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RHEOLOGICAL STUDIES OF HIGH-CONCENTRATION CELLULOSE SULFATE-ACETATE SOLUTIONS

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With the method of homogeneous synthesis, various salt forms of cellulose sulfate-acetate containing Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, *and* Co^{2+} *as compensating cations have been obtained. The flow curves, the concentration and temperature dependences of the shear viscosity of aqueous solutions of cellulose sulfate-acetate have a form characteristic of liquid-crystal systems. For solutions of all salts except for potassium salt, spontaneous formation of the anisotropic phase in the form of individual spherulites, spherulite bands, structures of the fingerprint type, and other more complex formations has been registered. A new hydrodynamic criterion that permits predicting the realization of lyotropic mesomorphism in solutions of cellulose derivatives is proposed.*

At the Scientific-Research Institute of Physicochemical Problems of the Belarusian State University, for the first time a polymer electrolyte containing in each anhydroglucose link an acetate and a sulfate group and, as compensating counterions, one- and two-charge cations Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Co^{2+} has been synthesized and isolated from solution of cellulose sulfate-acetate (CSA) in the salt form.

Synthesized salts of cellulose sulfate-acetate are characterized by a high solubility in water (up to 70 mass %). High-concentration aqueous solutions of salt forms of CSA, except for potassium salt, exhibit stable birefringence. In the stationary state and in flowing they opalesce, changing their color from yellow-red to violet, which is one of the outward signs of the cholesteric mesophase formation [1–3].

To register and predict the liquid crystalline (LC) ordering of cellulose sulfate-acetate salts, we have made rheological, polarization-microscopic, and hydrodynamic studies of their aqueous solutions in a wide range of concentrations.

Experimental. Cellulose sulfate-acetate in the salt form was obtained by the method of homogeneous synthesis [4]. The degree of substitution (DS) for sulfate and acetate groups was, respectively, 0.9–1.0 and 0.8–1.0, and the polymer molecular mass was 46,000.

Solutions of CSA salts were prepared by dissolving polymer samples previously dried to a constant mass at a temperature of $60 \pm 2^{\circ}C$ in water, water-salt and water-alcohol media at a different ratio of components. The dissolution process was considered to be completed under the condition of the absence of undissolved polymer fragments from the optical microscope field of view. Concentrated viscous solutions of CSA were deaerated for 48 h. The concentration of prepared solutions was refined by the gravimetric method [5]. To register the isotropic–anisotropic phase transition, a drop of the prepared solution was placed on a microscope slide and pressed by a cover glass. Then the thin solution layer obtained was observed in polarized light with an "Amplival" optical microscope equipped with two polaroids. The observed structural changes were recorded on a film by means of a photographic attachment.

Rheological studies of aqueous solutions of CSA were made with the use of a "Reotest-2" rotational viscometer with a cylinder–cylinder working unit in the temperature interval from 20 to 50° in the shear stress range from 1.6 to $3 \cdot 10^3$ Pa.

Viscometric studies of diluted solutions of CSA salts in water-salt and water-alcohol media were made with the use of a Ubbelohde viscometer at a temperature of $25^{\circ}C$. The characteristic viscosity was determined by the method of double extrapolation of the dependences $\eta_{sp}/c = f(c)$ and $\ln(\eta_{rel}/c) = f(c)$ to the zero concentration [6]. The Huggins constant k_H was calculated by the slope of the $\eta_{sp}/c = f(c)$ curve and the crossover concentration c^* — by the inflection of this curve [7].

