PHASE SEPARATION AND LIQUID-CRYSTAL STATE OF CELLULOSE TRIACETATE IN NITROMETHANE

A. B. Shipovskaya,[a] **G. N. Timofeeva,**[a] **N. O. Gegel',**[a] **and S. Yu. Shchegolev**[b]

UDC 544.015.4:544.022.5:547.458.81

The existence of the liquid-crystal state of cellulose acetate in nitromethane has been shown on the basis of the calculation data, rheological and x-ray structural analysis, and polarization- and electron-microexamination. The conditions for the formation of the lyotropic phase have been revealed and the states of its concentration-temperature boundary have been determined and marked on the diagram. It is shown that the ratio between acetate and hydroxyl groups in the polymer strongly influences the temperature and concentration ranges of realization of a highly oriented state.

Introduction. Earlier it was shown that under certain thermodynamic conditions the cellulose triacetate (CTA)–nitromethane system is characterized by the existence of both amorphous and crystalline types of phase separation [1, 2].

Formulation of the problem. The state diagram of this system obtained for CTA samples with close physicochemical characteristics but prepared under the conditions of different industrial enterprises is characterized by an upper critical mixing temperature (UCMT) (Fig. 1). In the range of values of the weight concentration C below ~10–12% and in the temperature range from the UCMT (52 and 57°C, Fig. 1a and b, respectively) to ~40°C (inside the binodal dome, curves 1), amorphous phase separation occurs. In this range, because of the high values of viscosity and duration of relaxation processes, incomplete phase separation is observed. As a result, jellies, whose characteristic feature is instability, are formed. The initially transparent jellies become turbid and synerize with time as a consequence of the processes of ordering and orientation [3]. Such behavior can be explained taking into account the specific features of the phase separation in solutions of crystallizable polymers, which is CTA. For such objects, first the state with the amorphous type of phase separation with subsequent transition to crystallization is often realized.

For $C \sim$ 12–15% (Fig. 1a) and ~10–12% (FIg. 1b) in the temperature range ~45–40°C, the diagram has a branch corresponding to the region of superposition on the amorphous equilibrium curve (curves 1) of the melting curve of crystal structures (curves 2). At $C >$ 12–15% in the range of room temperatures crystallization occurs, which is evidenced by the x-ray photographs of films obtained from such systems [4].

Below the curve of absolute instability of the system (Fig. 1, curve 3) for $C \cong$ 3–15% in the system two phases exist, and in the polymer-concentrated phase CTA is in the crystalline state [1, 2]. In [1], curve 3 was called the quasi-spinodal, since it has an unusual form: it does not touch the binodal (unlike the classical thermodynamics of solutions [5]), and its shape is suggestive of the melting curve of the crystalline polymer (liquidus curve). In [2], on the basis of experimental and calculated data it was shown that curve 3 is most probably the result of the superposition of two phase separation curves: the spinodal (curve 4 in Fig. 1b) and the vitrification curve.

Cellulose acetates belong to the class of linear polymers with a higher rigidity of the link and a high degree of asymmetry [6, 7]. For example, for CTA in ethyl acetate the Kuhn segment is equal to 260 Å [8]. According to our data, for CTA and cellulose diacetate (CDA) in nitromethane the value of the Kuhn segment is 300 and 100 Å, respectively. These estimates, as well as the data of [9], point to the fact that under certain thermodynamic conditions a spontaneous transition of macromolecules of cellulose acetate to the liquid-crystal (LC) state is possible in principle.
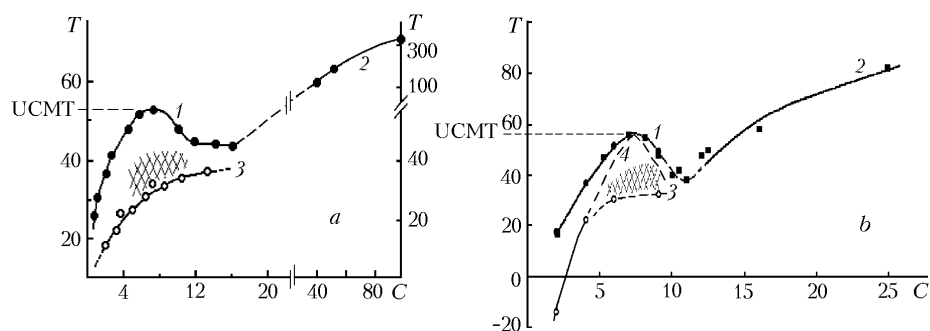
Fig. 1. Phase diagrams of the cellulose triacetate–nitromethane system obtained by the turbidity spectrum and differential-thermal analysis methods ($\gamma = 62.2\%$, $\overline{M}_\eta = 7.3{\cdot}10^4$, open stock company "Khimvolokno," city of Vladimir [1]) (a) and by the methods of polarization microscopy and turbidity spectrum ($\gamma = 62.2\%$, $\overline{M}_\eta = 7.0{\cdot}10^4$, open stock company "Khimvolokno," city of Engels [2] (b): 1) binodal; 2) liquidus; 3) absolute instability; 4) spinodal calculated by the Flory–Huggins lattice theory; the shaded region shows the concentration-temperature domain of existence of the LC state.

