

PECULIARITIES OF THE PHYSICOCHEMICAL PROPERTIES OF CHITOSAN SOLUTIONS

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The rheological, electrochemical, and surface properties of chitosan solutions in acetic acid were studied for several molecular masses and polymer and acetic acid concentrations. Changes in the viscosity, degree of structuring, and flow curve character of the solutions were observed when these were stored. The stability of the viscous properties was essentially influenced by the concentration and molecular mass of the polymer and by the ionic strength of the solution. The surface tension and conductivity of the solutions did not change in time. It is speculated that the kinetic instability of the rheological properties of chitosan is not associated with the occurrence of any destructive processes.

Keywords: chitosan solutions, rheology, surface tension, conductivity, kinetics

It is known that the operating performance of a ready polymeric product is defined in many respects by the physical–chemical properties of a forming solution. For large-capacity synthetic and also some natural and artificial polymers (e.g., cellulose and its derivatives), such regularities have been studied and generalized well enough [1, 2]. However, for chitosan (CT), a derivative of the natural polysaccharide chitin, this problem still remains topical, as the obtainment of quantitative data on the interrelation between the physical–chemical characteristics of a solution and those of a ready material is complicated by the compositional heterogeneity of samples of the polymer [3, P. 112–118], the kinetic instability of the viscous properties of solutions based on it [4–7], the absence of certified techniques to estimate the quality of the initial raw material, and so on.

Traditionally, CT has been used for manufacturing solutions, gels, and films, the preparation methods for which have been covered fully enough in the scientific and patent literature [3, 8, 9]. Recently, reports have appeared describing the obtainment of CT-based novel film composites [10, 11]; capsules [12]; fibrous biocatalysts [13]; nanofibers and nonwoven cloths [14, 15]; micro- and nanoparticles, with the use of carbon dioxide in the supercritical

state [16]; and so on. The general stage in the preparation of all these materials from CT is polymer dissolution in organic or mineral acids of differing concentrations. Therefore, research on the peculiarities of the physical-chemical parameters of CT solutions is of interest from both scientific and practical points of view.

The purpose of this work was to study the peculiarities of the rheological, electrochemical, and surface properties of acetic CT solutions, depending on the concentration and molecular weight of the polymer, the concentration of acetic acid, and the time for which a solution is stored under static conditions.

Materials and methods of research

In this work, we used industrial acid-soluble samples of CT with different molecular weights (\overline{M}_η) and with similar deacetylation degrees. The samples are characterized in table. As a solvent, we used aqueous solutions of acetic acid (concentration $C(\text{Ac}) = 2\text{--}70\%$), which were prepared by using chemically pure glacial acetic acid and distilled water. Acetic CT solutions with concentrations C of 0, 1–5 g/dl were used for study. Solutions were prepared by dissolving a sample of air-dry CT in water–acid medium at room temperature and normal atmospheric pressure for 1 day; moderately concentrated ($C = 2\text{--}5$ g/dl) solutions were additionally stirred on a magnetic stirrer. All systems were stored under static conditions at a temperature T of $22 \pm 2^\circ\text{C}$. Measurements of the physical and chemical parameters were made at intervals during several years.

Properties of the chitosan samples

Sample	Viscosity-averaged molecular mass \overline{M}_η (kDa)	Deacetylation degree (mol%)	Manufacturer
CT-87	87	83,6	CJSC «Bioprogress» (Shchelkovo, Russia)
CT-180	180	82,0	CJSC «Bioprogress»
CT-200	200	82,0	CJSC «Bioprogress»
CT-275	275	80,8	CJSC «Sonat» (Moscow, Russia)
CT-640	640	82,6	CJSC «Bioprogress»

Rheograms of viscosity (η , Pa·s) were read with a Rheotest RN-4.1 and, in some cases, a Rheotest-1 rotary viscometer, with cylinder–cylinder working units, at temperatures T of 20–50°C and shear stresses $\lg \tau$ of 1,2–3,5 [Pa·10⁻¹]. The degree of solution structurization was defined as

$$S = \frac{\eta_{\max} - \eta_{\min}}{\eta_{\min}} \cdot 100\%,$$

where η_{\max} is the greatest Newtonian viscosity (for classical flow curves) or the maximal value of viscosity on the rheological curve $\lg \eta = f(\lg \tau)$ (for systems with plastic flow curves); η_{\min} is the value of viscosity at the values of $\lg \tau$ beginning with which a sharp decrease in $\lg \eta$ (i.e. corresponding to the origin of the structural viscosity area) is observed. The apparent energy of activation of the viscous flow (ΔE_a , kJ/mol) was estimated by the Arrhenius–Frenkel–Eyring equation:

$$\eta = A \exp\left(\frac{\Delta E_a}{RT}\right),$$

where A is the constant, R is the universal gas constant (J/mol·K), T is the temperature (K), and $\eta = \eta_{\max}$.