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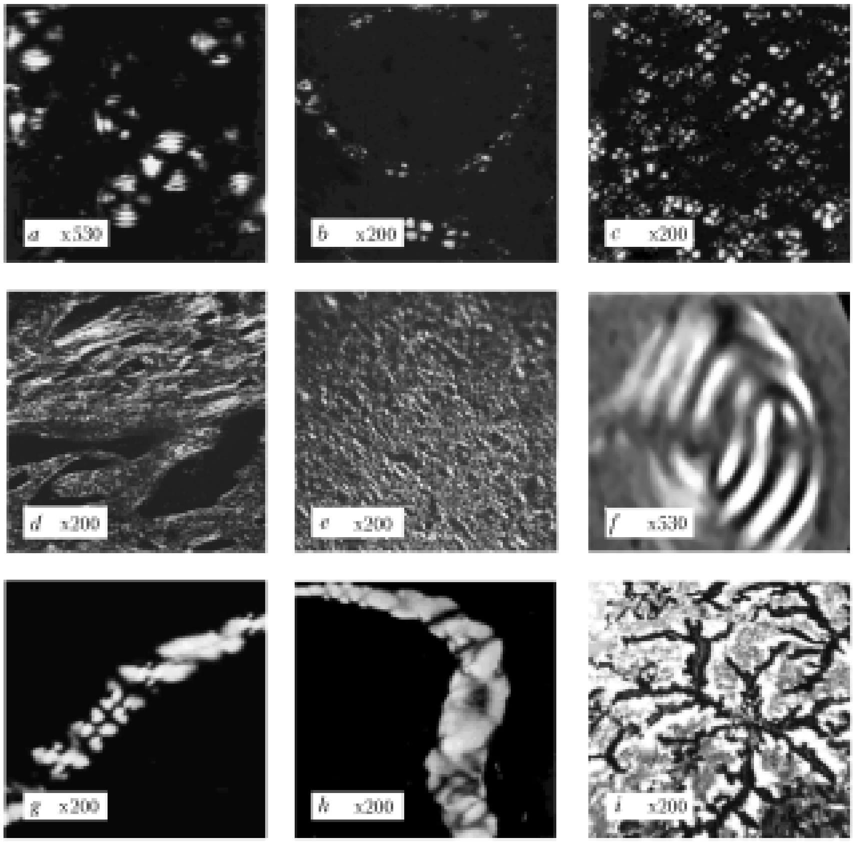
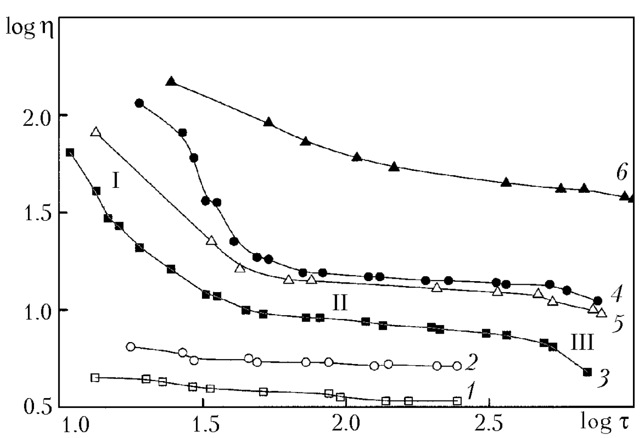


Fig. 1. Microphotographs of the structures arising in aqueous solutions of CSA at 20°C.

Results and Discussion. It has been found that aqueous solutions of Na^+–CSA up to 2 mass % are visually transparent and isotropic; in the range of concentrations between 2 and 42 mass % they are also isotropic but are no longer transparent, which points to the association of macromolecules without the formation of a certain order in their arrangement. With the method of polarization-optical microscopy in concentrated Na^+–CSA solutions (over 42 mass %), ordered structures distributed in an isotropic medium in the form of individual spherulites of diameter from 10 to 50 μm have been clearly recorded (Fig. 1a). With increasing content of the polymer in the solution, the spherulites aggregate in the form of bands and more complex structural formations (Fig. 1b, c). The spherulites have a clearly defined circular structure intercepted by a Maltese cross. Microheterogeneous systems containing such spherulites are thermodynamically unstable, and their storage for 1 month at 5°C leads to a clear separation of the solution into transparent and turbid layers, which corresponds, as to the structure, to the isotropic and anisotropic phases [1]. The appearance of a two-phase region in the Na^+–CSA solutions characteristic of other lyotropic LC systems [8] can be attributed to both the geometric anisotropy of the polymer chain and the change in its conformation in the process of solution concentration. At higher concentrations (over 52 mass %), the Na^+–CSA solution represents, as to its structure, a liquid-crystalline matrix containing small regions of isotropic inclusions (Fig. 1d), which completely disappear as the solution concentration is farther increased to the maximum value (58 mass %). In this case, in microphotographs a confocal texture of the solution (Fig. 1e) is recorded, which changes to a planar one upon displacement of the cover glass. Moreover, in the range of concentrations between 50 and 52 mass % we have registered a texture of the type of fingerprints specific for cholesteric liquid crystals (Fig. 1f).

Analogous phase transformations are also characteristic of Li^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Co^{2+}–CSA. For calcium salt of CSA the formation of structures of the shish-kebab type (Fig. 1g, h) and dendritic structures (Fig. 1i) has also been noted.



