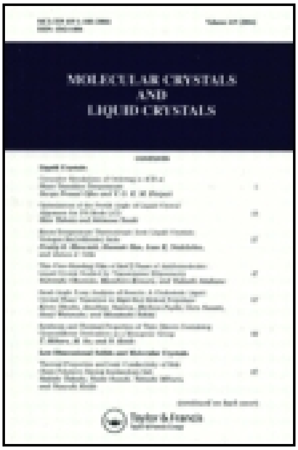

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Structural-Thermodynamic Characteristics of Non-Aqueous Solutions of Cellulose and Its Derivatives with LC-Order

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STRUCTURAL-THERMODYNAMIC CHARACTERISTICS OF NON-AQUEOUS SOLUTIONS OF CELLULOSE AND ITS DERIVATIVES WITH LC-ORDER

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Abstract The regularities of the influence of solvents, introduction of substituents (hydroxypropyl, acetyl, etc.) and degree of etherification of cellulose macromolecules on temperature-concentration boundaries of LC-state in rest and flow are studied. Set of hydroxypropylcellulose (HOPC) samples with the degree of mole substitution from 0.23 to 7.50, cellulose acetates and other lyotropic cellulose derivatives is applied. Individual and mixed nonaqueous solvents of different nature were used: polar aprotic (dimethylacetamide-DMAA, N-methylpyrrolydone, nitromethane), protonodonating (trifluoroacetic acid, acetic acid), water and others. The physico-chemical properties of solutions (phase equilibrium, rheologic, hydrodynamic and volumetric parameters are studied. A model for prediction of anisotropic-isotropic transitions in lyotropic solutions of cellulose derivatives is elaborated.

A sharp interest to liquid-crystalline polymers of cholesteric type is determined by a unique combination of optic properties - linear double refraction and circular dichroism, this yields possibilities to their wide practical usage.

In the scientific plane, actuality of investigations on LC-polymers on the base of cellulose derivatives makes it necessary to elaborate the principles of formation of LC-phases under the influence of chemical modification of cellulose; in practical plane, this

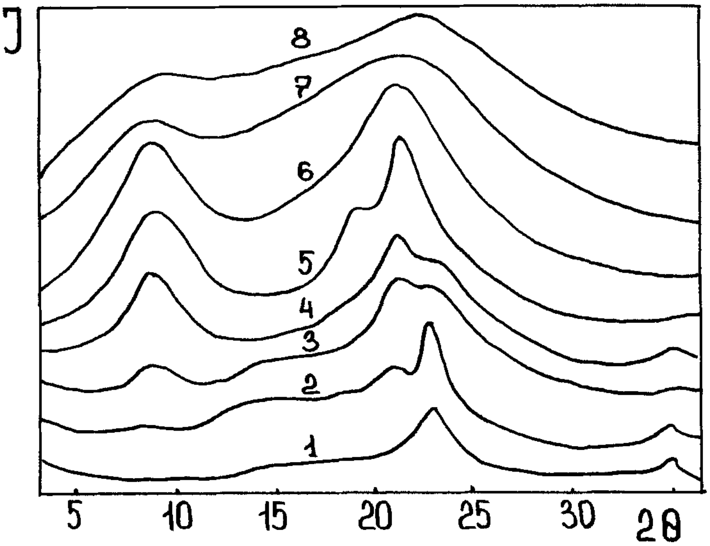

FIGURE 1 Diffractograms of HOPC samples with different mole substitution . MS = 0.3 (1); 0.6 (2); 1.6 (3); 2.3 (4); 3.2 (5); 4.7 (6); 5.2 (7); 7.0 (8).

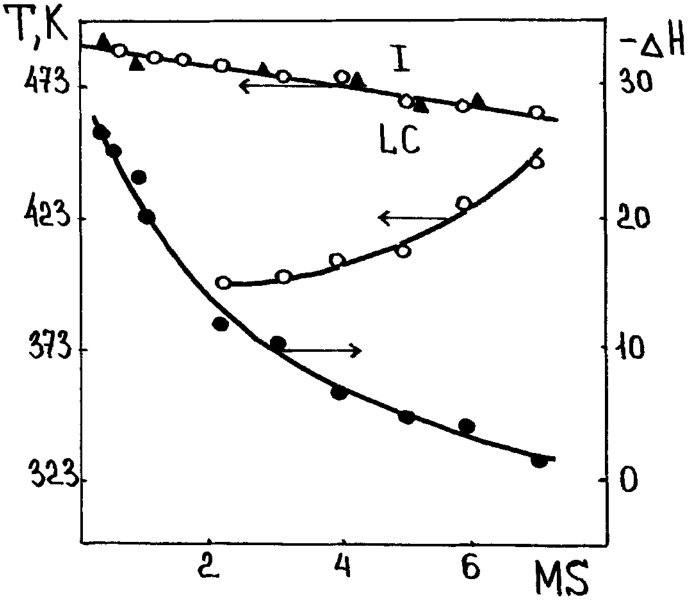

FIGURE 2 Dependence of temperatures and enthalpies of phase transitions on MS of HOPC samples (1, 2) synthesized according to /1/.

leads to new approaches to obtain the cellulose materials with required properties.

