

ELECTRICAL PROPERTIES OF WATER-NANOCELLULOSE SYSTEMS IN A WIDE TEMPERATURE RANGE

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Introduction

The formation of lyotropic liquid-crystalline phases in water suspensions of cellulose nanocrystals (NC) has led to a large number of studies of their rheological, optical and structural properties in the liquid state. Data on the physical, in particular electrical, properties of water-nanocellulose systems in the solid state are much less and they relate mainly to nanocellulose films with low water concentrations. An essential feature of the structure of solid nanocellulose-water systems is the spatial inhomogeneity of nanocrystals, which occurs when obtaining samples from water suspensions by evaporation or freezing. In the intercrystalline layers of ice or cellulose nanocrystals, ionic impurities are concentrated. In addition, the interface regions of nanocrystals in the polycrystals or agglomerates formed from them contain various structural defects. Nanoscale spatial inhomogeneities and structural defects can significantly affect phase transitions and relaxation processes, so the study of the physical properties of water-nanocellulose systems in the temperature range, including areas of phase transitions, is relevant.

Methods

Samples with different moisture content were obtained for the study: 1.5NC/H₂O (1.5g NC per 1 liter of water), 3NC/H₂O, 6NC/H₂O, 89.8NC/H₂O, 96.6 NC/H₂O, 97.3NC/H₂O. These samples were examined by thermogravimetry, IR spectroscopy and dielectric spectroscopy.

Results

The dependences of the real and imaginary parts of the complex dielectric constant in the temperature range $[-100; +50]^{\circ}\text{C}$ at frequencies $f = 5, 10, 20, 50$ kHz were obtained for the studied samples (Fig. 1,2).

For all studied nanocellulose-water systems, low-temperature dielectric relaxation is observed (Fig. 1,2). The dependences show that the dielectric constant for samples 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, in the temperature range above the relaxation process, increases with increasing nanocellulose concentration. For samples 96.6 NC/H₂O and 97.3NC/H₂O it is not possible to distinguish the relaxation process. From the dependences of the imaginary part of the dielectric constant for the studied samples it is seen (Fig. 2) that the position of the maximum is shifted towards low temperatures with increasing nanocellulose concentration.

It can be seen from the dependences (Fig. 3) that the process of dielectric relaxation shifts towards low temperatures with increasing nanocellulose concentration and its activation energy increases with the addition of cellulose compared to water (Table 1). Entropy of $\Delta S/k$ activation also occurs when nanocellulose is added to water.

We assume that the entropy of activation of the relaxation process is related to the probability of the formation of hydrogen bonds between the HC and the surrounding water molecules. The same values of $\Delta S/k$ (table 1) at different concentrations of NC are the result of the formation of a hydrate shell around the crystals of NC.

Table 1. Energy characteristics of relaxation processes of the studied samples.

	$\Delta S/k$	U, kJ/mol	V, kJ/mol	$\frac{N\mu^2}{3k\epsilon_0}, \text{K}$
H ₂ O	0	32.1±3.6	3.7±0.1	31152±180
1.5NC/H ₂ O	8.0±1.8	49.3±3.8	4.1±0.1	41488±200
3NC/H ₂ O	8.9±1.1	50.6±2.3	4.0±0.1	46106±112
6NC/H ₂ O	7.5±0.3	47.2±0.5	3.7±0.1	53153±362
96.6NC/H ₂ O	9.4±1.1	46.1±2.4	-	-
97.3NC/H ₂ O	9.7±1.2	47±2.1	-	-

