magnetic field. The value of ΔH* is estimated via the equation $\ln(\tau_1/\tau_2) = (\Delta H^*/R)(1/T_1 - 1/T_2)$ as ~ 4 kJ/mol, in qualitative agreement with rather low enthalpies of LC phase transitions (Chandrasekhar, 1977, Plate, 1988).
Figures 9 a – 9 c show the boundary curves measured for the HPC-3-DMAA, HPC-1 – ethanol and CEC–DMAA systems at various magnetic field intensities H.

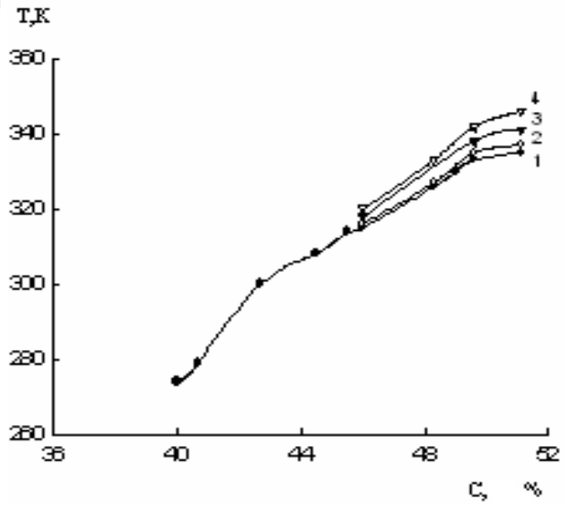

Fig. 9 a. Boundary curves for the HPC-3–DMAA system. H = (1) 0, (2) 3, (3) 5, and (4) 9 kOe.

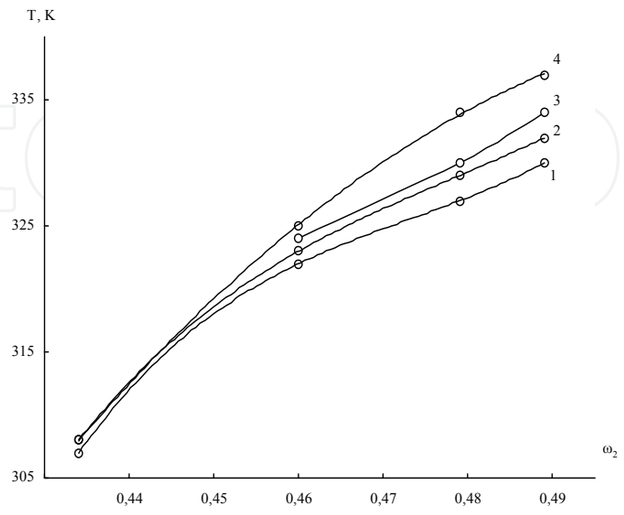

Fig. 9 b. Boundary curves for the CEC – DMAA system. H = (1) 0, (2) 3, (3) 5, and (4) 9 kOe.

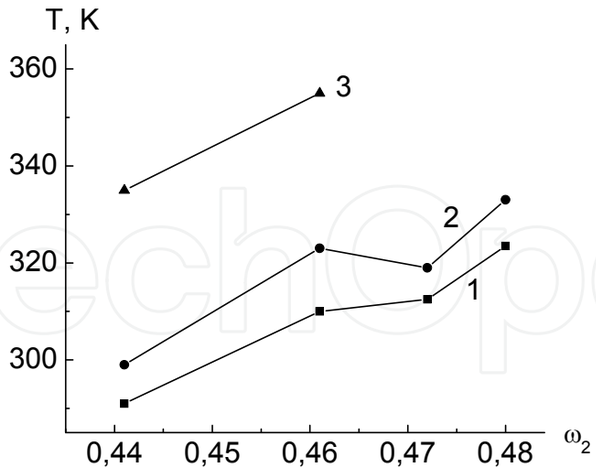

Fig. 9 c. Boundary curves for the HPC-1 – ethanol for system. H = (1) 0, (2) 3, (3) 5 kOe.