The surface tension coefficient (σ , N/m) was determined stalagmometrically at $T = 20^\circ\text{C}$. The error did not exceed $\pm 5\%$. We used a stalagmometer with an arched (L-type) capillary with a diameter d of

0,6 mm. The surface tension coefficient was found with the formula

$$\sigma = \sigma_0 \frac{n_0}{n},$$

where n and n_0 are the numbers of solution and solvent drops being formed and σ_0 is the surface tension coefficient for the solvent (acetic acid), which in preliminary experiments had been found to be $\sigma_0 = 6,9 \cdot 10^{-2}$ N/m for 2% acetic acid and $3,2 \cdot 10^{-2}$ N/m for 70% acetic acid. In parallel, we determined the time of formation and separation of solution (t, s) and solvent (t_0, s) drops from the stalagmometer's capillary.

The conductivity (γ , S/cm) was measured with an Anion 4120 conductometer (error, $\pm 4\%$).

Results of research and their discussion

Fig. 1, a and 1, b (curves 1) shows viscosity rheograms for fresh moderately concentrated CT solutions in 2% acetic acid. It can be seen that both dependences $\lg \eta = f(\lg \tau)$ are similar and are classic for polymer solutions: on the flow curves, it is possible to single out areas of the greatest Newtonian viscosity and the origin of structural viscosity. The viscosity increased with increasing concentration of CT in the solution ($C(\text{Ac}) = \text{const}$).

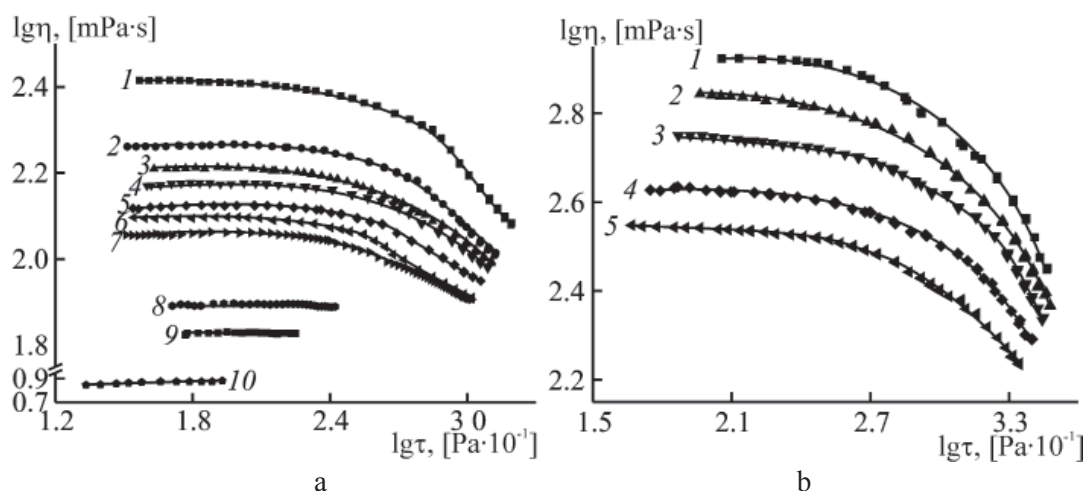


Fig. 1. Flow curves for CT-87 solutions in 2% acetic acid: (a) a solution ($C = 2$ g/dL) stored under static conditions ($T = 22 \pm 2^\circ\text{C}$) for 0 (1), 7 (2), 14 (3), 21 (4), 28 (5), 35 (6), 42 (7), 77 (8), 87 (9), and 800 days (10); (b) $C = 3$ g/dL, storage times of 0 (1), 2 (2), 5 (3), 9 (4), and 13 days (5)

With a simultaneous increase in the CT concentration in solution and in the concentration of acetic acid (solution ionic force I) and/or the molecular weight (\overline{M}_n) of the polymer, the character of the rheological curves underwent a change (Fig. 2 and 3, a and 3, b, curves 1). For example, CT solutions in acetic acid $C(\text{Ac}) \geq 4\%$, even at comparatively low

polymer concentrations (2 g/dl), were non-Newtonian liquids, for which a viscosity decrease was observed in the entire shear stress area studied. In the area of comparatively high $\lg \tau$ values, the viscosity decreased to a greater degree than it did in the area of low values, which is peculiar to the flow of pseudoplastic systems.