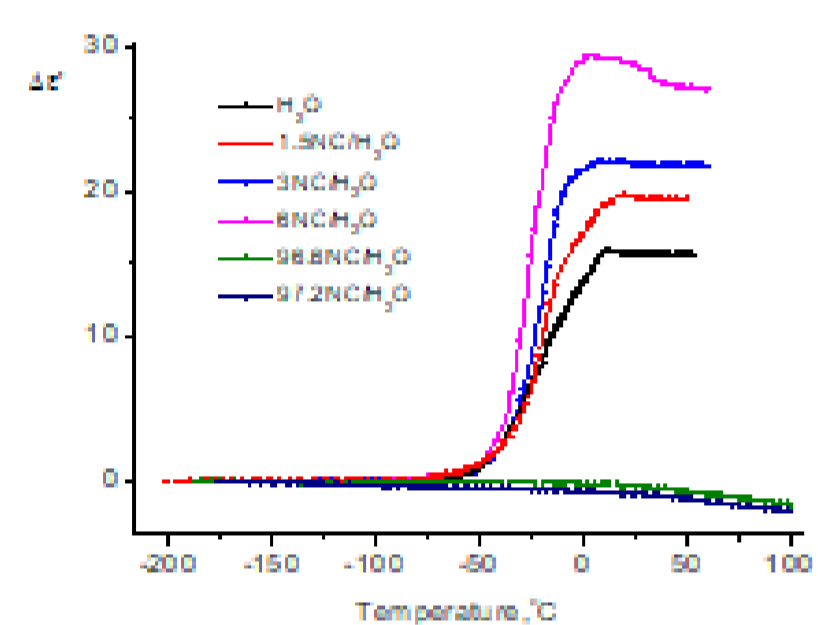


Fig. 1. Temperature dependence of the increment of the real part of the dielectric constant ($\Delta\epsilon'$) for H₂O, 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O and 97.3NC/H₂O at a frequency of 10 kHz

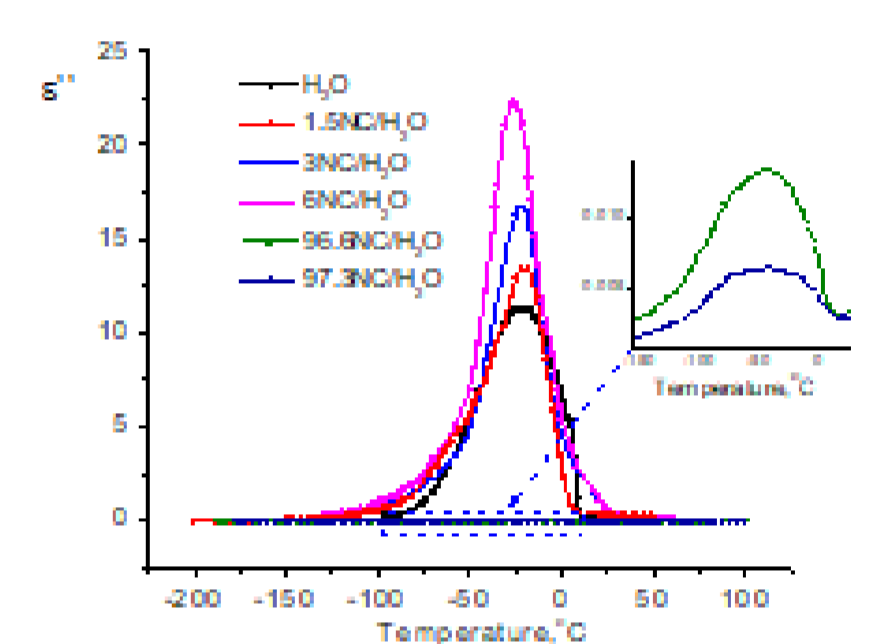


Fig. 2. Temperature dependence of the imaginary part of the dielectric constant for H₂O, 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O and 97.3NC/H₂O at a frequency of 10 kHz

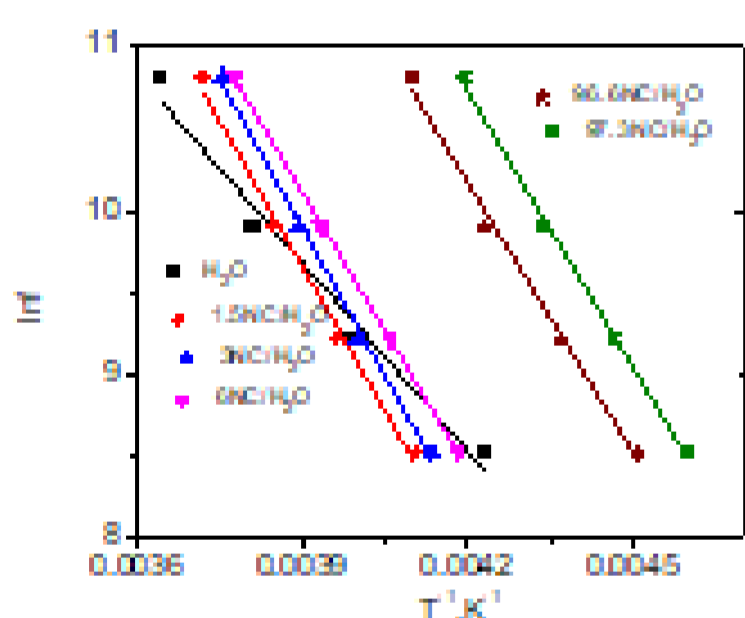


Fig. 3. Arrhenius dependencies for H₂O, 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O and 97.3NC/H₂O.