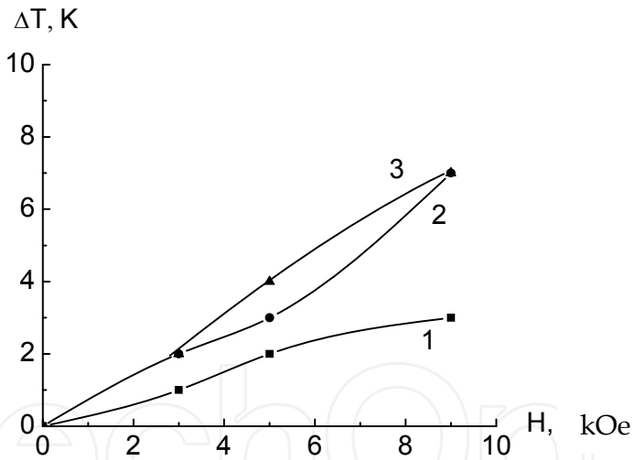

Fig. 10 a. ΔT vs magnetic field intensity for the CEC – DMA system. ω_2: (1) 0.46, (2) 0.48, (3) 0.49.

As is seen, with an increase in H, the temperature–concentration region of LC solutions widens. The higher the value of H, the more pronounced the shift of the boundary curves. A similar behavior was observed for solutions of CEC in DMF and PBG in DMF.

Figures 10 a – 10 e show the concentration dependences of ΔT for the cellulose ester – solvent systems (ΔT is the difference of phase transition temperatures in magnetic field and in its absence). It is seen, that as the magnetic field intensity H is increased, the ΔT value increases. It testifies about the macromolecule orientation increase.

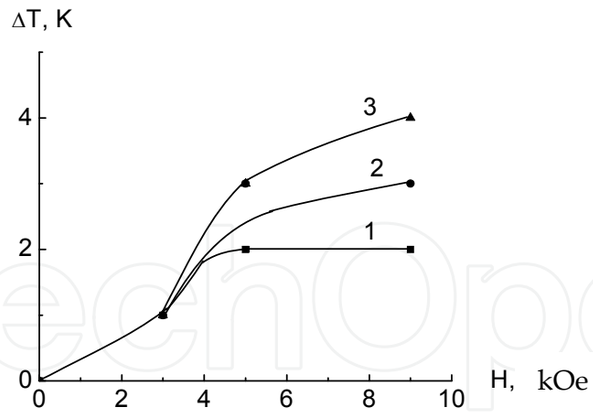

Fig. 10 b. ΔT vs magnetic field intensity for the CEC – DMF system. ω_2: (1) 0.47, (2) 0.49, (3) 0.50.

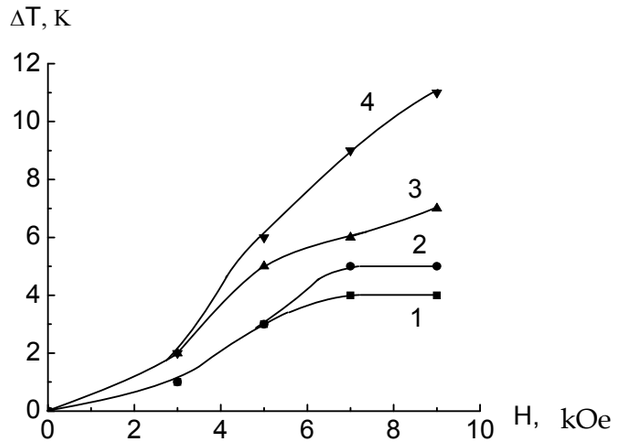

Fig. 10 c. ΔT vs magnetic field intensity for the HPC-3 – DMA system. ω_2: (1) 0.46, (2) 0.48, (3) 0.50, (4) 0.51.

