

**ELECTRIC PROPERTIES OF WATER.
NEW EXPERIMENTAL DATA
IN THE 5 HZ – 13 MHZ FREQUENCY RANGE**

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A b s t r a c t

The dielectric permittivity, conductivity and loss tangent of water were measured with non-blocking electrodes for different thicknesses of the sample and for various oscillator levels. The measurements were carried out in the 20-90°C temperature range with the 10°C interval. Domain Debye resonances in water, as well as changes in dielectric constants, relaxation times and conductivity with temperature were observed. The results show that water has domain structure in the studied temperature range. When the temperature grows, we observed growth of the domain dielectric constants, decrease the domain relaxation times, and growth of the relative width of the Debye resonances.

Key words: water electric properties, Debye resonance.

1. INTRODUCTION

Crystals with smaller coercive force, in which it is possible to change the direction of spontaneous momentum by applying electric field, are called ferroelectrics and are usually characterised by a large value of dielectric constant. All crystals at the ferroelectric state are piezoelectric (Kittel, 1966).

The dielectric measurements of solids which after melting give polar liquids show anomalous dispersion (Smyth and Hitchcock, 1932). For solids consisting of non-polar molecules, no appreciable dispersion within the range of radio frequencies has been found. On the basis of experimental data it was established that ferroelectric properties do not exist in dipole matter, although they have been detected in crystals with bounded water, in crystals with hydrogen bonding, and in ionic crystals of perovskite and ilmenite structure. It was established that ice and water are not ferroelectric.

Different values of dielectric constant for different frequencies can account for different polarisation mechanisms and related relaxation times. The concept of relaxation time means a characteristic range of time needed for the disturbed system to recover to the equilibrium state (Debye, 1945). The relaxation frequency changes in a wide range and can strongly depend on temperature. The changing state of matter can be accompanied by a change in relaxation processes and related relaxation times, as occurs, for instance, in water. For water at room temperature, the dipole relaxation frequency is about 3×10^{10} Hz. For ice at -20°C , the relaxation frequency is about 1 kHz (Smyth and Hitchcock, 1932). The results obtained by Smyth and Hitchcock (1932) and Debye (1945) provided too little information to draw conclusions regarding the nature of the observed Debye's relaxation and as a consequence, the nature of ice. The thermally stimulated depolarization currents technique is useful for investigating reorientation mechanisms (see, for instance, Vassilikou-Douva *et al.*, 1996).

The experimental results presented at 27th EGS General Assembly show that ice is ferroelectric and piezoelectric (Rusiniak, 2002). Water in various states of matter is one of the most common substances on the earth. The physical properties of water in a wide range of temperatures and pressures were the object of interest for a long time (Akerlof and Oshry, 1950; Owen *et al.*, 1961; Vidulich and Kay, 1962; Rushe and Good, 1966), and the knowledge of these properties in geophysics is of utmost importance (Sumi, 1961; Bigalke and Junge, 1999; Garambois and Dietrich, 2001). Field and laboratory experiments were carried out by Bigalke and Junge (1999) based on non-linear induced polarization (IP) phenomena. They used KCl solution in the experiments. Pure water should be polarized by contact with metal, as it was shown in paper of Rusiniak (2000; Fig. 1b). Simple dc resistivity measurement of pure water show non-linearity. The non-Debye feature of the frequency dependence of dielectric constant and the variation *versus* temperature were discussed by Varotsos (1974). The electric field variations of the earth that occur before earthquakes were investigated in Greece (Varotsos and Alexopoulos, 1984a, b), China (Walace and Teng, 1980), Japan (Rikitake *et al.*, 1980), and Russia (Sobolev, 1975). A field experiment of Garambois and Dietrich (2001) shows seismo-electric signals detected by electric field antennas in a porous medium. The only real source of such seismo-electric signals is piezoelectric substance. Water as a ferroelectric is piezoelectric. So the presence of water in porous structure should be a source of seismo-electric signals. Knowledge of electric

properties of water and saturated porous rocks at higher temperatures can be useful for investigation and monitoring of thermal and volcanic areas. Owen *et al.* (1961) using resonant frequency of a coaxial cavity at frequencies between 50 and 480 MHz, determined the dipole dielectric constant of water between 0 and 70°C and between 1 and 1000 bars. In previous papers (Rusiniak, 2000; 2002a), electric properties of water have been investigated at room temperature. Recently, the dielectric dispersion in hydrated rock was investigated in wide frequency range by Kyritsis *et al.* (2000; 2001).