From P. Flory's works it follows that the probability of transition of a polymer to a highly ordered state is determined by the flexibility parameter f, whose value should not exceed 0.63 [10]. For CTAs, even in the roughest calculations f varies from 0.1 to 0.2, i.e., it appears to be much smaller than the criterial value. The degree of asymmetry calculated according to [6] for a maximally acetylated CTA with a 62.2% substitution of hydroxyl groups and a viscosity-average molecular mass of $7.3{\cdot}10^4$ equaled ~140. The degree of asymmetry corresponds to the polymer concentration of 5.7%, beginning from which the LC-phase formation in solutions of CTAs is possible.

Assuming conditionally curve 3 (Fig. 1) as the boundary of the crystallization region, the authors [11] suggested that in the range of temperatures above the absolute instability curve inside the binodal dome the system can be in the transient LC-state. The possibility of formation of the latter in the right extreme part of the phase diagram was reported in [12–17]. Since the preparation of high-concentration solutions is connected with many difficulties, in these works the objects in investigations were obtained by swelling the polymer in solvent vapors. Thus, the initiation of orientation processes at sorption by cellulose acetate of small (no more than 8–10 mass %) quantities of nitromethane vapors is confirmed by the induction of optical anisotropy in films [12], the anomalous character of the swelling curves of fibers, films, and powdery polymer [13, 15], the radical transformation of the rheological properties with the realization of viscosity rheograms typical of lyotropic LC-systems [14], the increase in the intensity of reflections on diffractograms and the decrease in the disorientation angle [16], the spontaneous elongation of fibers and films [15, 17], which is a direct confirmation of the transition of the polymer-solvent system to the LC-phase [10], etc., as well as by the change in the spatial structure (optical activity) of the polysaccharide [12–17].

The aim of the present work was to investigate the processes of LC-phase formation in the CTA–nitromethane system in the opposite region of the state diagram (at relatively lower concentrations).

Experimental. For the investigation, we chose industrial samples of powdery CTAs of wooden origin obtained at the open stock company "Khimvolokno" (cities of Engels, Vladimir) and used for manufacturing acetate fibers. The CTA samples were characterized by the content of bound acetic acid $\gamma = 62.2\%$ and close values of the viscosity-average molecular mass: $\overline{M}_\eta = (7.0\text{–}7.3){\cdot}10^4$. We also used samples with $\gamma = 60.2$ and 58.1% obtained by saponifying the initial CTA with $\gamma = 62.2\%$ manufactured by the open stock company "Khimvolokno" (city of Engels).

For the solvent, we used analytically pure nitromethane, $d = 1.14$ g/cm^3, $T_{boil} = 101.2^{o}$C. Nitromethane is an electron-donor, dipolar, aprotic solvent [18]. It interacts specifically with the functional groups of cellulose acetate solvating mainly hydroxyl groups [19, 20].

We investigated the CTA–nitromethane system in the range of concentrations $C = 4\text{–}25$ mass % and in the temperature range $T = 20\text{–}80^{o}$C. The objects of investigation were prepared by swelling the polymer sample in the solvent for 24 h with subsequent dissolution on a water bath at 80 ± 5°C until a visually transparent homogeneous solution was obtained. The thus prepared mixture was stored at room temperature and normal atmospheric pressure. Prior
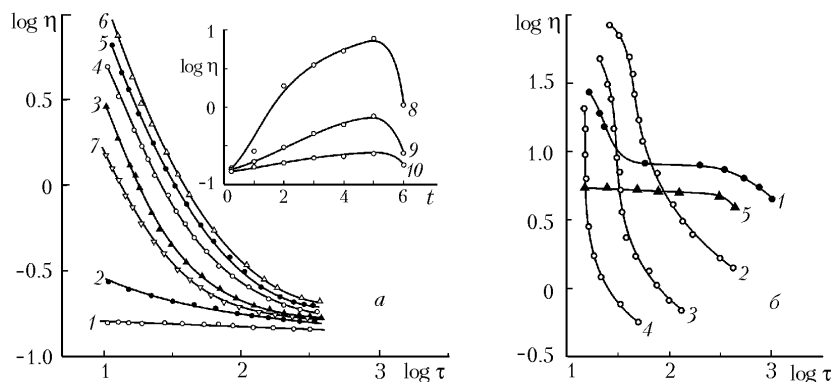
Fig. 2. Flow curves of the CTA–nitromethane system with a 5% concentration of the polymer at $T = 40^{\circ}$C for various thermostating times: a) [1] 0.25 h; 2) 1; 3) 2; 4) 3; 5) 4; 6) 5; and 7) 6; the insert shows the viscosity change in the same system at log τ: 8) 1.1; 9) 1.7; and 10) 2.3]; rheokinetics of the phase transition in the CTA–nitromethane system with $C = 11\%$ at $T = 35^{\circ}$C for various thermostating times (b): [1) 1 h; 2) 3; 3) 5; 4) 7; 5) at $T = 60^{\circ}$C] ($\gamma = 62.2\%$, $\overline{M}_{\eta} = 7.3 \cdot 10^{4}$, open stock company "Khimvolokno," city of Vladimir).

to experiments, the mixture was heated to 80°C, and thermostated for 1 h. Then a portion of the solution was sampled and placed in the operating unit of the device used, thermostated again for 1 h at 80°C, and then cooled at a constant rate down to the experimental temperature.

