Dielectric relaxation of solid water solutions of hydroxypropylmethylcellulose: the role of ions.

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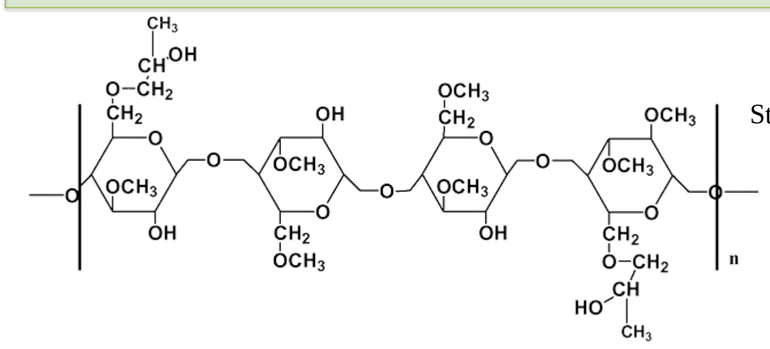
Motivation

The formation of lyotropic liquid-crystalline phases in water-HPMC systems attracts considerable attention from researchers. The rheologic, optical and structural properties of water-HPMC systems are thus well known. However, most of this research focuses on the water-HPMC systems in liquid state, and the data on the physical (electric in particular) properties of such systems in solid state is lacking. Moreover, the research describing the role of ions in the electrical properties of such systems is practically non-existent.

An essential feature of the structure of solid water-HPMC systems is its spatial heterogeneity arising due to aggregation or co-crystallization of HPMC. This happens when samples are obtained from aqueous suspensions by evaporation or freezing. During this process ions are concentrated in the intergranular layers of ice. At the same time, the interfaces of individual nanocrystals in a polycrystal or agglomerate contain various structural defects. As nanoscale spatial heterogeneities and structural defects can significantly affect phase transitions and relaxation processes, so the study of the electrical properties of water-HPMC systems in the temperature range which includes phase transition regions, constitutes a significant interest. Thus, in the present work we describe dielectric properties of aqueous and NaCl-water solutions of hydroxypropyl methyl cellulose of different concentrations in a wide temperature range.

Materials

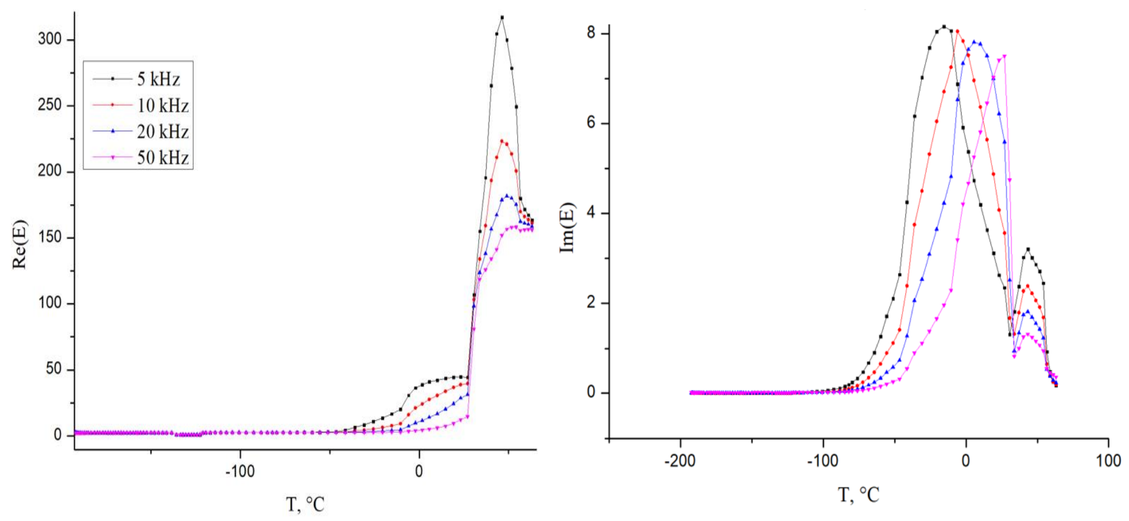


Structural formula of **hydroxypropylmethylcellulose** (HPMC)