We found that water has a large dielectric constant ($\epsilon' \sim 10^6$). Basing on the results obtained, we developed a model of water with domain structure. The aim of the present investigation is to test the model at various temperatures. The measurements were made at frequencies between 5 Hz and 13 MHz under isochoric conditions. The changes of domain dielectric constant, conductivity, relaxation time and width of the resonance curve with temperature were measured. We also measured the loss tangent. The measurement was limited to 90°C by the materials used to build the measurement chamber. We were unable to extend the measurement range and attain the critical temperature T_c .

2. EXPERIMENTAL SETUP AND PROCEDURE

The dielectric permittivity and conductivity values were obtained from measurements in a parallel plate condenser with the sample between the plates. Sometimes, an additional guard electrode is used to eliminate fringing field (Scott *et al.*, 1967). The terminals can make a significant contribution to the measured data. This effect can be eliminated by short terminals or by using four terminals: two current terminals and two potential ones (Locker and Byerle, 1985). The four electrode method is useful only for conductivity measurement. Measurement of samples with different thicknesses is useful for verifying whether the result of measurement of dielectric constant is not of contact nature. Capacity measurement can also be disturbed by parasite resonance at high frequency associated with the inductance of the sample. The reliability of capacity measurement at low frequency range is not questionable (Brand *et al.*, 2000; Homes *et al.*, 2001; Schneider *et al.*, 2001; Rusiniak, 2002a, b). The electric properties of water have been measured using a Hewlett Packard LF impedance analyzer HP 4192 A. The capacity was measured with minimal accuracy of 5% and resistance with minimal accuracy of 2% at 5 Hz frequency. To eliminate accidental errors, the measurement was conducted continuously from 20 to 90°C. The electrodes were cleaned in benzine and later in acetone. To minimise errors due to incomplete filling and resulting from in-series connected air condenser, the sample was placed in vertical position. The frequency range was 5 Hz to 13 MHz and the oscillator levels were as follows: $OL = 1$ V, $OL = 0.1$ V, $OL = 10$ mV and $OL = 5$ mV. The oscillator levels were chosen in the working range of the instrument. A change in the oscillator level means a change of force acting on domains. The small oscillator level in certain cases

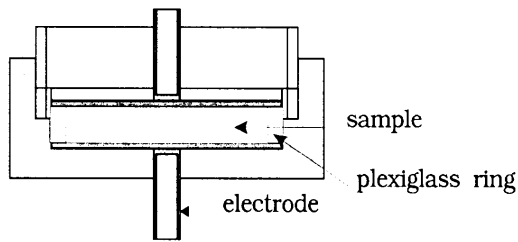


Fig. 1. A schematic diagram of the arrangement for measurement.

can falsify results of the measurement. The instrument was operated with a PC computer through a GPIB interface. Gold plated non-blocking electrodes with diameters of 40 mm and 30 mm were applied. The sample holder was constructed of two parts of plexiglass connected by a screw junction (Fig. 1). The container for a water sample creates a ring of plexiglass locked by elec-

trodes. To seal the sample chamber, the ring was covered by a thin layer of silicone grease. The sample chamber was inserted into brass thermostat. The thermostat was connected to a ground terminal of LF impedance analyzer. The temperature was controlled by a Unipan temperature controller of type 660 working with PT100 sensor.

