

Influence of ions on dielectric properties of nanostructured water-cellulose-NaCl systems in a wide temperature range

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Introduction

The lyotropic liquid-crystalline phases in water suspensions of cellulose nanocrystals have received much attention, leading to the extensive research of their liquid state rheological, optical, and structural properties. However, few researchers have studied the properties of water-nanocellulose systems in the solid state. Moreover, existing data mainly concerns the nanocellulose films with low water concentrations. An essential feature of the solid water-nanocellulose system structure is the spatial heterogeneity of its nanocrystals, which arises when samples are prepared by evaporation or freezing. Different types of ionic impurities concentrate in inter-crystalline layers of ice or cellulose nanocrystals, which can significantly affect phase transitions and relaxation processes. Therefore, the study of the physical properties of water-nanocellulose systems in the temperature region near the phase transition constitutes a significant interest.

Methods

Samples with different moisture content were obtained for the study: 0.08NC/NaCl (0.8g NC per 1 liter of 0.9NaCl-water solution), 0.15NC/NaCl, 0.3NC/NaCl, 0.15NC/H₂O (1.5g NC per 1 liter of water), 0.3NC/H₂O, 0.6NC/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 $[-100\div 0]^{\circ}\text{C}$ at frequencies $f = 5, 10, 20, 50$ kHz were obtained for the studied samples (Fig. 1,2).

For all studied nanocellulose-water-NaCl systems, low-temperature dielectric relaxation is observed (Fig. 1,2). The dependences show that the dielectric constant for samples 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, 0.15NC/H₂O, 0.3NC/H₂O, 0.6NC/H₂O, in the temperature range above the relaxation process, increases with increasing nanocellulose concentration. 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). With the addition of cellulose to NaCl solution, activation energy decreases.

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 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 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl but has a lower value than for NaCl. Therefore, it can be argued that the nature of the relaxation process in 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl differs from H₂O and water-nanocellulose systems, 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.

Temperature decrease in the dielectric relaxation of the water-nanocellulose-NaCl system in comparison with the water-nanocellulose systems associated with the influence of ions on the hydrogen bonds system. The obtained data are in agreement with the results of photoluminescence and optical transmission studies.

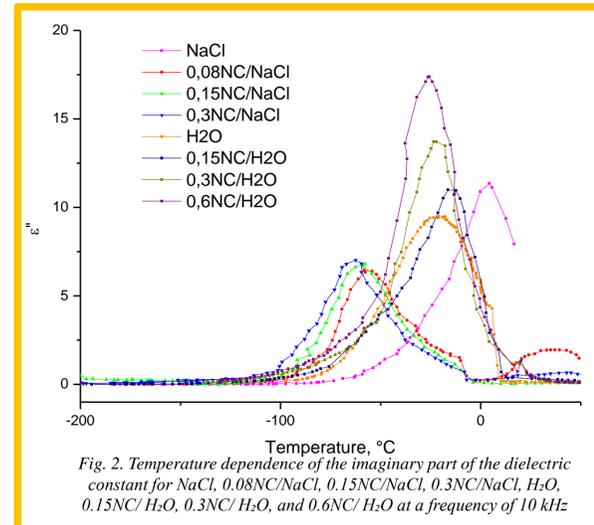


Fig. 2. Temperature dependence of the imaginary part of the dielectric constant for NaCl, 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, H₂O, 0.15NC/H₂O, 0.3NC/H₂O, and 0.6NC/H₂O at a frequency of 10 kHz

Table 1. Activation energies of relaxation processes of the studied samples

Sample	U, kJ/mol
NaCl	52.6±6.2
0.08NC/NaCl	28.2±1.7
0.15NC/NaCl	29.1±1.9
0.3NC/NaCl	29.8±3.2
H ₂ O	30.6±5.2
0.15NC/H ₂ O	54.1±3.3
0.3NC/H ₂ O	52.0±1.7
0.6NC/H ₂ O	42.4±2.8

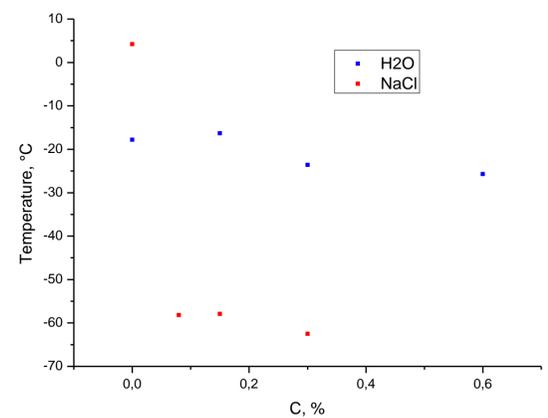


Fig. 4. Dependence of the maximum temperature of the imaginary part of the dielectric constant on concentration for NaCl, 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, H₂O, 0.15NC/H₂O, 0.3NC/H₂O, and 0.6NC/H₂O at a frequency of 10 kHz