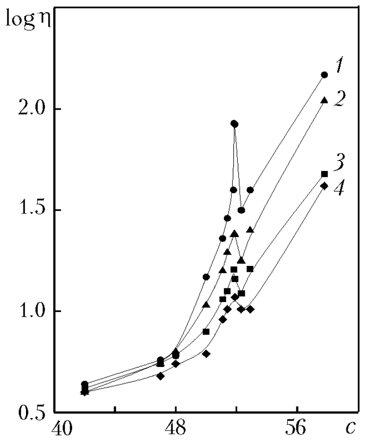


Fig. 2. Viscosity versus shear stress for aqueous solutions of Na^+–CSA with a concentration (mass %) of: 42 (1), 47 (2), 50 (3), 52 (4), 52.5 (5), 58 (6).

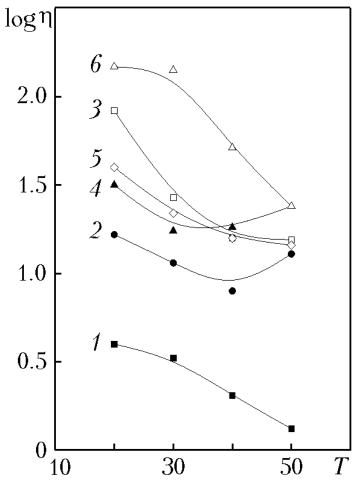
Fig. 3. Viscosity of Na^+–CSA solutions versus concentration (mass %) at 20°C and a shear stress of 25 (1), 40 (2), 250 (3), and 660 Pa (4).

It is known [9] that among the most important criteria for classifying solutions of polymers with liquid-crystalline ones are their characteristic rheological properties, in particular, the presence of the yield point, the absence of the region of viscosity constancy on the rheological curves, and the extreme character of the concentration and temperature dependence of the shear viscosity.

Na^+–CSA solutions with concentrations of 42 and 47 mass % under shear deformation show an abnormally viscous behavior characteristic of structured systems (Fig. 2, curves 1 and 2). The rheological curves of Na^+–CSA solutions with a concentration over 50 mass % show three sections. In region I there is a sharp decrease in viscosity at small shear stresses with a yield point whose value increases with increasing concentration of the solution. This section reflects the polydomain flow of the system associated with the decrease in the size of the domains and the increase in their number. Region II — a "quasi-Newtonian section" — indicates that in reality there is an insignificant but continuous decrease in the viscosity and characterizes the flow of the broken domain structure in a continuous molecular medium. In this case, motion in the flow of aggregates equal in size, whose orientation changes but slightly in shear, occurs. In the section of rheogram III with increasing shear stress a sharp decrease in the viscosity is observed again, which corresponds to the changeover to the molecular (monodomain) mechanism of flow (curves 3–5). Such a character of flow is inherent in solutions containing two phases: isotropic and anisotropic ones. The passage to a completely anisotropic solution (58 mass %) is followed by the disappearance of the third section from the flow curve (curve 6).

The viscosity–concentration dependence (Fig. 3) plotted on the basis of the data of the rheological investigations for Na^+–CSA solutions has a maximum characteristic of LC systems [9] at a concentration of 52 mass %, which shifts to 52.5 mass % as the temperature is increased from 20 to 50°C. The maximum height tends to decrease with increasing rate of shear deformation, which points to the breakage of the LC domains under this type of external action on the system and to the spontaneity of the process of ordering of Na^+–CSA macromolecules in the solution in its absence. The ascending branch of the dependence $\log \eta = f(c)$ pertains to isotropic solutions in which elements of ordered structures begin to nucleate (Fig, 1a–c). The viscosity maximum is characteristic of the moment at which inversion of the iso- and anisotropic phases occurs (Fig. 1d). The descending branch of the viscosity–concentration dependence describes the behavior of solutions in which the volume concentration of the isotropic phase sharply decreases. At a concentration of 52.5 mass % and higher the solution is completely anisotropic (Fig. 1e) and the viscosity increases again.

Figure 4 shows the viscosity–temperature dependence of Na^+–CSA solutions of different concentrations. In one-phase systems, at Na^+–CSA concentrations of 42 and 58 mass % the viscosity naturally decreases with increasing temperature, and for two-phase solutions (50–52.5 mass %) the temperature dependence has an extreme character, noted also for other LC systems [9]. The minimum in the viscosity–temperature dependence can be explained as follows. As the temperature is increased, two competing processes proceed: a decrease in the viscosity due to the inten-



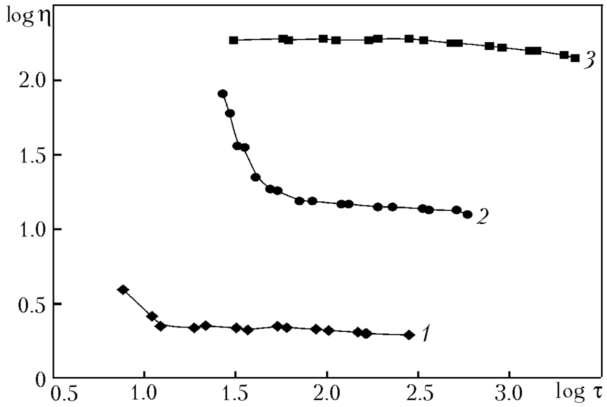


Fig. 4. Temperature dependence of the viscosity of Na^+–CSA solutions with concentrations (mass %) of: 42 (1), 50 (2), 52 (3), 52.5 (4), 53 (5), and 58 (6) at a shear stress of 25 Pa.