3. SAMPLES

The objects of our examination were samples of distilled, not degassed water. Disk-shaped samples have diameters of 20 mm or 28 mm and thicknesses of 3.93 mm, 1 mm or 0.2 mm. The relaxation Debye resonance depends on sample thickness. For a thick sample, only a wing of resonance curve is visible in the measurement frequency range. For $h = 0.2$ mm, we observe full resonance curve and we can see how the relaxation time changes with temperature. A thicker sample means that forces acting on unit volume of water are weaker. The behaviour of water is in this case also interesting, but to analyze it, we should make measurement at lower frequency range. The relaxation time should also depend on sample diameter as it is seen from the model (Rusiniak, 2000). But in this measurement, the diameters of the sample were accidental. The sample holder was earlier used for rock samples with diameter $d = 43$ mm and thickness $h = 3$ mm.

4. EXPERIMENTAL RESULTS

The dielectric permittivity, conductivity and loss tangent were measured at 20–90°C with 10°C interval. The four oscillator levels, $OL = 1$ V, 0.1 V, 10 mV, 5 mV, were used on three samples of thicknesses $h = 3.93$ mm, 1 mm, 0.2 mm.

Dielectric permittivity

The dielectric permittivity and conductivity of water, measured at various temperatures, are shown in Fig. 2 as functions of frequency; the example shown was measured

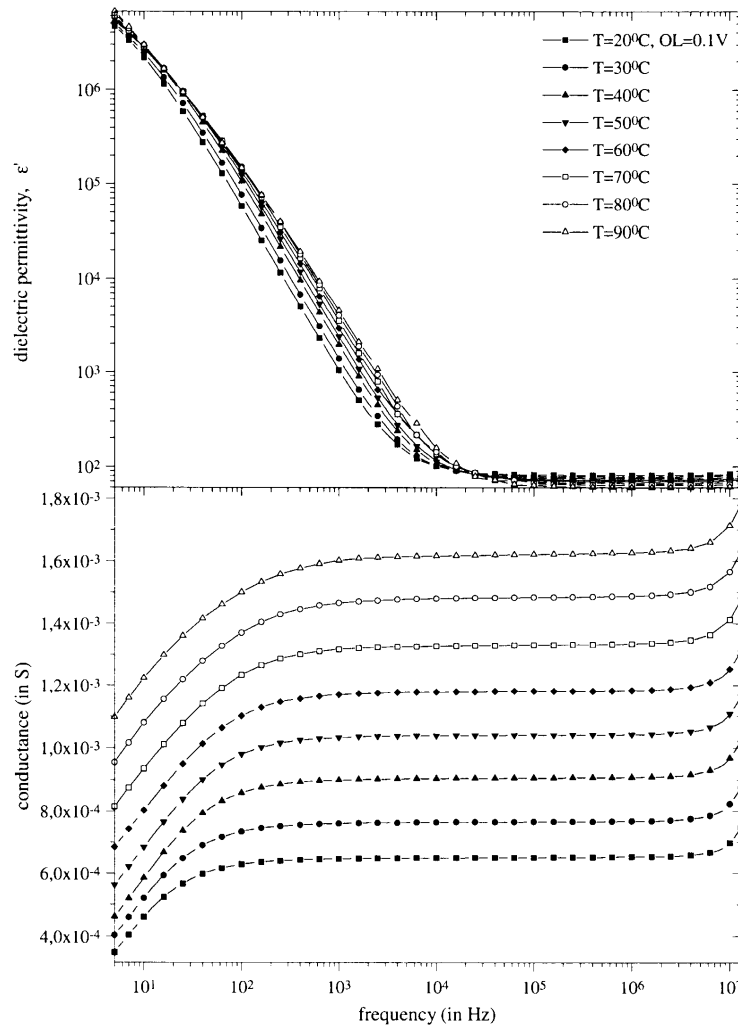


Fig. 2. Measured relative dielectric permittivity and conductivity of water at various temperatures as a function of frequency for oscillator level $OL = 1$ V. Diameter $d = 28$ mm and thickness $h = 3.93$ mm.