The table shows that with increasing concentration of cellulose nanoparticles in the solution increases the concentration of relaxants, the movement of which contributes to the dielectric relaxation. Comparing the values of the activation energy U, we see that its value is almost the same for 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O and 97.3NC/H₂O, but has a greater value than for H₂O. Therefore, it can be argued that the nature of the relaxation process in 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O and 97.3NC/H₂O differs from H₂O, and is the result of the superposition of two relaxation processes, one of which is related to relaxation process in H₂O, and another with relaxation on the surface of NCC crystals surrounded by a hydrate shell.

For 96.6NC/H₂O and 97.3NC/H₂O films, the intensities of the maxima at 10 kHz on the temperature dependence of the imaginary part of the dielectric constant decrease with decreasing water concentration (Fig. 4). When approximating the dependence of the peak intensity of the imaginary permittivity of water concentration, we find that the intensity decreases to zero when the concentration of water about 2%. That is, it can be assumed that the dielectric relaxation will be absent for the anhydrous NC film.

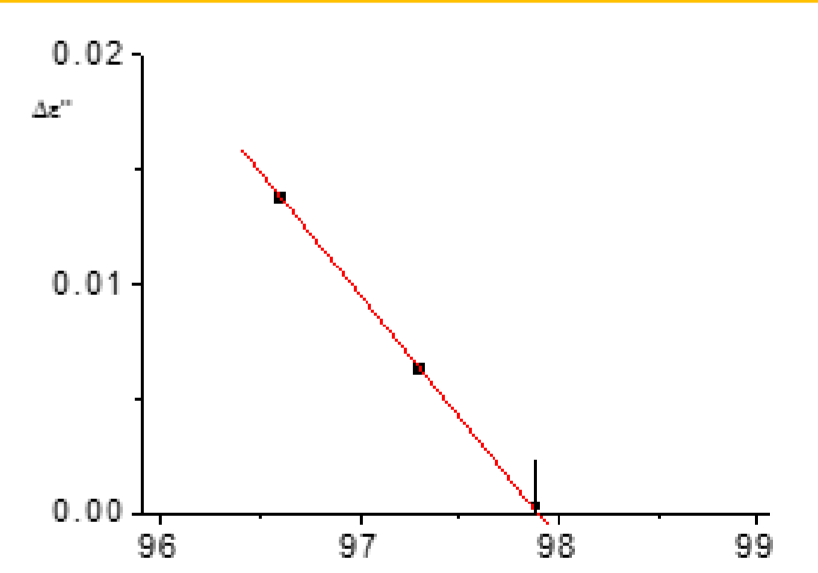


Fig. 4. Dependence of the magnitude of the peak intensity of the apparent dielectric constant for dielectric relaxation on the water concentration.

Conclusions

It is shown that for solutions of 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O, 96.6NC/H₂O, 97.3NC/H₂O in the $[-100; +0]^{\circ}\text{C}$ region, a dielectric relaxation is observed, the nature of which differs from the dielectric relaxation in water and which associated with dipole thermal polarization. It is shown that the intensity of dielectric relaxation decreases with decreasing water concentration and when it is approximated from the concentration, it goes to zero. That is, we can assume that no dielectric relaxation is observed in dried NC crystals (in crystals without a hydrate shell). Therefore, it can be stated that the relaxation process in 1.5NC/H₂O, 3NC/H₂O and 6NC/H₂O solutions and 96.6NC/H₂O, 97.3NC/H₂O films is associated with the surface layers of nanocellulose particles, which are surrounded by a hydrate shell. Relaxers move between equilibrium positions, the energy difference between which is $V \approx 4$ kJ/mol and overcome the energy barrier of the order of $U \approx 50$ kJ/mol. Also for this relaxation process in 1.5NC/H₂O, 3NC/H₂O, 6NC/H₂O solutions there is a contribution of the entropy of activation of the relaxation process which is absent in H₂O. The presence of the entropy of activation of the relaxation process is associated with the probability of formation of hydrogen bonds of the relaxer with the surrounding water molecules of the hydrate shell. Its same value for solid systems 1.5NC/H₂O, 3NC/H₂O and 6NC/H₂O (table 1) indicates the same average number of water molecules surrounding the relaxants on the surface of nanocellulose particles.