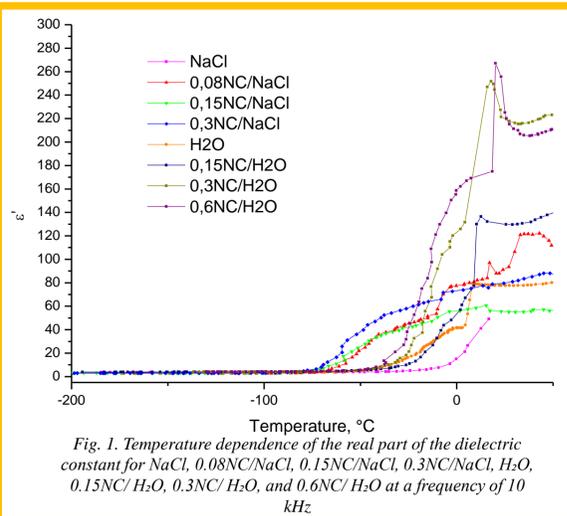


Fig. 1. Temperature dependence of the real part of the dielectric constant for NaCl, 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, H₂O, 0.15NC/H₂O, 0.3NC/H₂O, and 0.6NC/H₂O at a frequency of 10 kHz

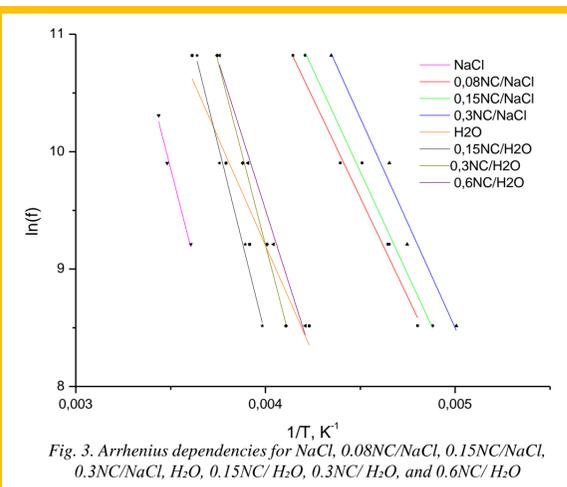


Fig. 3. Arrhenius dependencies for NaCl, 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, H₂O, 0.15NC/H₂O, 0.3NC/H₂O, and 0.6NC/H₂O

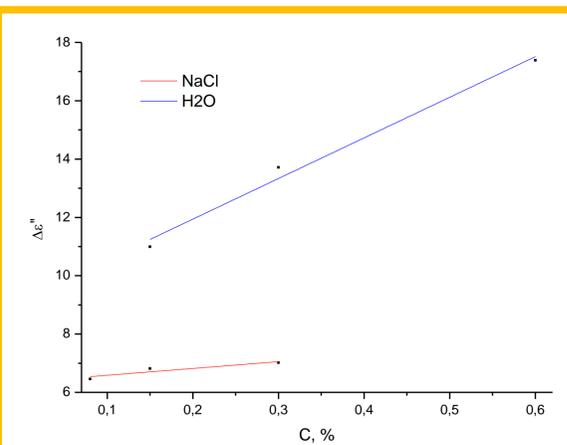


Fig. 5. Intensity of the maximum of the imaginary part of the dielectric permittivity for samples with different cellulose concentration

Conclusions

It is shown that for solutions of 0.08NC/NaCl, 0.15NC/NaCl, 0.3NC/NaCl, in the $[-100\div 0]^{\circ}\text{C}$ region, a dielectric relaxation is observed, the nature of which differs from the dielectric relaxation in water and water-nanocellulose systems and which associated with dipole thermal polarization. It was found that the relaxation process in the solid water-nanocellulose-NaCl system is associated with the surface layers of nanocrystals, which are surrounded by a hydrate shell. It has been shown that when NaCl salts are added to the water-nanocellulose system, the ions, in the solid state of the solution, surround the nanocellulose molecule and change the effect of the hydrate shell of the biopolymer on the hydrogen bond network. At the same time, the ions also affect the network of hydrogen bonds in the ice, which manifests itself in the form of a shift of the relaxation process towards low temperatures.