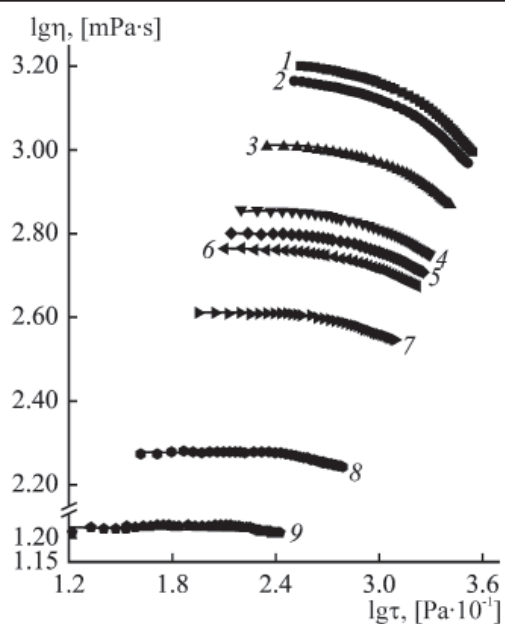


Fig. 2. Flow curves for a CT-200 solution ($C = 5$ g/dL) in 70% acetic acid after storage under static conditions for 0 (1), 2 (2), 7 (3), 21 (4), 28 (5), 35 (6), 49 (7), 92 (8), and 363 days (9)

A study of the temperature dependence of viscosity of CT solutions showed that with increasing temperature, η decreased (Fig. 3). The shape of the rheological curves did not change essentially. From the obtained dependences $\ln \eta = f(RT)^{-1}$, the apparent activation energy for the viscous flow of CT solutions was calculated (Fig. 4,a, a point on the ΔE_a axis). The obtained value ≈ 28 – 30 kJ/mol is typical of solutions of semirigid chain polymers, of which CT is one.

The comparatively high durability of the structure of the systems being studied was also confirmed by the high values of the structurization degree (Fig. 4,b, a point on the S axis). Similar S values were found by Nud'ga et al. [17] for moderately concentrated CT solutions in acetic acid. With increases in C , \bar{M}_n , and I , the degree of the solution's structural organization (the ability of the structure to withstand the application of a mechanical field) increased.

It is known that the viscosimetric properties of CT solutions are unstable in time [4–7]. In this connection, we examined the rheological properties of solutions stored in the absence of an external field.

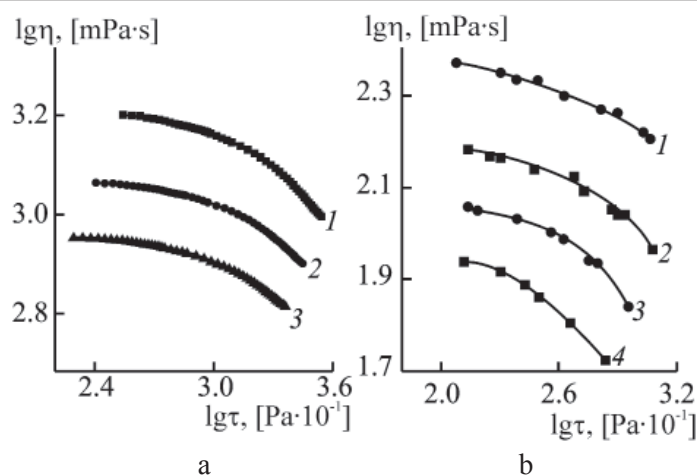


Fig. 3. Viscosity rheograms: (a) CT-200 ($C = 5$ g/dL) in 70% acetic acid at a temperature $T = 20$ (1), 25 (2), and 30°C (3); (b) CT-275 ($C = 2$ g/dL) in 4% acetic acid (Rheotest-1) at $T = 20$ (1), 30 (2), 40 (3), and 50°C (4)