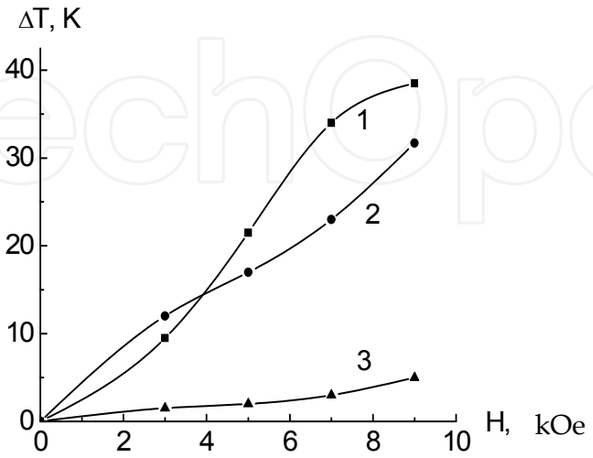

Fig. 10 d. ΔT vs magnetic field intensity for the HPC-1 – DMA system. ω_2: (1) 0.49, (2) 0.52, (3) 0.55.

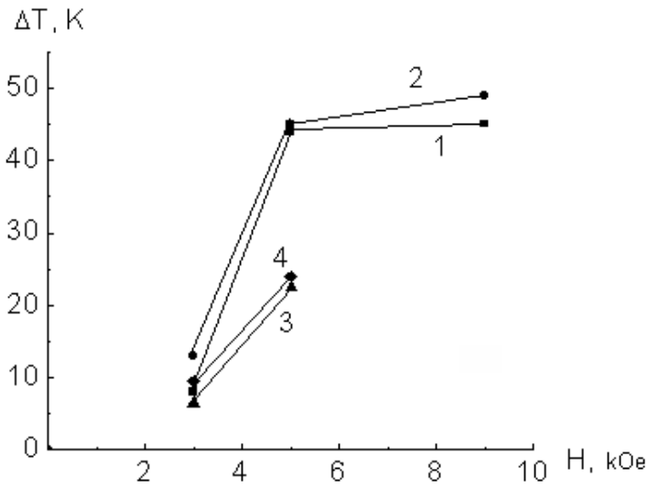

Fig. 10 e. ΔT vs magnetic field intensity for the HPC-1 – ethanol system. ω_2: (1) 0.44, (2) 0.46, (3) 0.47, (4) 0.48.

2.3 HPC solutions in water

Aqueous solutions of HPC belong to systems with strong electron-donor (hydrogen) bonds (Belousov & Panov, 1983). Because of the presence of two mobile protons and two unshared electron pairs at the oxygen atom, a water molecule may function both as an electron donor and an electron acceptor and form four hydrogen bonds with an energy of 20 kJ/mol. Therefore, a loose structure with a large free volume is formed in water. In the case of water, the fraction of nonspecific interaction is as low as 7%. Intermolecular interactions of HPC with water may be determined by both the hydrophilic hydration giving rise to hydrogen bonding between a polymer and a solvent and the hydrophobic hydration of water, which consists in densification of water structure around nonpolar methyl and methylene groups of HPC molecules during formation of solutions. Many studies were devoted to phase equilibrium in the HPC–water system, and the LCST values were reported in a number of papers (Vshivkov et al., 2007, Fischer et al., 1995, Kagemoto et al., 1970, Nystrom & Bergman, 1978, Werbowyi & Gray, 1976, 1979, 1980, Nishio et al., 2002, Fortin & Charlet, 1989, Ryotarou & Yoshiyuki, 2003, Guido, 1995, Furusawa & Tagawa, 1985, Suto et al., 1989, Lu & Schwartz, 2002, Bergman & Sundelof, 1977). Figure 11 a displays the phase diagram measured for the HPC-1–water system. This diagram is largely consistent with the phase diagrams described for this system. Four regions can be distinguished in the diagram: (I) the region of isotropic transparent solutions; (II) the region of anisotropic transparent solutions; (III) the region of heat-induced phase separation giving rise to formation of a white anisotropic precipitate; and (IV) the region of anisotropic solutions opalescent over the entire volume (the colorless solutions are observed, which is typical of cholesterol LC solutions. (1* refers to colorless solutions and 2* refers to blue solutions, which is typical of cholesterol LC solutions (Kapustin, 1978). According to Fisher et al. (1995), the crystal solvates are formed in solutions at an HPC concentration of ~ 80 % or above. The boundary curve 1 that characterized the heated induced phase transition has a binodal shape. It appears that the breakdown of hydrophilic and hydrophobic hydration of HPC initially leads to the amorphous phase separation of solutions and formation of two coexistent dilute and concentrated phases (the LCST is 298 K). Simultaneously, anisotropic crystal solvates precipitate in the concentrated phase.