Rheological investigations were made on a Höppler and a Rheotest-1 viscosimeters in the range of shear stresses log $\tau < 1$ and log $\tau = 1.0$–3.2, respectively. Superimposing of deformations at each temperature was carried out periodically at fixed time intervals. Between the deformation cycles the system was at rest in the operating unit of the viscosimeter under isobaric-isothermal conditions.

Optical observations of the birefringent structures were made with an MPSU-1 polarization microscope. Electron-microscopic photographs of the CTA isolated from the LC liquid were obtained with an EM-5 electron microscope. Replicas were sputtered by means of an UZDN-1 ultrasonic low-frequency disperser. The structure of precipitates isolated from the polymer solution was characterized with the aid of a Tesla-242E electron microscope. As CTA precipitants, ethyl alcohol and analytically pure hexane were used. X-ray photographs were obtained on an URS-50 IM diffractometer with Cu–K$_{\alpha}$ radiation.

The Flory–Huggins interaction parameter (χ_1) was calculated according to [21] and expressed in terms of the entropic (ψ_1) and enthalpic (k_1) components:

$$\chi_1 = \frac{1}{2} + k_1 - \psi_1 \, ,$$

where ψ_1 is the slope of the straight line $(T_{\mathrm{cr}})^{-1} = f\left(X^{1/2} + \frac{1}{2}X^{-1}\right)$; $k_1 = \Theta\psi_1/T_{\mathrm{cr}}$. The calculation of χ_1 for the CTA sample with $\gamma = 62.2\%$ was made with the use of the experimental data of [1], $\gamma = 60.2\%$ [22].

Results and Discussion. In [23], it was noted that in the process of thermostating of the CTA–nitromethane system in the concentration range 5–7% in the phase separation region at temperatures 5–7°C below the binodal dome an increase in viscosity η with time at small shear stresses took place. This effect was explained by the appearance of a space lattice of the jelly.

Having repeated some of these experiments and widened the temperature-concentration range, as well as having increased the number of samples, we investigated the rheological properties of the CTA–nitromethane system both outside and inside the phase separation region.

In the region of thermodynamic compatibility, this pair forms true stable solutions with a time-invariable dependence log $\eta = f(\log \tau)$ which for the investigated concentrations is described by the classical (for polymer solu-
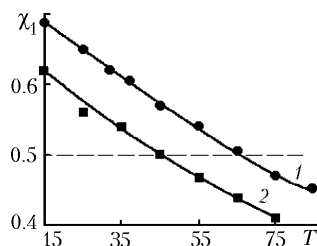
1224

Fig. 3. Temperature dependence of the Flory–Huggins parameter for the CTA–nitromethane system: 1) $\gamma = 62.2\%$; 2) 60.0.

tions) flow curves (Fig. 2a, curve 1; Fig, 2b, curve 5). With decreasing temperature and on passing through the binodal viscosity, rheograms characteristic of structured solutions are realized (Fig. 2a, curves 2–7; Fig. 2b, curves 1–4). This may be due to both the jellification process and the formation in the solution of a highly ordered LC phase. Taking into account that the realization of the LC phase for a crystallizing polymer may be relatively slow, we estimated the time dependence of all rheological characteristics.

The investigation of solutions with concentrations of 5–11% at small thermostating times (0.25 h) has shown that upon cooling of the system down to the absolute instability curve the usual flow curves are observed (Fig. 1, curve 3). At longer thermostating times (>1 h), flow curves of structured systems are realized at relatively high temperatures. For example, for a 5% solution at short thermostating times classical viscosity rheograms are observed up to 30°C. Only upon reaching this temperature does a sharp increase in the viscosity occur in the region of small shear stresses. At longer thermostating times such an effect manifests itself already at 40°C.

Figure 2a representing the viscosity kinetics of the CTA ($\gamma = 62.2\%$)–nitromethane system with $C = 5\%$ in the thermostating process at $T = 40^{\circ}$C clearly shows an anomalous decrease in η at log $\tau = 1.0$–1.3. Here the dependence log $\eta = f(\log \tau)$ of the system varies with time. During 4–5 h the viscosity increases (curves 1–6). Such behavior was noted in [23] and explained by the jellification process proceeding by the mechanism of incomplete phase layering [24, 25]. It is not excluded that the increase in η with time is due to the densification of the structures formed in the jelly. However, despite the high viscosity value, this structure has a marginal ultimate strength and fails easily upon a small increase in the shear stress. Our kinetic estimates show that with time in the system there occur structural changes accompanied by both an increase in the viscosity in the domain of small τ and its sharp decrease at log $\tau > 1.3$.

A further thermostating (>5 h) revealed a new effect — a decrease in viscosity on going from curve 6 to curve 7 (Fig. 2a), i.e., the kinetics of η at various values of τ has an extreme character (insert in Fig. 2a, curves 8–10). Such a decrease in viscosity can no longer be explained by jellification alone and points to a change in the flow mechanism itself when the structures formed exhibit a lower resistance. It is natural to suppose that the decrease in η is due to the formation of a highly ordered phase whose viscosity can be much lower than the isotropic one [6, 7].