at $OL = 0.1$ V. The sample thickness was $h = 3.93$ mm. It is seen from the figure that the ϵ' curves increase at low frequency and decrease at high frequency when the temperature is increased. When the temperature increases, the ϵ' curve shifts as a whole to a higher frequency. These dispersion curves are smooth. In Fig. 3, the dielectric permittivity dispersion curves are given for $OL = 1$ V and the sample thickness $h = 0.2$ mm (it is to be compared to $OL = 20$ V for $h = 3.93$ mm). It is seen that in the low frequency region, the dielectric permittivity increase with temperature is the great-

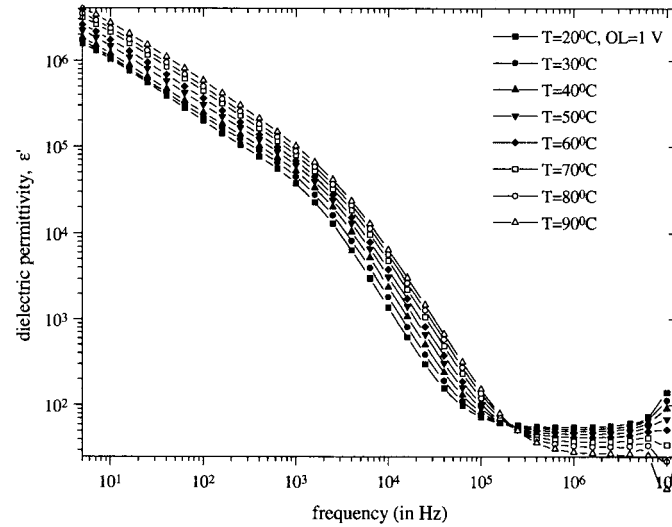


Fig. 3. Measured relative dielectric permittivity of water at various temperatures as a function of frequency for oscillator level $OL = 1$ V. Diameter $d = 28$ mm and thickness $h = 0.2$ mm.

est. The dielectric permittivity dispersion, loss tangent and conductivity curves measured on this sample for $OL = 0.1$ V are plotted in Fig. 4. (It is to be compared to $OL = 2$ V for $h = 3.93$ mm.) When temperature is increased, the domain dielectric constants also increase and the domain relaxation times decrease. This can be interpreted in terms of the model of the dipole liquid with domain structure (Rusiniak, 2000). The domain relaxation times depend on viscosity. The domain dielectric constants as a function of temperature are plotted in Fig. 5. We see that the domain dielectric constants of the oxygen ion domains and proton domains (for $h = 0.2$ mm) give linear change with temperature in the measured temperature range. The dipole dielectric constant decreases when temperature grows, as it has been presented by Owen *et al.* (1961); and Vidulich and Kay (1962).

Conductivity

In Figs. 2 and 4, the conductivity dispersion curves measured at various temperatures on samples of thicknesses $h = 3.93$ mm and $h = 0.2$ mm, respectively, at $OL = 0.1$ V are plotted. It is seen from these figures that the amplitudes of Debye resonance, frequency and resonance width increase when temperature is increased. The conductivity outside the resonance is mainly of domain nature. We should keep in mind that we are dealing with superposition of two overlapping resonances: oxygen ion domains and proton domains. The proton domains resonance is prevailing. From the measurement we can obtain the temperature dependence of the resonance frequency, the resonance