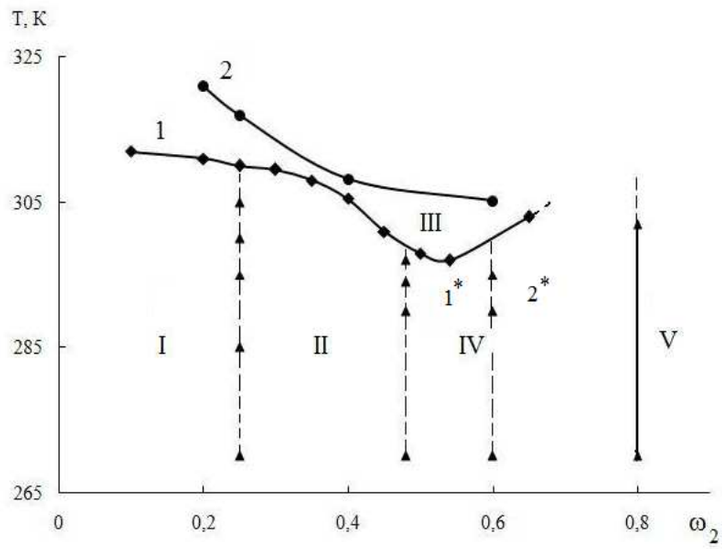

Fig. 11 a. Phase diagram for the HPC-1–water system. Shear rate γ = 0 (1) and 12 s^{-1} (2). See text for explanations.

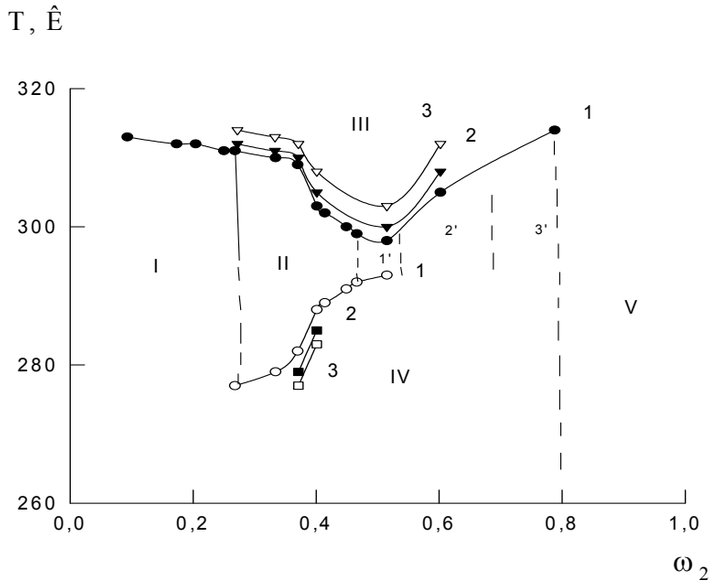

Fig. 11 b. Boundary curves for the HPC-2–water system at γ = (1) 0, (2) 12, and (3) 60 s–1. Color of the solutions: (1') red, (2') green, (3') violet. Comments are given in text.

Figures 11 b and 12 show the phase diagrams for the HPC-2–water and HPC-3–water systems measured under static conditions and in the shear field. The phase diagram of the HPC-2 – water system virtually coincides with that of the HPC-1–water system, since a difference in the molecular masses of these samples is insignificant; the LCST is 298 K. The diagram comprises the regions similar to those characteristic of the HPC-1–water system.