When CT solutions were stored under static conditions, their viscosity declined essentially (Fig. 4). The higher was the solution polymer concentration (curves 3 and 4), the larger was the decline in the system's viscosity (η/η_0 , where η_0 is the initial viscosity of the solution) in time, in agreement with the data of Sklyar et al. [7]. However, for a system with a higher polymer concentration and a higher solution

ionic force (curve 2), the viscosity decrease was somewhat smaller in comparison with that observed in a solution with lower C and I values. Thus, the lower is the acid concentration in the solvent, the larger is the decrease in η with time. An increase in the molecular weight of CT, with other things being equal, probably makes the decline in the solution η larger (curve 1).

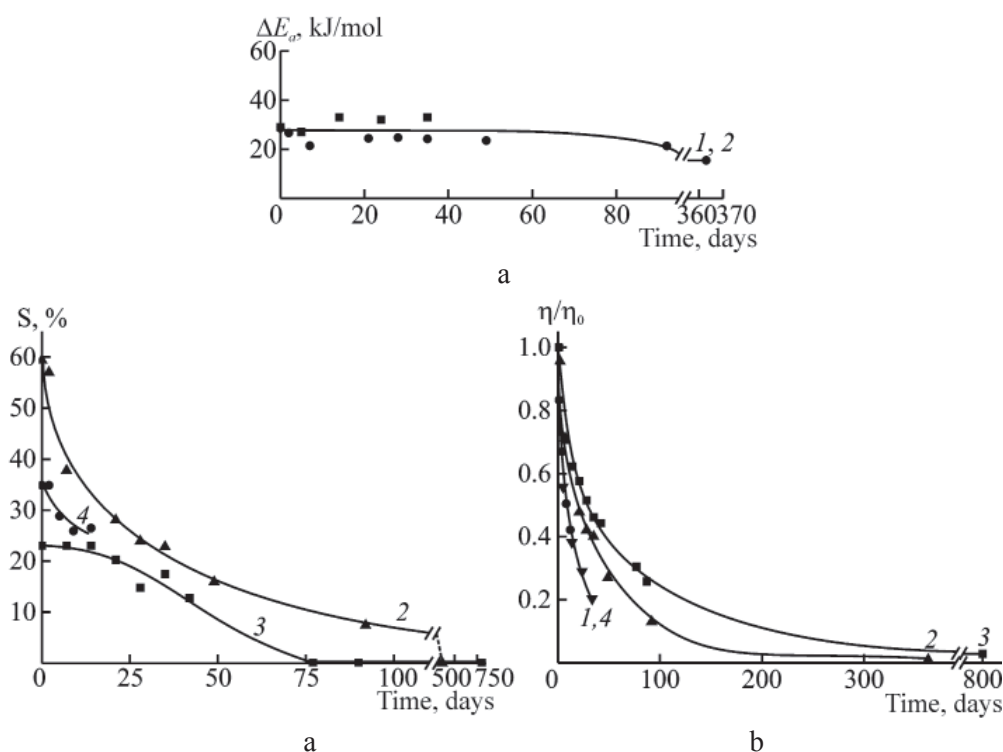


Fig. 4. Kinetics of the activation energy of the viscous flow (a), the degree of structurization (b), and the relative viscosity (c) for solutions of CT-275 ($C = 2$ g/dL) in 4% acetic acid (1), CT-200 ($C = 5$ g/dL) in 70% acetic acid (2), and CT-87 ($C = 2$ and 3 g/dL) in 2% acetic acid (3, 4)

With time, changes were observed not only in η but also in the character of the viscosity rheograms. Specifically, for the flow curves of CT solutions in 2% acetic acid that had been stored for a period of time, in comparison with fresh solutions, the shear stress range in which viscosity is constant was observed to expand (Fig. 1, curves 2–7) to the point of realization of the dependence $\lg \eta = f(\lg \tau)$ for Newtonian liquids (Fig. 1, a, curves 8–10). For pseudo-plastic systems, the non-Newtonian character of the flow was retained for up to ~21 days of storage of CT solutions under static conditions (Fig. 2, curves 2–4). At a longer storage time, the realization of classic flow curves (curves 5–7) was observed. At a storage time of more than ~75 days, the dependence of viscosity on shear stress was already linear ($\lg \eta \sim \lg \tau$; curves 8–10).