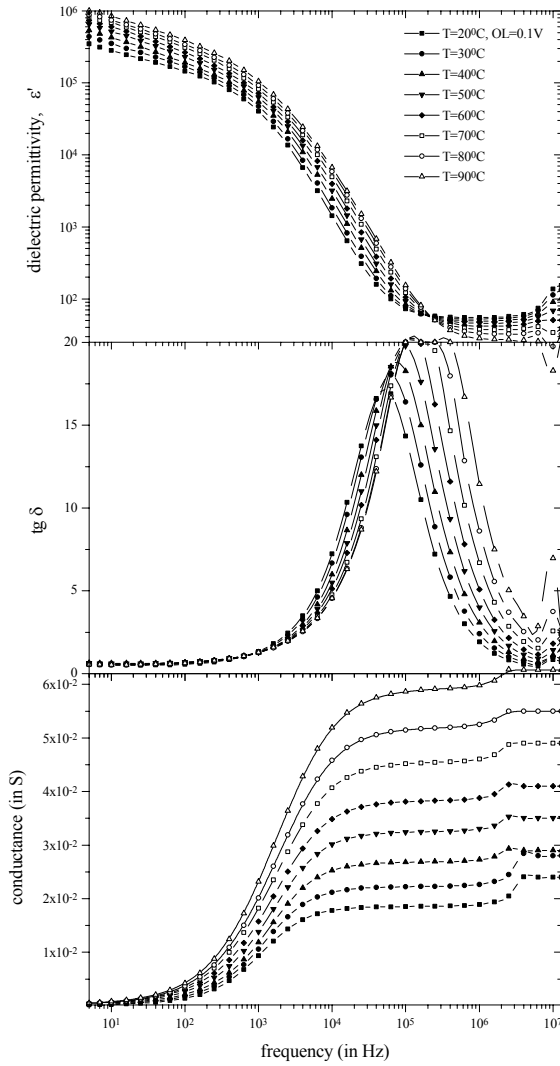


Fig. 4. Measured relative dielectric permittivity, loss tangent and conductivity of water at various temperatures as a function of frequency for oscillator level $OL = 0.1$ V. Diameter $d = 28$ mm and thickness $h = 0.2$ mm.

width and the conductivity after the resonance. Figure 6 shows the resonance frequency of the light domains as a function of temperature for $h = 0.2$ mm at $OL = 1$ V and $OL = 5$ mV. It is seen from this figure that the resonance frequency changes linearly with temperature. In Fig. 7 the relative width of the proton domains resonance as a function of temperature is represented by the ratio of the frequency for left side and right side resonance

$$A_L = \frac{f_{0.25}}{f_r}, \quad A_R = \frac{f_{0.75}}{f_r},$$

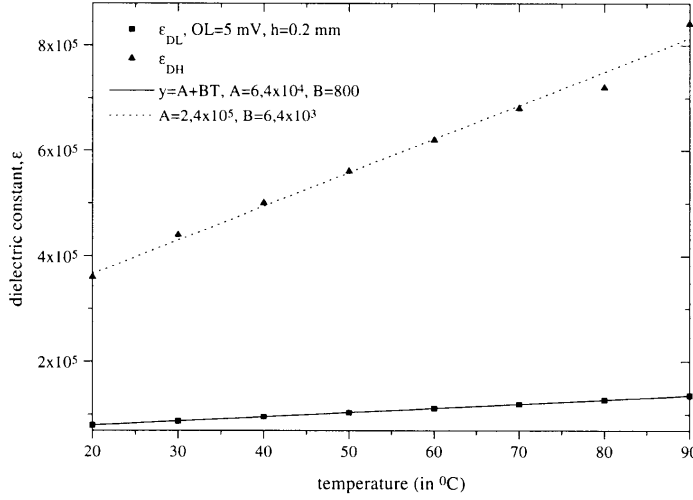


Fig. 5. Variation in domain dielectric constants with temperature (diameter $d = 28$ mm, thickness $h = 0.2$ mm and oscillator level $OL = 5$ mV). The triangles indicate the oxygen domains dielectric constant, the squares indicate the protons domains dielectric constant.