The distinctive feature is a change in the color of solutions with the weight fraction of the polymer $\omega_2 > 0.45$. The observed color transition from red to violet through green may be related to a reduction in the cholesteric helix pitch with an increase in the polymer concentration in solutions. Also note that, in contrast to HPC-1 solutions, in the case HPC-2 solutions, the curve delimiting regions II and IV shifts toward lower polymer concentrations at low temperatures. The molecular mass of the HPC-3 sample is almost an order of magnitude higher than that of the HPC-1 and HPC-2 samples, therefore we failed to prepare HPC-3 solutions in a wide concentration range because of its poor solubility. Three regions may be distinguished in the phase diagram: (I) the region of isotropic solutions; (II) the region of transparent anisotropic solutions; and (III) the region, where heating causes phase separation accompanied by formation of the while anisotropic precipitate. A comparison of the phase diagrams indicates that an increase in the molecular mass of the polymer leads to a shift in the boundary curve reflecting the formation of anisotropic LC solutions to lower concentrations. This fact is consistent with the current theoretical concepts [20].

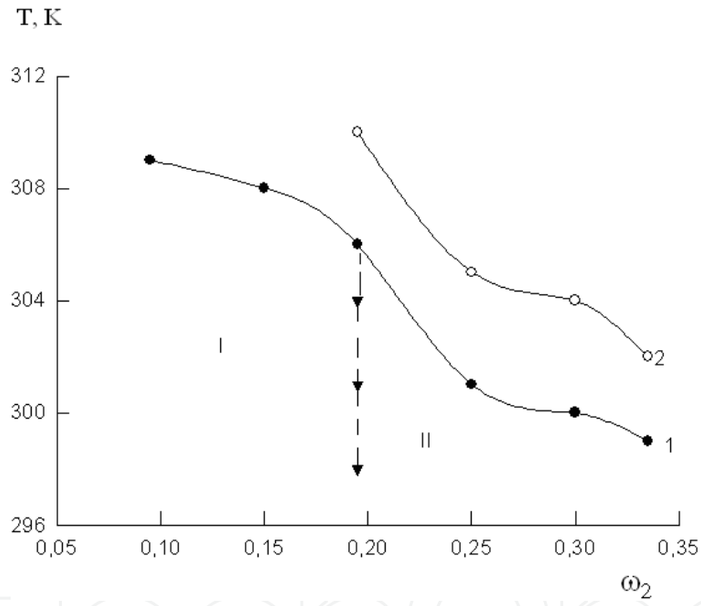

Fig. 12. Boundary curves for the HPC-3–water system at γ = (1) 0 and (2) 12 s–1. Comments are given in text.

2.3.1 Influence of the shear stress field on the liquid crystalline phase transitions

The deformation of these systems increases the temperatures of heat-induced separation and decreases the temperatures of transition from region II to region III. As the shear rate is increased, the absolute value of ΔT increases for both transitions and achieves 7 K (ΔT is a difference between phase transition temperatures under dynamic and static conditions). This phenomenon may be explained by the breakdown of nuclei of a new phase under the action of the mechanic field, as was observed for a number of polymer – solvent systems characterized by amorphous and crystalline phase separation (Vshivkov et al., 1998, Vshivkov & Rusinova, 2001).

2.3.2 Influence of the magnetic field on the liquid crystalline phase transitions

Application of magnetic field causes an increase in the phase transition temperature under heating, which is likely associated with a change in the orientation of macromolecules in solution (fig. 13).

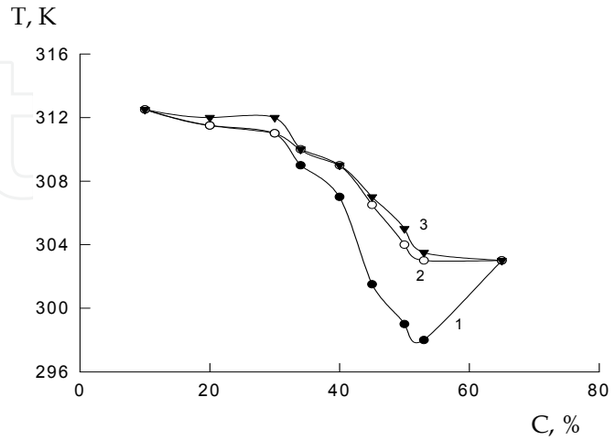

Fig. 13. Boundary curves for the HPC-1–water system. H = (1) 0, (2) 5, and (3) 9 kOe.