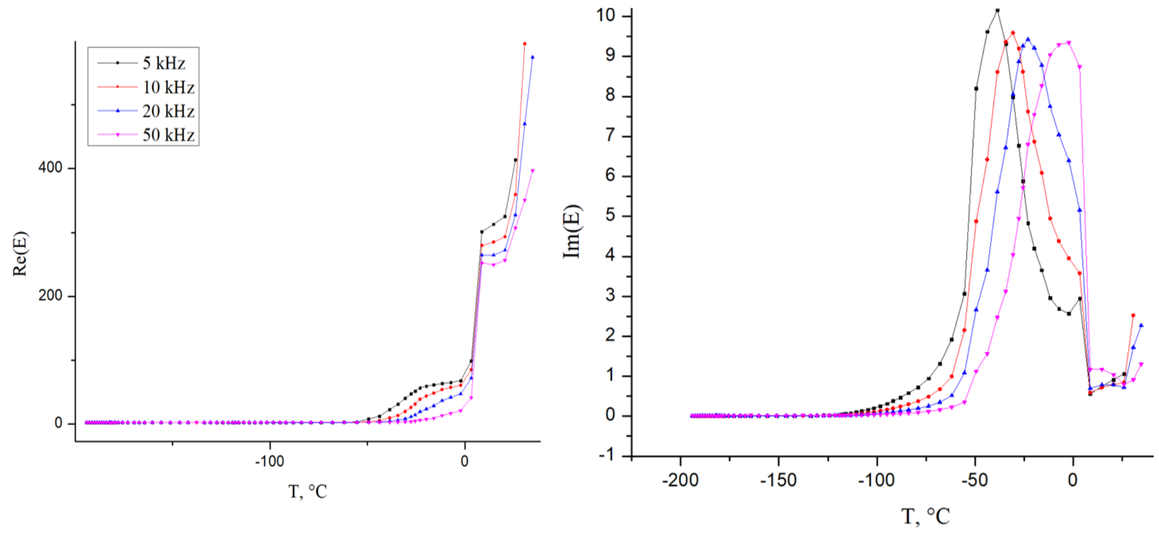
We studied HPMC solutions of the following concentrations:

Water solutions: 0.1%, 0.4% 2%, 2.5%, та 3% (HPMC)
NaCl-water solutions: 0.9% NaCl+0.1%, 0.9% NaCl +0.4% ,
0.9% NaCl +2%, 0.9% NaCl +2.5%,
0.9% NaCl +3%.

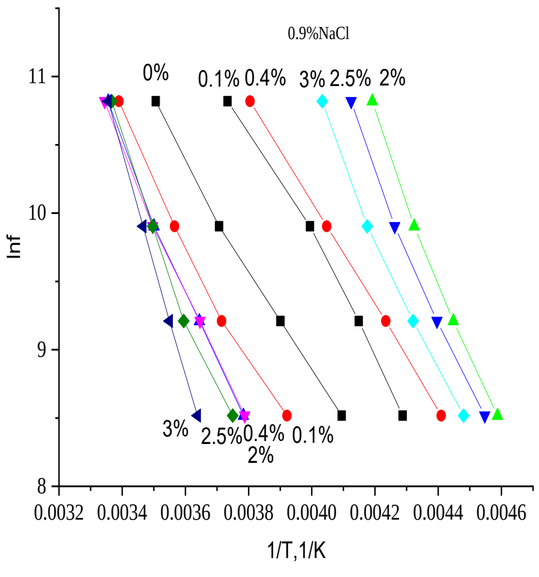
Experimental results



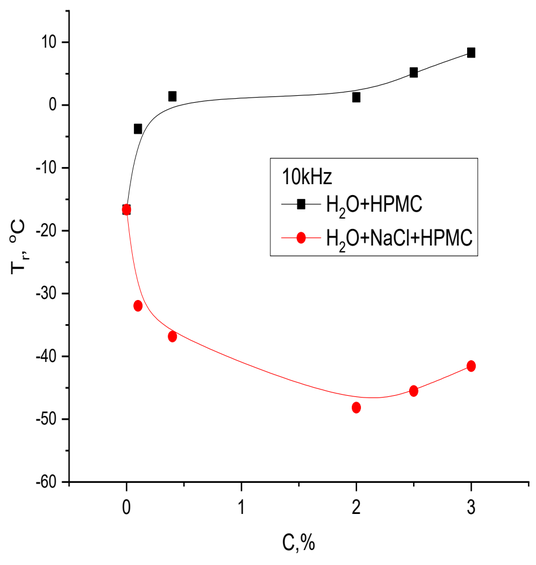
Real and imaginary parts of the dielectric permittivity for 0.1% water-HPMC solution at frequencies 5, 10, 20, and 50 kHz.