Particularly illustrative from this point of view is Fig. 2b representing the dependence log $\eta = f(\log \tau)$ for the CTA–nitromethane system with $C = 11\%$ at $T = 35^{\circ}$C. This case corresponds to a state more distant from the binodal compared to the 5% mixture at $T = 40^{\circ}$C. The lower temperature of the experiment makes it possible to follow visually the dynamics of structural transformations taking place in the system in the process of phase separation. First a lattice of the jelly is formed (curve 1), which corresponds to the steady state of the system at higher temperatures (as was observed for the 5% mixture at 40°C). Then with time a strengthening of the supermolecular structures followed by a drastic increase in the viscosity at log $\tau < 1.5$ occurs (curves 2–4). However, the structures formed turn out to be very labile (which was noted above) and fail at log $\tau > 1.5$. Moreover, in the process of phase separation, first there is a certain increase in the yield strength τ_{cr} and then its monotonic decrease (although insignificant since the τ_{cr} values themselves are relatively small). In addition, there is a considerable decrease in the viscosity, which becomes lower than its value corresponding to a higher temperature (60°C, region of homogeneous solutions, curve 5). Most probably, it is in this period that the isothermal transition of macromolecules to the oriented state occurs and not individual supermolecular formations, but anisometric plane aggregates representing fragments of the ordered polymeric phase become the structural elements of the system determining the viscous flow. It may be supposed that the internal friction coefficient at viscous motion of such fragments is smaller than in the case of isotropic solutions. Visually, at this stage
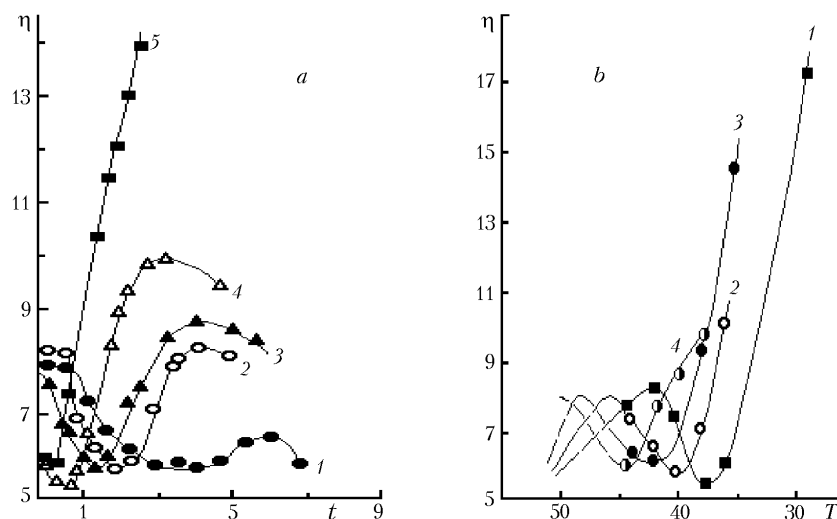
Fig. 4. Dependence of viscosity of the CTA–nitromethane system at an 11% concentration of the polymer: a) on the thermostating time [1) $T = 44^{\circ}$C; 2) 42; 3) 40; 4) 38; 5) 36]; b) on the temperature [1) $t = 0.5$ h; 2) 1; 3) 2; 4) 4] ($\gamma = 62.2\%$, $\overline{M}_{\eta} = 7.3 \cdot 10^{4}$, open stock company "Khimvolokno," city of Vladimir).

the system represents a flowing turbid mass. The effective value of the parameter χ_1 at $T = 35^{\circ}$C is equal to 0.61 (Fig. 3, curve 1).

Below we discuss the results of the observations aimed at answering the question: is this transition a result of an external action or does it occur spontaneously under the given conditions and rheology permits only ascertaining this fact.

To weaken the influence of relatively large shear stresses, we measured the viscosity values of the systems on a Höppler viscosimeter at log $\tau < 1$ in the temperature range of 30–45°C. Figure 4a shows the viscosity change with time for the 11% system at various temperatures. The formation and accumulation of highly ordered structures at 44°C begins 1 h after the beginning of measurements (curve 1). After 5 h the viscosity increases. Going to lower temperatures leads to a decrease in the viscosity after shorter time intervals (curves 2–5) and in shorter times: 42°C — 1.5 h, 40 — 1.0, 38 — 0.5, 36 — 0.25 h. It should be noted that for the given system at temperatures of 44 and 42°C at the beginning of measurements the usual (for isotropic polymer systems with UCMT) dependence $\eta = f(T)$ is observed, i.e., as the temperature decreases, the viscosity increases (curves 1 and 2). But beginning with 40°C (curve 3) the solution is enriched with an ever increasing number of anisotropic structures, and the turbidity and viscosity decrease already at the initial moment of measurements. At 38°C (curve 4) intensive formation of the largest number of ordered structures takes place, and to this there corresponds the deepest minimum on the kinetic curve of viscosity. At 36°C (curve 5) the solution transforms to a solid white substance and the viscosity increases with no limit.

Thus, the rate of formation of highly ordered structures is higher the lower the temperature. Measurements in time make it possible to ascertain "inertia" of the process of formation of highly oriented structures, which appears as their partial manifestation at sufficiently high temperatures (Fig. 4a, curves 1 and 2), the transformation into a matrix at lower temperatures (curves 3, 4), and, finally, the subsequent changeover of the whole of the polymer into a continuous solid anisotropic matrix characterized by an unlimited increase in the viscosity (curve 5).