Fig. 5. Viscosity versus shear stress for aqueous solutions of Li^+–CSA (1), Na^+–CSA (2), and K^+–CSA (3) with a concentration of 52 mass %.

TABLE 1. Calculated and Experimental Values of the Critical Concentration of Transition to the LC State of Various Salt Forms of CSA

Counterion	c_m, mass %	A	x	φ_{2calc}	c_{calc}, mass %	c_{exp}, mass %
Li^+	70	20	26.7	0.28	39	35
Na^+	58	22	28.5	0.26	37	42
Ca^{2+}	55	24	29.5	0.25	36	30
K^+	52	12.5	15.8	0.44	57	Not revealed

sification of the thermal motion and its increase due to the increase in the volume concentration of the isotropic phase in the system. When the second process begins to dominate, the viscosity, after passing through the minimum, increases again.

Analogous laws have also been established for solutions of lithium and calcium salts, whereas for solutions of potassium salt the rheological criteria of the system transition to the LC state have not been revealed. The character of the flow of K^+–CSA solutions in shear is practically Newtonian and the flow curves have no yield point (Fig. 5). Unlike the Li^+, Na^+, and Ca^+–CSA solutions, the K^+–CSA solutions were one-phase and isotropic — in polarized light the formation of ordered supermolecular structures has not been registered throughout the investigated range of concentrations (1–52 mass %).

We have made estimates of the dynamic rigidity of the CSA macromolecule in various salt forms, whose quantitative characteristics are the Kuhn-segment length and the axial ratio in accordance with the method of [10] (Table 1). This has made it possible to calculate by the Flori equation [8] the polymer concentration in the solution (φ_{2calc} and c_{calc}) at which LC ordering is realized. A fairly good correlation between the theoretical and experimental concentrations corresponding to the initial appearance of the mesophase in concentrated solutions for Li^+, Na^+, and Ca^{2+}–CSA has been established. At the same time, in the case of K^+–CSA the ability of the polymer to show lyotropic mesomorphism is absent.

The aim of the next step of the work was to establish correlation dependences between the hydrodynamic characteristics ($[\eta]$, k_H, and c^*), the chain-rigidity parameters (A or x), and the fact of LC phase formation in concentrated solutions of CSA. For the investigation, we chose the three-component Na^+–CSA–water-alcohol systems, since

TABLE 2. Influence of the Solvent Composition on the Hydrodynamic Characteristics and Parameters of Thermodynamic Rigidity of Na^+–CSA in Water-Alcohol Media

Solvent	vol. Q, %	$[\eta]$, 100 cm^3/g	k_H	c^*, g/100 cm^3	$[\eta]k_Hc^*$	A	x	φ_{2calc}	Presence of LC phase
Water	0	0.44	0.66	1.70	0.49	22	29	0.26	+
Water–ethanol	5	0.52	0.68	2.28	0.81	17	22	0.33	+
	10	0.46	0.71	2.55	0.83	16	21	0.34	+
	20	0.45	0.54	3.80	0.92	12	16	0.47	+
	30	0.45	0.40	6.05	1.09	8	10	0.64	–
Water–isopropyl alcohol	5	0.54	0.60	3.50	1.13	13	17	0.42	–
	10	0.50	0.62	5.43	1.68	9	12	0.83	–
	20	0.45	0.74	7.87	2.62	7	9	0.69	–
	30	0.31	1.25	Precipitation occurs at $c \geq 5$ g/100 cm^3					–
Water–glycerol	10	0.57	0.81	1.90	0.88	20	26	0.29	+
	50	0.61	0.39	8.80	2.09	6	8	0.75	–

TABLE 3. Hydrodynamic Characteristics of Aqueous Solutions and Rigidity Parameters of Salt Forms of Cellulose Sulfate-Acetate