The degree of structurization of the solutions also decreased during their storage (Fig. 4). The zero value of S , characteristic of Newtonian liquids with $\lg \eta \sim \lg \tau$, was realized for less concentrated solutions at a much smaller time of their storage under static conditions. The viscous flow activation energy for the solutions remained almost unchanged (Fig. 4), except after 363 and more days of storage.

Apparently, the described regularities of temporal change in the character of the flow curves, viscosity, and the degree of structurization of CT solutions are not a consequence of destructive processes, as all these changes occurred most intensively in solutions with lower acetic acid concentrations.

Because there has been no unequivocal explanation for what causes the decrease in viscosity of CT solutions in time [4–7], it was of interest to also follow the kinetic stability of other physical–chemical parameters of the systems under study, in particular surface tension and conductivity. The totality of these parameters, together with the value of viscosity, essentially determines the fiber-forming ability of polymer solutions during fiber electroformation [18].

We first consider the surface properties of CT solutions. In special experiments, we explored the concentration dependence of the surface tension coefficient for CT solutions in 2 and 70% acetic acid. In aqueous acetic acid, this polymer displayed the property of a surfactant: with increasing solution concentration of the polymer, σ decreased, reaching a constant value at $C \geq 0.2$ g/dl. With increasing acetic acid concentration, σ decreased substantially (Fig. 5, a, points on the ordinate); the character of the $\sigma = f(C)$ dependence was similar.

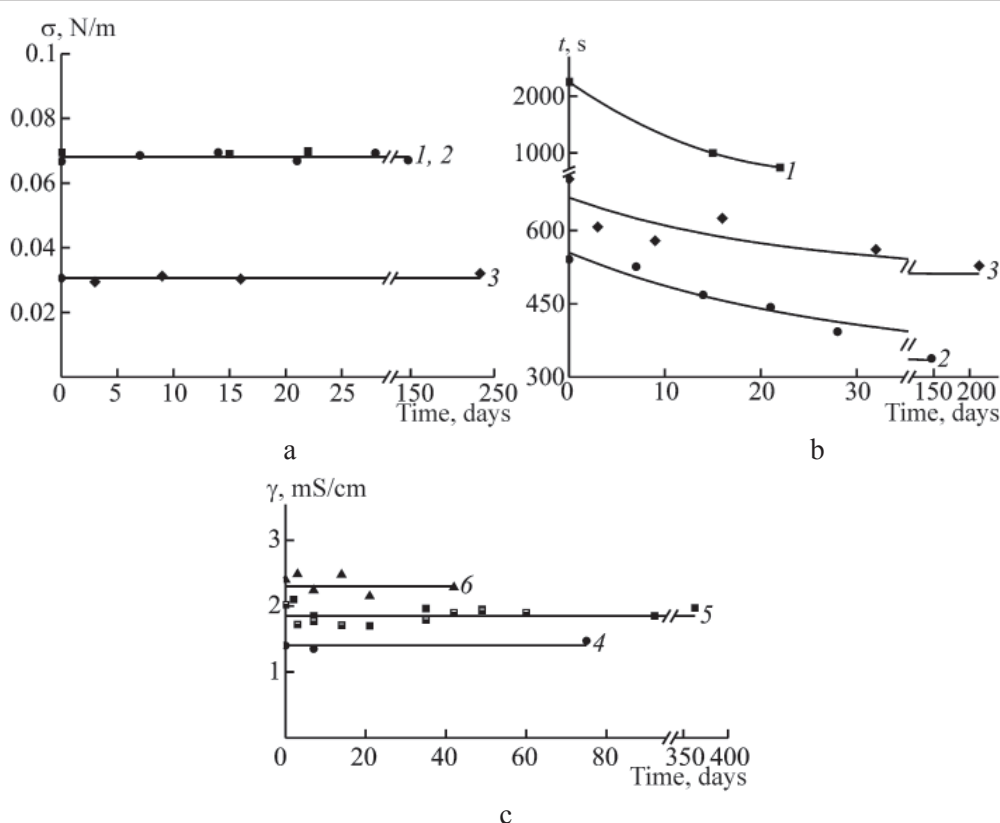


Fig. 5. Kinetics of the surface tension (a), the time of outflow of a fixed volume of liquid from the stalagmometer's capillary (b), and the conductivity (c) for solutions of CT-640 (1), CT-200 (2–5), and CT-180 (6). Concentrations: $C = 0.25$ (2) and 0.5 g/dl (1) in 2% acetic acid; $C = 0.25$ (3), 3 (4), and 5 g/dL (5, 6) in 70% acetic acid

For estimating the influence of the kinetic factor on the surface tension coefficient, we used CT solutions with concentrations for which the condition $\sigma(C) = \text{const}$ was met. Observations on the kinetics of σ allowed the conclusion that the surface tension of water–acid solutions of CT does not change in time (Fig. 5,a).