The best graphical representation of the change in η with temperature at various thermostating times for $C = 11\%$ is given in Fig. 4b. At larger thermostating times the formation of anisotropic structures shifts into the region of higher temperatures. However, above 50°C the time factor (at least within 7 h) is immaterial. This seems to be natural, since according to the state diagram (Fig. 1) at $T > 50^{\circ}$C the system goes into the region of single-phase homogeneous solutions.

A similar behavior is also observed for systems with a lower concentration with the difference that the characteristic decrease in the viscosity occurs in different temperature ranges. For example, for the system with $C = 5\%$ it is 31.0–34.5°C; with $C = 7\%$ — 35.0–40.0°C; and with $C = 10\%$ — 36.0–42.0°C. The relatively narrow temperature

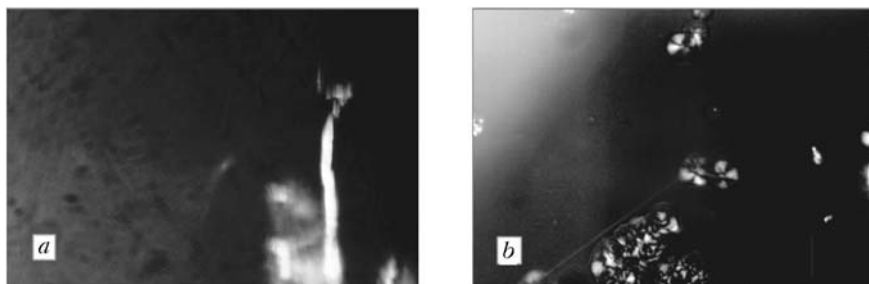Fig. 5. Photographs of the CTA–nitromethane system taken in polarized light: a) solution with $C = 9\%$ at $T = 45^{\circ}$C; b) $C = 5\%$ at $T = 25^{\circ}$C ($\gamma = 62.2\%$, $\overline{M}_{\eta} = 7.0 \cdot 10^{7}$, open stock company "Khimvolokno," city of Engels).
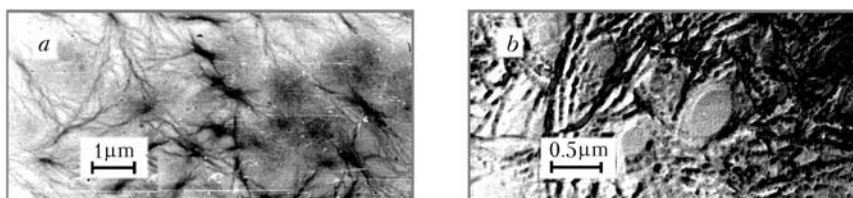

Fig. 6. Electron-microscopic photographs of the sediment obtained from the anisotropic CTA–nitromethane system: a) by setting out in ethyl alcohol; b) by deposing on mica ($\gamma = 62.2\%$, $\overline{M}_{\eta} = 7.3 \cdot 10^{4}$, open stock company "Khimvolokno," city of Vladimir).

range of viscosity decrease may turn out to be not registered at the traditional step of 10°C on the temperature scale and the final result of the sharp increase in the viscosity will become determining. Then the dependence log $\eta = f(T^{-1})$ will have not two inflections (which takes place for ether-cellulose systems in the process of isotropic and anisotropic phase inversion [7]), but only one inflection pointing to a sharp increase in the viscosity and being likely due to the previous crystallization.

Thus, the presented measurements of η at small shear stresses show that the anomalous behavior of the systems manifests itself also at small deformations, and the external action plays likely an additional role in the self-organization of the structures. This is evidenced by the higher temperatures at which a marked decrease in η occurs in the case of the application of the shear field.

Our attempts to investigate the rheokinetics of the phase transition for systems of completely acetylated cellulose ester–nitromethane with $C > 11.5$–12% were vain because of the larger values of η. Moreover, the process of preparation of homogeneous solutions of so high concentrations corresponding to the region of mutual superposition of the amorphous and crystalline phases is inhibited even at high temperatures. Once cooled, the systems become turbid, which can be due to the formation of both LC-type structures and the process of crystallization.

The formation of the anisotropic phase is confirmed by the investigations in polarized light. In the temperature range corresponding to the anomalous decrease in η, in the CTA–nitromethane system structures exhibiting a clearly defined optical anisotropy arise. At mutually perpendicular direction of the analyzer and polarizer planes isotropic solutions heated to 70–80°C look dark. As they cool down, the appearance of birefringent formations is observed (Fig. 5a), and their iridescent glow is enhanced by slightly pressing and shifting the microscope slides. The anisotropic structures are mobile, and they have an extinction angle of 40–50°. In individual cases, anisotropic droplets with a Maltese cross are noted (Fig. 5b). Heating of the solutions to above 55°C leads to the disappearance of the birefringence effect.