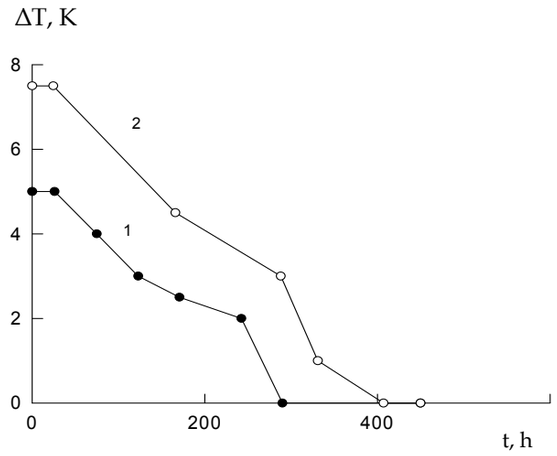

Fig. 14. Time dependence of ΔT for HPC-1 solutions in water. c = (1) 53.5 and (2) 49.6%. H= 5 Oe.

Like the HPC and CEC solutions in organic solvents, the HPC – water system possesses memory: an increased T_{ph} is preserved for many hours after the magnetic field is switched off (fig. 14). The calculated time of relaxation necessary to achieve the initial orientation of macromolecules is τ = 260 h (*c* = 53.5%) and 103 h (*c* = 49.6%). With an increase in the concentration of the polymer, the time of relaxation grows, since the viscosity of the system increases.

3. Conclusion

Phase diagrams have been constructed for the cellulose ester – water systems under static conditions, in the shear stress and magnetic fields. As the molecular mass of the polymer is

increased, the curves delimiting isotropic and anisotropic solutions shift to lower concentrations. The deformation causes the formation of domain structure, the changes in the type of the liquid crystal, and in the phase transition temperatures of solutions both upon heating and cooling. As the molecular mass of the polymer increases, the ability of macromolecules to orient under the shear stress field decreases. The concentration and dependence ΔT is described by the curve with maxima. The formation of domains in solutions was observed under the shear stress field.

The magnetic field also widens the temperature–concentration region of the existence of the LC phase. This effect is related to the cholesteric liquid crystal – nematic liquid crystal phase transition and the orientation of macromolecules in the direction parallel to the magnetic field lines. In this case, large supramolecular structures (domains) develop in solutions. The effect of magnetic field on the variation in LC transitions with the polymer concentration in solution shows an extremal pattern. Figures 15 and 16 demonstrate the concentration dependences of ΔT for HPC1– DMAA, HPC-3–DMAA, and HPC-1–water systems measured at various magnetic field intensities.

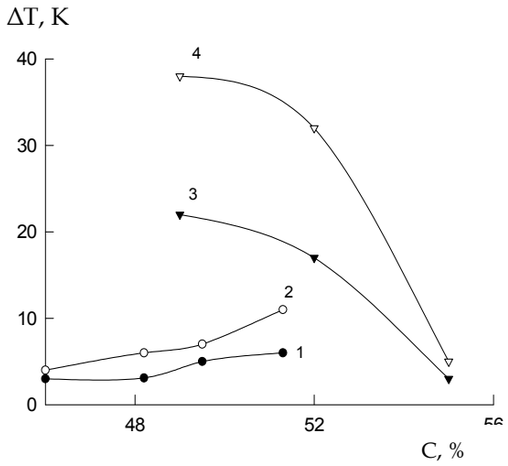

Fig. 15. Concentration dependence of ΔT for solutions of (1, 2) HPC-3 and (3, 4) HPC-1 in DMAA. H =(1, 3) 5 and (2, 4) 9 kOe.