Counterion	$[\eta]$, 100 cm^3/g	k_H	c^*, g/100 cm^3	$[\eta]k_Hc^*$	A	x	φ_{2calc}	Presence of LC phase
Li^+	0.72	0.25	1.77	0.32	20	26.7	0.28	+
Na^+	0.44	0.66	1.70	0.49	22	28.5	0.26	+
K^+	0.66	0.55	3.84	1.39	12.5	15.8	0.44	–
Ca^{2+}	0.47	0.32	1.84	0.28	24	29.5	0.25	+
Mg^{2+}	0.42	0.40	1.85	0.31	22	27.7	0.26	+
Zn^{2+}	0.44	0.52	2.16	0.49	23	27.3	0.27	+
Co^{2+}	0.42	0.62	2.30	0.60	22	24.8	0.30	+

Table 4. Hydrodynamic Characteristics of Solutions of Cellulose and Its Derivatives and Polyacrylic Acid

Polymer	Solvent	$[\eta]$, 100 cm^3/g	k_H	c^*, g/100 cm^3	$[\eta]k_Hc^*$	Presence of LC phase
Cellulose	CF_3COOH	3.10	1.18	0.58	2.12	–
Cellulose acetate (C3 = 1.5)	CF_3COOH	2.43	0.65	0.50	0.79	+
Cellulose acetate (C3 = 2.5)	CF_3COOH	1.70	0.56	0.40	0.38	+
Cellulose acetate (C3 = 2.5)	CH_3COCH_3	1.80	0.40	0.96	0.69	+
Cellulose acetate (C3 = 2.9)	CF_3COOH	1.60	0.56	0.40	0.36	+
Cellulose acetate (C3 = 2.9)	CH_2Cl_2	1.40	0.80	1.50	1.68	–
Hydroxypropylcellulose	H_2O	2.80	0.86	0.34	0.82	+
Cellulose acetobutyrate	$CH_3CON(CH_3)_2$	1.80	0.51	0.20	0.18	+
Ethylcellulose	CH_3COOH	2.00	0.31	0.20	0.12	+
Polyacrylic acid	H_2O—NaCl	3.20	0.32	2.05	2.10	–

for them the regions of the two-component solvent compositions, for which the property of LC ordering of the polymer shows up, and the regions for which the LC ordering was not revealed had been determined.

Table 2 presents the results of determining the characteristic viscosity, the Huggins constant, and the crossover concentration, as well as the calculated parameters: the Kuhn constant and its axial ratio for Na^+–CSA in water-alcohol media. From the correlation analysis performed, it follows that each parameter taken separately cannot be used to predict the orientation ordering of macromolecules in concentrated solutions. Therefore, as a new criterion, we suggest using the product of the three quantities $[\eta]$, k_H, and c^*, which takes into account the polymer–solvent and polymer–polymer interactions and the degree of filling a unit volume of the solution with polymer macromolecules, respectively. This parameter is dimensionless and should not exceed unity in LC systems as well, as follows from the analysis of the data of Table 2.

It should be noted that for other salt forms of CSA the given criterion also clearly predicts the ability to form the LC phase upon their dissolution in water (Table 3).

The use of the empirical product $[\eta]k_Hc^*$ to predict if the polymer–solvent system will exhibit the property of lyotropic mesomorphism turned out to be possible also for nonionogenic cellulose derivatives, as well as for the synthetic polyelectrolyte–polyacrylic acid (Table 4).

CONCLUSIONS

1. As a result of the polarization-optical studies, the conditions for the formation of LC structures in aqueous solutions of Li^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Co^{2+} forms of CSA have been determined. It has been shown that the LC state is formed in high-concentration solutions at a polymer content from 35 to 70 mass %.

2. As an empirical parameter permitting prediction of the realization of LC ordering in solutions of cellulose derivatives, it is suggested to use the product of the three quantities $[\eta]k_Hc^*$. The numerical value of this criterion for LC systems should not exceed unity.

NOTATION

A, Kuhn-segment length, nm; c, concentration, g of polymer/100 cm^3 of solution; c^*, crossover concentration, g of polymer/100 cm^3; c_m, concentration corresponding to the maximum solubility of the polymer, mass %; c_{calc}, calculated value of the critical concentration of transition to the LC state, mass %; c_{exp}, experimental value of the concentration corresponding to the transition to the LC state, mass %; k_H, Huggins constant; Q, content of alcohol, vol. %; T, temperature, ^oC; x, axial ratio; η, shear viscosity, Pa·sec; $[\eta]$, characteristic viscosity, 100 cm^3/g; η_{rel}, relative viscosity; η_{sp}, specific viscosity; η_{sp}/c, reduced viscosity, 100 cm^3/g; φ_{2calc}, calculated volume concentration of polymer corresponding to the transition to the LC state; τ, shear stress, Pa. Subscripts: rel, relative; m, maximum; calc, calculation; sp, specific; exp, experimental.

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