Electron-microscopic analysis has revealed that sedimentation of LC-state structures, for example, in ethyl alcohol (Fig. 6a) or hexane leads to the formation of fibrous sediments, which is an additional criterion of the realization of the LC phase [6]. The electron-microscopic photographs of the CTA sediment isolated from the anisotropic solution by deposition on mica and tinged with carbon have the form of prolate fibrils oriented in different directions (Fig. 6b). The diffractograms of the films formed from the concentration-temperature domain of existence of anisot-
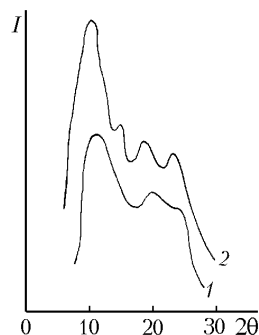
Fig. 7. Diffractograms of films obtained from different concentration-temperature ranges: 1) homogeneous solutions; 2) anisotropic state ($\gamma = 62.2\%$, $\overline{M}_\eta = 7.0 \cdot 10^4$, open stock company "Khimvolokno," city of Engels).

ropic systems (Fig. 7, curve 2) have a large number of intense and clearly defined reflections (unlike films formed from the domain of homogeneous solutions, Fig. 7, curve 1).

The experimental material obtained has made it possible to determine the concentration-temperature domain of existence of the LC state of the CTA–nitromethane system (shaded portion of the diagram in Fig. 1). We can ascertain its relatively small extent as to both the temperature and the concentration, which complies with the theoretical notions of Flory [10] and the experimental data for other systems: complex or simple esters of cellulose–solvent [7, 26–28]. Interestingly, the values of the threshold concentration (~5%), beginning with which in a given system anomalous rheograms, critical shear stresses, properties of anisotropy, etc. are registered, was also predicted by calculations (see above).

Let us emphasize that a distinctive feature of the CTA–nitromethane system is the specific solvation of the functional groups of the polymer by the solvent [19, 20]. According to the classical notions, a more active polymer-solvent interaction should be expected at temperatures above the curve of phase separation with UCMT (Fig. 1), with which our rheological tests results agree (Figs. 2 and 4). As the temperature decreases, the thermodynamic quality of nitromethane as a CTA solvent drops, which shows up as an increase in the Flory–Huggins interaction parameter for this system calculated from the phase equilibrium curve (Fig. 3, curve 1). The value of the quantity χ_1 varies from 0.51 (near the Θ-conditions, $\Theta = 68^{\circ}$C [1]) to 0.65 at $T = 25^{\circ}$C. It is likely that in the phase separation region desolvation of polymer molecules and strengthening of dipole-dipole contacts occur. In so doing, by virtue of the fact that the hydroxyl groups have already been solvated by nitromethane, intermolecular interaction occurs mainly between free acetate groups, providing a gradual orientation of macromolecular chains and their domains.

From the above specificity it follows that in addition to the rigidity of the macromolecule itself the number and type of functional groups in it can play a significant additional role promoting or inhibiting the formation of ordered structures. In this case, the higher the degree of acetylation the larger (under the existing conditions) the number of intermolecular contacts. All other characteristics being equal, an increase in the number of OH-groups in the CTA should lead to a better solvability of the polymer in nitromethane and to a limitation of polymer–polymer contacts. Indeed, the CTA–nitromethane system with compositions equivalent to those used in the present paper form at room temperature visually transparent homogeneous solutions [29].

One can also come to such a conclusion on the basis of the dependence $\chi_1 = f(T)$ for a CTA sample with a lower degree of esterification (Fig. 3, curve 2) and the calculation of the value of the Θ-temperature. For example, as the degree of esterification is decreased from 62.2 to 60%, the Θ-temperature calculated in [22] decreases from 68 to 46°C. Consequently, the smaller the number of acetate groups in the cellulose ether, the more active the manifestation of the interaction of nitromethane with the hydroxyl groups of the polymer and the higher the polymer concentration and the lower the temperature required for creating the conditions for the transition of the cellulose acetate–nitro-methane system to the LC state.

Indeed, for the other samples characterized by the same $\overline{M}_\eta$ as in the above-considered CTA but with $\gamma = 60.2$ and 58.1%, all the above properties and dependences were also revealed beginning with $C = 14$ and 25%, respectively, at lower temperatures. As an example, Figure 8 shows the rheokinetics of the phase transition in a system with
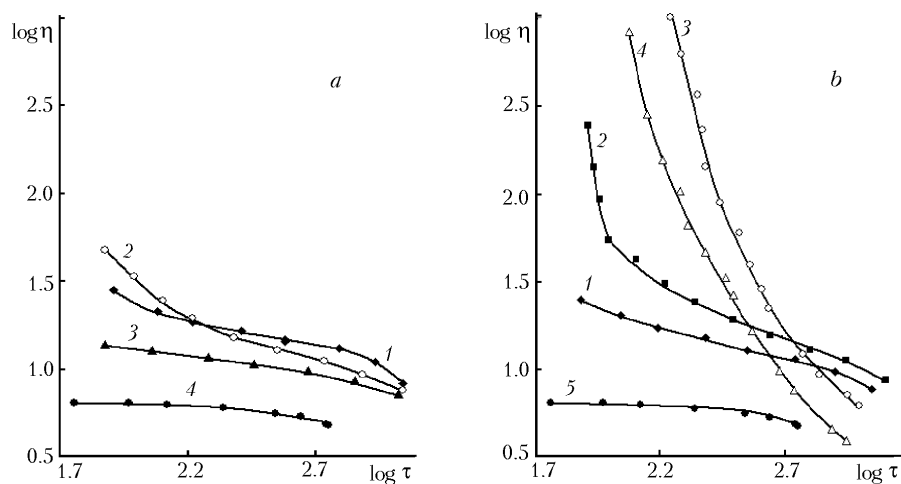
1228