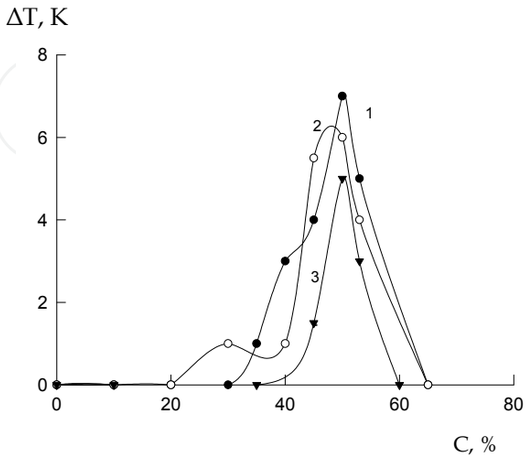

Fig. 16. Concentration dependence of ΔT for HPC-1 solutions in water. H = (1) 5, (2) 9, and (3) 13 kOe.

In analyzing the effect of the polymer concentration on magnetic field-induced changes in phase transition temperatures, two factors should be taken into account. First, as concentration increases, the number of macromolecules capable of orientation in the magnetic field grows; as a consequence, T_{ph} should increase. Second, a rise in the polymer concentration in solution facilitates densification of the fluctuation network of entanglements. This impedes the occurrence of orientation processes and weakens the effect of the magnetic field. On the whole, the concentration dependence of ΔT is apparently described by a curve with a maximum.

It should be noted that for solutions of an HPC-1 sample with a lower molecular mass, the value of ΔT is much higher. This observation indicates a more distinct orientation of smaller molecules in the magnetic field, in agreement with the data from (Kol"tsov et al., 1995).

Figures 17 and 18 plot ΔT as a function of lnE for HPC-1–DMAA, HPC-3–DMAA, and CEC – DMAA systems. It is seen that these dependences are described by straight lines. The analogous dependence is determined for the PBG – DMF system. With an increase in the magnetic field energy stored by solutions, the value of ΔT increases. The effect of field on the phase transitions shows a threshold character: a change in T_{ph} begins from a certain critical intensity of the field H_{cr}. These values are 2.3 and 2.0 kOe for the HPC – DMAA and CEC –DMAA systems, respectively, and 2.3 kOe for the PBG – DMF system. In order of magnitude, these values are consistent with H_{cr} necessary for the nematic liquid crystal - cholesteric liquid crystal phase transition (Papkov & Kulichikhin, 1977, Chandrasekhar, 1980). In this case, $\Delta T = K\ln(E/E_0)$ or T_{ph} ($H > H_{cr}$) = $T_{ph}(H = 0) + K\ln(E/E_0)$. Coefficient K depends on the molecular mass of the polymer and its concentration in solution.

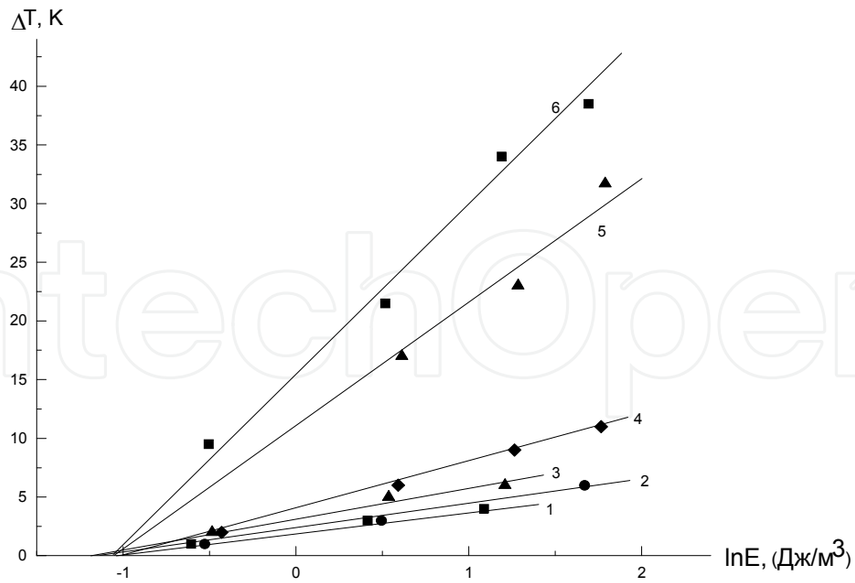

Fig. 17. Plot of ΔT vs. lnE for solutions of (1–4) HPC-3 and (5, 6) HPC-1 in DMAA c = (1) 46.1, (2) 48.3, (3) 49.6, (4) 51.3, (5) 52.0, and (6) 49.0%.