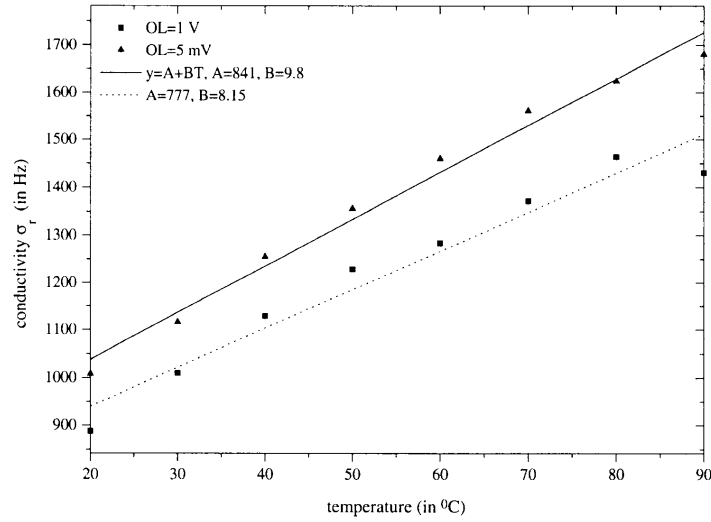


Fig. 6. Variation in resonance frequency of the protons domains with temperature for $h = 0.2$ mm at $OL = 1$ V and $OL = 5$ mV (obtained from conductivity dispersion curves).

where $f_{0.25}$, $f_{0.75}$ are frequencies for 0.25 and 0.75 of the conductivity value outside the resonance, and f_r is the resonant frequency for 0.5 of the conductivity value. The resonance line width increases when Δ_L decreases and Δ_R increases. From this figure it is seen that the relative resonance width increases when the temperature is increased. For oscillator level $OL = 1$ V the relative resonance width is greater than that for $OL = 5$ mV. This means that the oscillator level also changes the proton domains resonance width. Figure 8 shows the conductivity at 250 kHz as a function of temperature. From this figure it is seen that the conductivity exponentially grows with temperature.

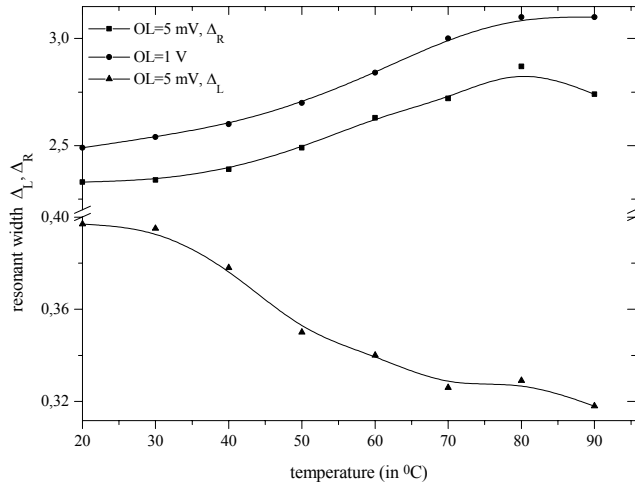


Fig. 7. Variation relative left side and relative right side conductivity dispersion curves of the protons domains with temperature for a sample of thickness $h = 0.2$ mm.

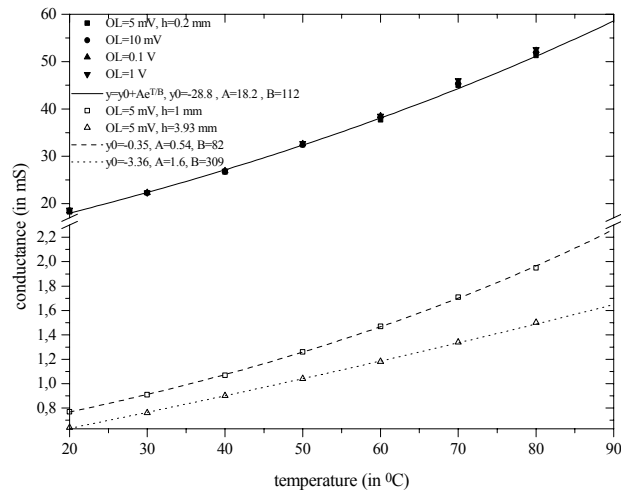


Fig. 8. Conductivity at 250 kHz as a function of temperature.