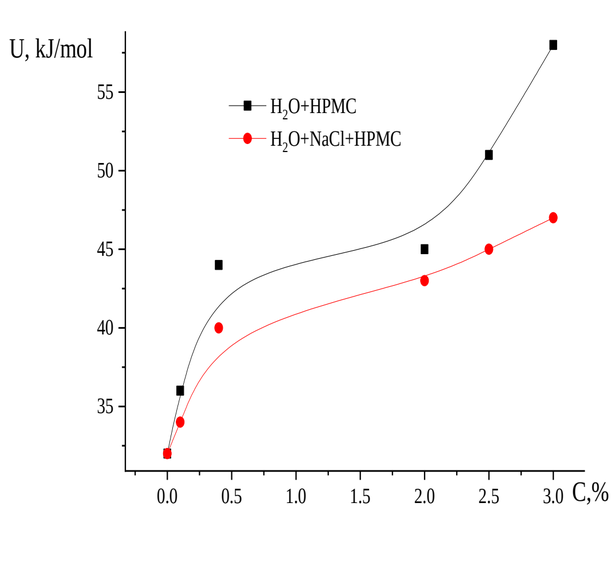
Real and imaginary parts of the dielectric permittivity for 0.9% water-NaCl solution with 0.1% water-HPMC concentration at frequencies 5, 10, 20, and 50 kHz.



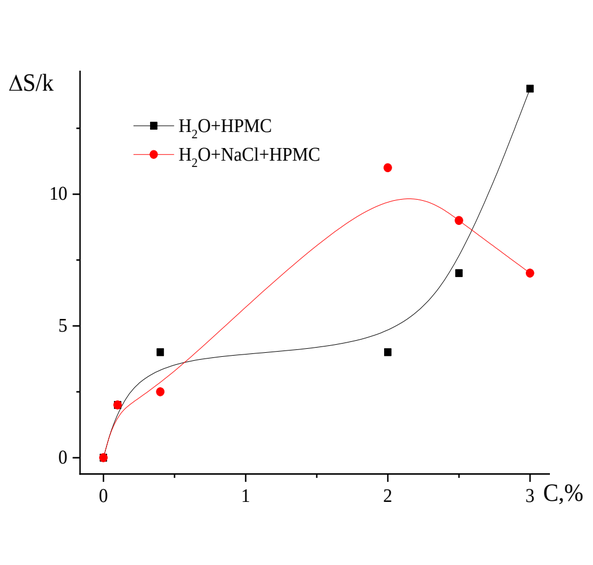
Arrhenius equation ln f (1/T) for pure water, 0.1%, 0.4%, 2%, 2.5% and 3% water-HPMC, and water- NaCl HPMC solutions.



Maxima of the dielectric relaxation at 10 kH for pure water, water-HPMC solution and water-NCl HPMC solutions of increasing concentrations.



Activation energy of dielectric relaxation vs. concentration for pure water, water-HPMC and water-NaCl HPMC solutions



Activation entropy of dielectric relaxation vs. concentration for pure water, water-HPMC and water-NaCl HPMC solutions

We fit Arrhenius equation for solutions using the following equation $ln\ f = -ln\ \pi\ \tau_0 + \frac{\Delta S}{k} - \frac{U}{kT}$

Conclusions

All systems were found to undergo low-temperature dielectric relaxation. When HPMC is added to water, a hydration shell, affecting the network of hydrogen bonds in ice, is formed. Adding polymer impurities into ice leads to the increase in the entropy and energy of the activation process, shifting its maximum towards higher temperatures.

When NaCl is added to water-HPMC system, ions in the solid state surround HPMC molecule and change the way hydration shell affects the network of hydrogen bonds in ice. These ions also affect the hydrogen bond network elsewhere in ice, shifting the relaxation process towards lower temperatures.