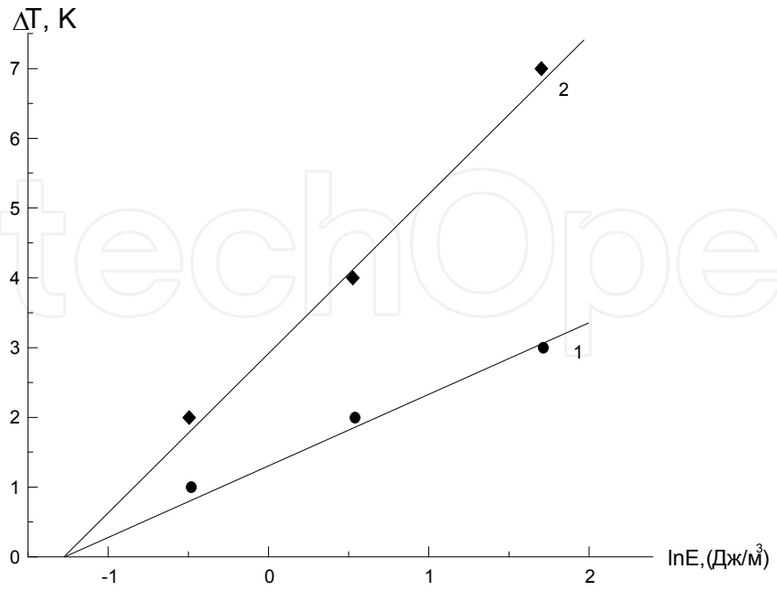

Fig. 18. Plot of ΔT vs. lnE for CEC solutions in DMAA. c = (1) 46.0 and (2) 48.8%.

Thus it is revealed a perfect analogy in influence magnetic and mechanical fields in their influence on phase liquid crystal transitions in solutions of rigid chain polymers.

4. Chart of symbols

- PBG – poly(γ-benzyl-L-glutamate, DMF – dimethylformamide, DMA – dimethylacetamide, Hc – a critical field strength,
- p_0 - zero field pitch, $\Delta\chi_m$ - diamagnetic anisotropy of the liquid crystal, K_{22} - the twist elastic constant, LC – liquid – crystalline, CEC – cyanoethyl cellulose, HPC – hydroxypropyl cellulose, T_{ph} - phase-transition temperature, X – coefficients of magnetic susceptibility, H – magnetic intensity, E – energy of the magnetic field stored by the solution volume unit, η – viscosity , φ_2* – critical concentration of a polymer, , above which the LC order arises,
- x – asymmetry of macromolecules, φ – ionization potential, ΔT – the difference of phase transition temperatures under dynamic and static conditions , γ – shear rate, ΔT – the difference in LC phase transition temperatures in the presence and absence of magnetic field, τ – times of relaxation, ΔH* – enthalpy of activation for the nematic liquid crystal–cholesteric liquid crystal transition, ω_2 - mass portion of polymer,

5. Acknowledgment

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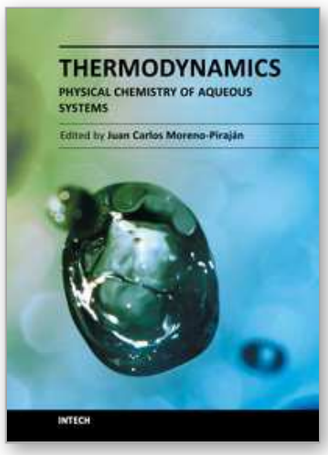

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