Loss tangent

The loss tangent on a water sample with thickness $h = 0.2$ mm at $OL = 0.1$ V, measured at various temperatures, is shown in Fig. 4 as a function of frequency. We see that when the temperature is raised, the maximum of the curves shifts to higher frequency, and the width and amplitude of the curves grow. Figure 9 shows the loss tangent measured on a sample of thickness $h = 0.2$ mm in low frequency range at various temperatures at oscillator levels $OL = 5$ mV, 0.1 V and 1 V, respectively. In Fig. 9a we see two maxima of loss tangent, $\text{tg}\delta_1$ and $\text{tg}\delta_2$, for proton and oxygen ion domains, respectively. Measurements carried out at $OL = 10$ mV give similar results. In

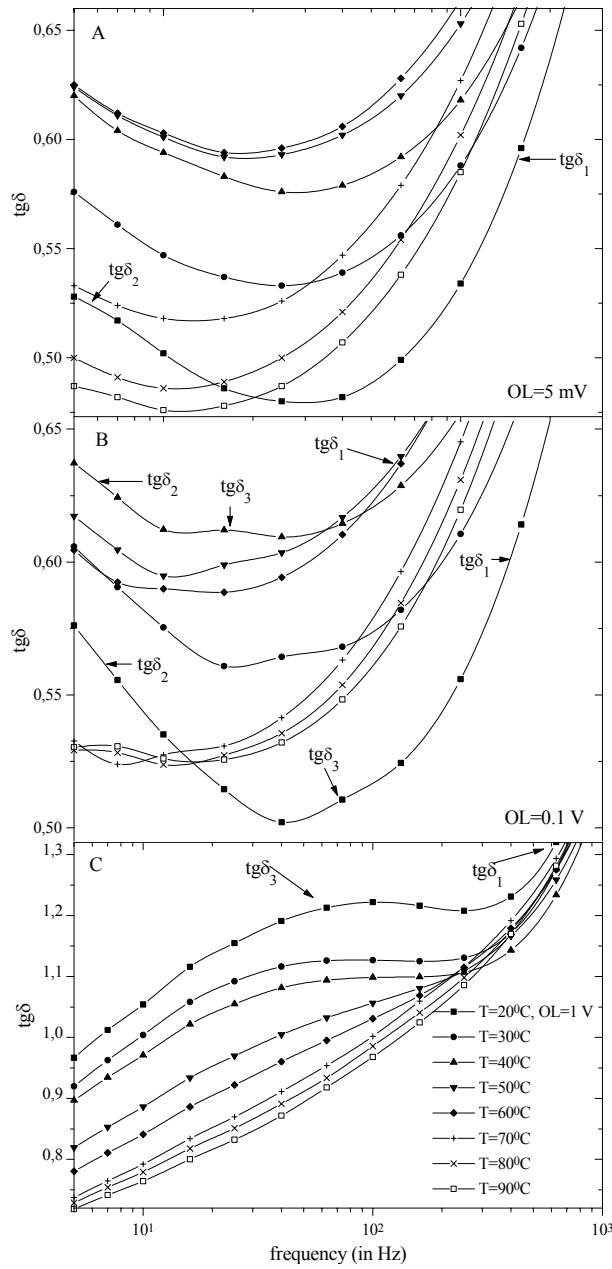


Fig. 9. The loss tangent measured on a sample of thickness $h = 0.2\text{ mm}$ in low frequency range at various temperatures, with oscillator level $OL = 5\text{ mV}$ (a), $OL = 0.1\text{ V}$ (b), and $OL = 1\text{ V}$ (c).