Fig. 8. Rheokinetics of the phase transition in the CTA (γ = 60.2%)–nitrome-thane system with a 15% concentration of the polymer: a) at T = 35°C for various thermostating times [1) 0.25 h; 2) 1.5), and 3) 4; 4) at T = 70°C]; b) at T = 30°C for various thermostating times [1) 0.25 h; 2) 0.5; 3) 1; and 4) 1.5; 5) at T = 70°C.
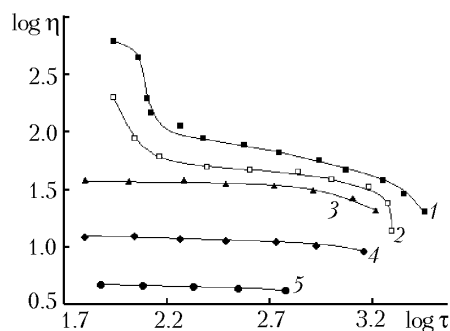

Fig. 9. Viscosity rheograms of the CTA (γ = 58.1%)–nitromethane system with a 25% concentration of the polymer at various temperatures: 1) T = 20°C; 2) 25; 3) 30; 4) 50; 5) 70; the thermostating time was 1 h at each temperature.

C = 15% at temperatures 35 and 30°C for a sample with γ = 60.2%, and Fig. 9 gives the viscosity rheograms of a system with C = 25% at T = 20–70°C for a sample with γ = 58.1%. One would also expect that at an even lower content of acetate groups in the polymer the LC phase will be realized under harder conditions: at low temperatures and larger threshold concentrations of the polymer.

Conclusions. The investigation of the CTA–nitromethane system has shown that it is characterized by a diversity of physical states (homogeneous and anisotropic solutions, jellies, visually observable two-phase systems) in a relatively narrow temperature range (20–60°C). The transition to the LC state is realized upon reaching the threshold concentration-temperature conditions and is protracted. The rate of formation of highly oriented structures is higher the lower the investigated temperature inside the found interval of mesophase formation.

Moreover, the specificity of the interaction of nitromethane with the polar groups of the polymer shifts the boundaries of the domain of existence of the LC phase with decreasing degree of esterification of samples into the region of lower temperatures and high concentrations. Consequently, in investigating the conditions for the formation of the lyotropic LC phase in cellulose acetate, it is necessary not only to be guided by their general solvability in a particular solvent, but also take into account the possibilities of selective solvation by a low-molecular liquid of the functional groups of the polymer.

NOTATION

C, solution concentration of the polymer, mass %; d, solvent density, g/cm^3; f, equilibrium degree of curvature of chains; I, scattering intensity, rel. units; k_1, enthalpic component of the interaction parameter χ_1; $\overline{M}_\eta$, viscosity-average molecular mass, average statistical quantity; T, temperature, $^{\mathrm{o}}$C; T_{boil}, boiling temperature of solvent, $^{\mathrm{o}}$C; T_{boilNM}, boiling temperature of nitromethane, $^{\mathrm{o}}$C; T_{cr}, critical temperature of binodal corresponding to the UCMT, $^{\mathrm{o}}$C; T_{meltCTA}, melting temperature of cellulose triacetate, $^{\mathrm{o}}$C; t, time, h; X, degree of polymerization; χ_1, Flory–Huggins polymer-solvent interaction parameter characterizing the surplus free interaction energy per one molecule of solvent in solution; γ, degree of acetylization of the polymer, %; η, viscosity, Pa·sec; Θ, temperature at which a diluted solution of the polymer in a given solvent exhibits properties of the ideal solution, $^{\mathrm{o}}$C; 2θ, diffraction angle; τ, shear stress, Pa; τ_{cr}, critical shear stress or yield stress, Pa; ψ_1, entropic component of the interaction parameter χ_1. Subscripts: boil, boiling; cr, critical; NM, nitromethane; melt, melting.