The aim of the work is to establish the regularities of the influence of solvents, type of substituent and degree of etherification of cellulose macromolecule on temperature-concentration boundaries of LC-state in rest and flow.

To study the influence of the degree of mole substitution on thermotropic mesomorphism, diffractograms ("Dron-3.0") of hydroxypropylcellulose (HOPC) samples with various mole substitutions from 0.23 to 7.50 were obtained; temperatures and heats of the phase transitions ("Seteram") were defined. The appearance of intensive Bragg reflections in region 2θ 5-8 grad on the diffractograms of HOPC samples (Fig. 1) with mole substitution above 2.3 is a convincing testimony of the existence of near dimeric order (together with transformation of reflection of the amorphous-crystalline part of cellulose at $2\theta=22.5$ grad). The data on temperatures and heats of phase transitions given in Fig.2 show that in 2.3 to 3.5 region of mole substitution there is a change in the tangent of dH/dMS function slope.

Cellulose derivatives are characterized by manifestation of lyotropic mesomorphism. Phase diagram of HOPC-N-methylpyrrolydone in Fig.3 serves as an example. Like for other cellulose derivatives, manifestations of numerous phase transitions are observed depending on polymer concentration and temperature.

As marked earlier, critical concentration C* for the cellulose derivatives depends on pK for acidic and on molar volume for basic solvents. We propose to use the function of the donor and acceptor numbers of

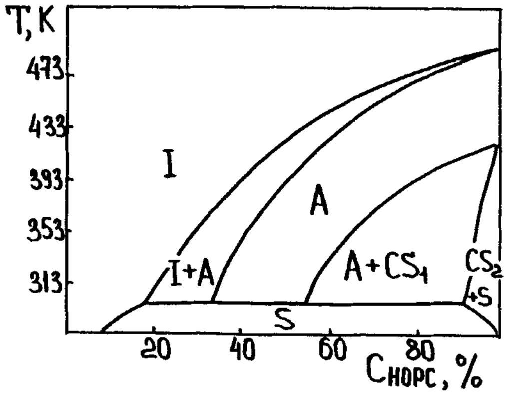

FIGURE 3 Phase diagram of HOPC-N-methylpyrrolydone system.

nonaqueous solvents. Fig.4 shows the linear correlation between C* and half-sum of donor and acceptor numbers in cellulose acetate- and HOPC-nonaqueous solvent systems. This is a general approach to the quantitative evaluation of solvent influence on anisotropic-isotropic transition in a wide variety of individual solvents: from acceptor to donor and from acidic to basic ones. Such an approach is applicable to the systems with solvation phenomena upon solution where there is no chemical modification of cellulose derivatives. In the case of mixed solvents, the model below is proposed for prediction of anisotropic-isotropic transitions on the base of multiple regressional analysis using EC-1060 /3/:

$$C^* = A_1 [\eta] + A_2 V + A_3 T, \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity of a solution; V is the molar volume, T is the temperature. For this model, Fisher criterion $F = 107$.

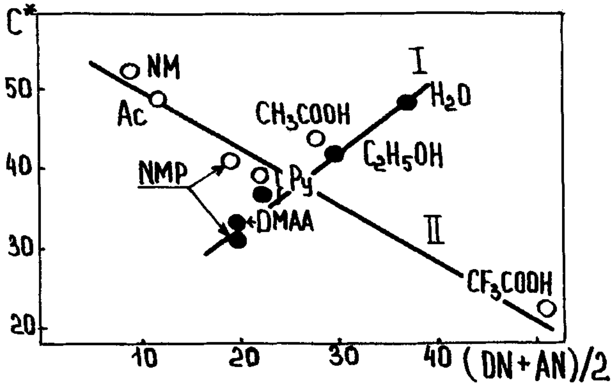

FIGURE 4 Dependence of C* of formation of anisotropic phase in HOPC (I) and AC (II) solutions on donor-acceptor properties of solvents.

Rheologic behaviour of lyotropic cellulose derivatives can be presented in the form of convexo-concave surfaces of viscosity in triple coordinates: $\lg\eta$-C-T and $\lg\eta$-C-X (where C is the polymer concentration, T is the temperature, X is the solvent composition) and approximated by the equation of the type below:

$$\lg\eta = \frac{A_0 + A_1 t + A_3 t^2 + A_5 C + A_7 C^2 + A_9 tC}{1 + A_2 t + A_4 t^2 + A_6 C + A_8 C^2 + A_{10} tC}, \qquad (2)$$

where η (Pa•C) is the solution viscosity; $A_0 - A_{10}$ are the coefficients related to nonaqueous solvent properties.

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