The stalagmometer method is based on the determination of the weight of a drop of liquid that comes off the capillary under the action of gravity. Traditionally, in the determination of the solution σ , this method is used to experimentally find the number of solution and solvent drops coming off the capillary when a liquid is slowly flowing out of the stalagmometer. The time of formation and separation of the liquid drops is usually left uncontrolled. We established that for fresh systems, the drop outflow time depends on the solution concentration of CT, the of the polymer, and the ionic force of the solution (Fig. 5,b, points on the ordinate).

From a study of the surface tension kinetics for water–acid solutions of CT, an interesting fact emerged. For stored solutions, the time

(t) of the formation and separation of drops of the liquid flowing out of the stalagmometer decreased essentially (Fig. 5,b). Because this supervision is nontrivial, similar experiments were run that used the binary system water–acid. It was found that the time of formation and separation of drops was the same for both freshly made acetic acid (t_0) and that stored for different periods.

A large decline in t occurred during ~ 28 – 30 days of storage (Fig. 5,b). At a longer time of solution storage, the change in t was not so essential. The rate of the decrease in t increased with increasing molecular weight of CT.

Traditional views hold that the time of outflow of a liquid from a capillary is proportional to the viscosity of that liquid. In view of this and by comparing Fig. 4,c and 5,b, it is easy to see a correlation between the temporal change in viscosity of moderately concentrated solutions, measured with a rotary viscometer, and the time of outflow of dilute CT solutions through the capillary of the stalagmometer. Indeed, in either case, a quantity is being measured that characterizes, to one degree or another,

er, the coefficient of friction of the liquid layers moving during the flow process.

Because these effects were observed when the solution was in a steady state, we believe that the decrease in η and t is connected with a change in the structure of the systems under study – possibly with a change in macromolecular shape in solution, giving rise to such conformations whose resistance to the flow is less than that in the initial freshly made system.

However, not all authors share this assumption. For example, in the works [4, 6], the decrease in the viscosity of CT solutions was explained by a hydrolytic breakdown of glycosidic linkages in the macromolecules. The dissolution of CT in water–acid medium is caused by the protonation of the polymer's amino groups, owing to which the macromolecule takes on the properties of a macrocation. If it is true that there are destructive processes occurring in CT solutions, the quantity of macroions in stored CT solutions should increase.

To elucidate this question, we investigated the conductivity of CT solutions, because this parameter is proportional to the number of charged particles present in a system. A typical dependence of γ kinetics is given in Fig. 5, c by using the example of CT solutions in 70% acetic acid. It can be seen that the conductivity of CT solutions stored for a long time under static conditions did not change (Fig. 5). The temporal variation in the γ values was within the measurement error.

Conclusions

The obtained result has allowed us to ascertain that the above-considered regularities of decrease in the viscosity, structurization degree, and outflow time of stored CT solutions do not stem from destructive processes. This is also in agreement with the fact of the less significant decrease in the viscosity of solutions with higher concentrations of acetic acid, found both in this work and by Sklyar et al. [7]. A possible cause for such behavior is as follows: An increase in the ionic force of a moderately concentrated solution increases the probability of interchain contacts between macromolecular coils and promotes the structural stabilization of the system. As noted by Sklyar et al. [7], it is difficult to imagine a breakdown of the glycosidic linkage taking place in dilute acetic acid (2 or 4%) and this process being absent in 70% acetic acid. It is more natural to associate all these changes with structural reorganizations.

Thus, our research has established the kinetic stability of the surface tension and conductivity of acetic CT solutions and the instability of their rheological properties. The stability of the viscous properties of solutions

is largely affected by the concentration and molecular weight of the polymer and also by the ionic force of the solution (acetic acid concentration). In the systems studied, no destruction of macromolecular chains occurs.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant no. 09-03-12193 ofi_m).

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