REFERENCES

1. G. N. Timofeeva, V. M. Aver'yanova, and V. I. Klenin, Thermokinetic study of the phase separation in the cellulose triacetate–nitromethane system, *Vysokomol. Soedin. B*, **19**, No. 1, 7–11 (1977).
2. N. O. Gegel', G. N. Timofeeva, and A. B. Shipovskaya, On the phase state of cellulose triacetate in nitromethane, in: *Structure and Dynamics of Molecular Systems*, Institute of the Physics of Molecules and Crystals, Educational-Scientific Center of the Russian Academy of Sciences, Ufa (2006), Issue 13, Pt. 1, pp. 236–239.
3. A. B. Shipovskaya and G. N. Timofeeva, Specific features of the phase separation in the system cellulose acetate of different degrees of acetylation–mesophasogenic solvent–nitromethane, in: *Structure and Dynamics of Molecular Systems*, Issue 10, Pt. 2, Izd. Kazansk. Univ., Kazan' (2003), pp. 222–225.
4. G. N. Timofeeva, E. S. Sveshnikova, and A. B. Shipovskaya, Orientational phenomena in the system cellulose acetate of different degrees of substitution–nitromethane, in: *Collected papers of the Int. Conf. "Composite-2004"* [in Russian], Izd. SGTU, Saratov (2004), pp. 336–341.
5. V. I. Klenin, *Thermodynamics of Systems with Flexible-Chain Polymers* [in Russian], Saratovsk. Gos. Univ., Saratov (1995).
6. S. P. Papkov and V. G. Kulichikhin, *Liquid-Crystal State of Polymers* [in Russian], Khimiya, Moscow (1977).
7. V. G. Kulichikhin and L. K. Golova, Liquid-crystal state of cellulose and its derivatives, *Khim. Drevesiny*, No. 3, 9–27 (1985).
8. K. Kamide, M. Saito, and H. Suzuri, Persistence length of cellulose and its derivatives in solution, *Macromol. Chem.*, *Rapid Commun.*, **4**, No. 1, 33–39 (1983).
9. S. M. Aharoni, Effects of the nature of the solvent on the lyotropic mesomorphicity of cellulose acetate, *Mol. Cryst. Liquid Cryst.*, **56**, No. 7, 237–241 (1980).
10. P. J. Flory, Statistical thermodynamics of semiflexible chain molecules, *Proc. Roy. Soc. London A*, **234**, No. 1, 60–72 (1956).
11. G. N. Timofeeva and A. B. Shipovskaya, Concentration-temperature conditions for the formation of the liquid-crystal phase of cellulose triacetate in nitromethane, in: *Structure and Dynamics of Molecular Systems*, Issue 10, Pt. 2, Izd. Kazansk. Univ., Kazan' (2003), pp. 28–31.
12. G. N. Timofeeva, I. V. Fedusenko, N. A. Lashek, and A. B. Shipovskaya, Induced optical anisotropy in cellulose acetate films under the influence of vapors of certain solvents, *Vysokomol. Soed. B*, **37**, No. 6, 1093–1095 (1995).
13. A. B. Shipovskaya and G. N. Timofeeva, Change in the structure and optical activity of cellulose acetates under the action of vapors of certain solvents, *Vysokomol. Soed. A*, **43**, No. 7, 1237–1244 (2001).
14. A. B. Shipovskaya and G. N. Timofeeva, Rheological properties and optical activity of modified cellulose acetate, *Vysokomol. Soed. B*, **45**, No. 1, 101–105 (2003).
15. A. B. Shipovskaya and G. N. Timofeeva, Liquid-crystal state in the system polysaccharide–mesophasogenic solvent, *Inzh.-Fiz. Zh.*, **79**, No. 1, 139–147 (2006).

16. A. B. Shipovskaya, O. F. Kazmicheva, and G. N. Timofeeva, Optical activity of the system cellulose acetate–mesophasogenic solvent upon the formation of the lyothropic liquid-crystal phase, *Biofizika*, **51**, No. 2, 256–266 (2006).

17. A. B. Shipovskaya, S. L. Shmakov, and G. N. Timofeeva, Phase processes and energetics of the spontaneous change in the dimensions of acetate fibers in nitromethane vapors, *Vysokomol. Soed. A*, **48**, No. 5, 801–814 (2006).

18. Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim (1988).

19. W. R. Moor and J. Schuttlewort, Solvation of cellulose derivatives, *J. Polym. Sci. B*, **132**, No. 1, 89–91 (1964).

20. A. S. Buntjakov and V. M. Averyanova, The structure of solution and films of cellulose acetate, *J. Polym. Sci. C. Morphol. Polym.*, No. 38, 109–120 (1972).

21. P. J. Flory, *Principles of Polymer Chemistry*, Ithaca Cornell Univ., New York (1953).

22. V. M. Aver'yanova, N. I. Panina, and G. N. Timofeeva, Estimation of the thermodynamic solubility parameters in the gelatinous cellulose triacetate–nitromethane system, *Vysokomol. Soed. B*, **21**, No. 7, 502–504 (1979).

23. G. N. Timofeeva and V. M. Aver'yanova, Study of the phase separation kinetics in the gelating cellulose triacetate–nitromethane system by a rheological method, *Kolloid. Zh.*, **42**, No. 2, 393–397 (1980).

24. P. V. Papkov, *Gelatinous State of Polymers* [in Russian], Khimiya, Moscow (1974).

25. A. Ya. Malkin and V. G. Kulichikhin, *Rheology in the Processes of the Formation and Transformation of Polymers* [in Russian], Khimiya, Moscow (1985).

26. R. S. Werbowij and D. G. Gray, Ordered phase formation in concentrated hydroxypropylcellulose solutions, *Macromolecules*, **13**, No. 1, 69–73 (1980).

27. S. Yu. Belov and V. V. Myasoedova, Characteristic features of the phase equilibrium and conformational state of cellulose triacetate in mixed flowing solvents, *Izv. Akad. Nauk SSSR*, *Ser. Fizicheskaya*, **55**, No. 9, 1789–1793 (1991).

28. U. Vogt and P. Zugenmaier, Investigation of lyotropic mesophase system: tricarbanylate cellulose — methyl ethyl ketone, *Macromol. Chem.*, *Rapid Commun.*, **4**, No. 12, 759–765 (1983).

29. A. B. Shipovskaya and G. N. Timofeeva, Study of the phase transformation kinetics of cellulose diacetate and triacetate in nitromethane by a rheological method, in: G. V. Pyshnograi and Yu. A. Altukhov (Eds.), *Urgent Problems of Rheology* [in Russian], Izd. Altaisk. GTU, Barnaul (2003), pp. 136–138.