Fig. 9b, at $OL = 0.1\text{ V}$ a small peak $\text{tg}\delta_3$ appears between $\text{tg}\delta_1$ and $\text{tg}\delta_2$. This peak moves to lower frequency when the temperature is risen. For measurement at oscillator level $OL = 1\text{ V}$, as it is seen in Fig. 9c, loss tangent peaks, $\text{tg}\delta_1$ and $\text{tg}\delta_3$, are ob-

served. The loss tangent peak $\text{tg}\delta_3$ vanishes when the temperature is raised. The results suggest that the structure of water changes as the oscillator level is raised above some value. The loss tangent of proton domains goes out of the measurement range, so an analysis of width and position of the peaks is difficult. The minimal loss tangent accuracy is about 0.1% at frequency 5 Hz.

5. DISCUSSION

Hydrogen at solid state is a substance with mechanical and electrical properties typical for metal. From physical point of view, water is a metal oxide in liquid state with semicrystalline structure. In solid state, it crystallizes in the hexagonal system having four molecules per unit cell. Ice is a crystal with hydrogen bonding. The bond angle of molecule should be seen as a result interaction of two forces on protons: electrostatic repulsion and proton magnetic moment attraction. The bond angle of molecule has been increasing from 104.5° in vapor, 105° in liquid to 109.5° in solid. The idea of dipole momentum of molecule was first introduced by Debye (1945) to explain the thermal dependence of electric permittivity. Debye used earlier orientation theory of permanent magnetic moments, given by Langevin. The frequency dependence of electric permittivity and conductivity for the gas and dilute solution was given by Debye (1945). The dependence was found for a simple relaxation model with a single relaxation time. For substance with many relaxation times, the dispersion curves are a superposition of Debye resonances. It is only in the vapor that the water molecule can be treated as a rigid dipole with a possibility of rotation. In liquids and particularly in solids such a possibility does not exist. As it was shown by Rusiniak (2000), rotation in gas should be substituted in liquid and in solid by translation as a possible mechanism of polarisation. Translation of any ion in solid and in liquid is possible only if a neighbouring ion moves. So we see that it is only the collective movements that are now possible: the domains movements. The liquid can be called a superplastic state. In this state, of special importance are thermal vibrations of protons. In liquid, the vibrations give a possibility for a fast change of average values of dipoles in the external electric field direction. In ice near the melting point, we observed two Debye resonances and dipole dielectric constant $\epsilon'_d > 0$ (Rusiniak, 2002). Mechanically, ice behaves as a visco-elastic substance flowing slowly under small pressure. The Debye relaxation theory has a general meaning for relaxation processes.

The presence of salt and other impurities can modify the dielectric permittivity and conductivity of water in the measurement frequency range. But this is a very wide subject and now we can only speculate. The effect should depend on ionic radius and concentration of ions. Also the result depends on whether or not the introduced substance reacts with water. Ionic radius, charge and the value of nuclear magnetic moment are very important because they decide where the impurity in semilattice of liquid will be present and how it will be acting on the lattice. The problem needs independent systematic investigation.

The measurements of dielectric permittivity, conductivity and loss tangent show that water has a stable domain structure in the temperature range of our measurement. The dielectric constants of domains grow linearly with growing temperature. The domain relaxation time decreases when the temperature increases as a result of the water viscosity changes. The conductance dispersion grows with increasing temperature. The domain structure changes when the oscillator level is too big. The isochoric measurement of water at higher temperatures would allow us to find the critical temperature. To make such measurements we have to design a new measurement chamber.

6. CONCLUSIONS

The conclusions can be summarised as follows:

- In the analysed temperature range, water is ferroelectric and piezoelectric.
- The domain dielectric constants grow with growing temperature.
- The domain relaxation times decrease with growing temperature.
- The conductance dispersion grows with growing temperature.
- The conductivity after Debye resonance grows exponentially with temperature.
- The structure of water changes at high oscillator level.

The measurements at higher temperatures need to be continued. The results can be useful in geophysical investigations.

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