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Formation of water nanodrops in cellulose impregnated with insulating oil

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Abstract This article presents results on the DC conductivity of moist pressboard impregnated with insulating oil and its dependence on the moisture and temperature of the samples. The transfer of charges was found to take place because of electron hopping between potential wells produced by water nanodrops. The average dimension of the nanodrops was around 2.32 nm, forming approximately 220 water molecules.

Keywords Pressboard · Insulating oil · Moisture · DC conductivity · Electron hopping · Water nanodrops

Introduction

The article investigated the DC conductivity of cellulose impregnated with insulating oil, with water concentrations in the range 1.5–6.7 wt%. This is a

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seemingly unusual object, but it has been widely used in constructing insulation for high-voltage power transformers for decades. After production, the power transformer was vacuum-dried to the moisture level in the cellulose insulation, which was higher than 0.8 wt%. Then the transformer was filled with insulating oil of moisture not higher than 2 ppm. The insulating oil impregnated the dried paper and pressboard. Operating the power transformer for a long time, the moisture in the cellulose gradually rose to more than 5 wt%. There are two primary sources of moisture entering the cellulose-insulated component of transformers. Moisture partially creeps from the outside and partially appears directly in cellulose as one of the sources of deterioration processes, namely pyrolysis, hydrolysis and oxidation.

Until now, it was thought that in an electrotechnical paper and pressboard impregnated with oil, the DC conductivity occurred by ion conductivity, which can be described by the Pool-Frank or Schottky models, presented, for example, in the paper by Mott and Gurney (1950). Recently, in a study by Żukowski et al. (2014), it was found that the conductivity depends on moisture much more strongly than on the linear dependence described by the ion conductivity models. This article presents the DC conductivity of damp pressboard impregnated with insulated oil, which was determined by the moisture content and occurred because of electron hopping (tunneling). There are models based on the hopping mechanism of

electrons describing DC (Mott and Davis [1979]; Shklovsky and Efros [1984]) and AC conductivity (Kołtunowicz et al. [2013]; Koltunowicz et al. [2014]) in semiconductors or metal-insulator nanocomposites with high precision. The result obtained in a study by Żukowski et al. ([2014]) described the possibility to unravel the problem of the moisture level in oil-impregnated cellulose. Taking into account the quantum mechanics potential of the wells between which tunneling takes place, they are close to atomic size (nanometrical). This means that the water in oil-impregnated cellulose may be in the form of single molecules or small associations—nanodrops. Therefore, in this article we used DC conductivity analysis to determine the sizes of water nanodrops in moist pressboard impregnated with insulating oil.

Research subject and DC conductivity measurement method

Weidemann electrotechnical pressboard T IV with a density of 1,000 kg/m³ was used. We used a well-known method of sample preparation, which was described in by Gäfvert et al. ([1997]). Samples of 215×215-mm² size with 1- or 2-mm thickness were dried in a vacuum chamber at the temperature of 353 K until their weight stopped reducing. The method of chemical titration (the so-called KFT method) required the sample moisture X to be measured, and it was $X \approx (0.575 \pm 0.025)$ wt%. Then, the samples were saturated with moisture from free air at the temperature T of 295 K at relative air saturation moisture ζ equal to (70 ± 5) %. The weight of the samples was monitored and controlled until moisture saturation was reached. This was followed by impregnating the samples with insulated oil at the $T = 348$ K and at relative air saturation moisture ζ of 15 % for 72 h. The pressboard impregnation with oil and equalization of moisture within its volume were done during this process. Conductivity of the pressboard was measured using a flat-plate three-electrode configuration (Fig. [1]). The voltage electrode (top) was loaded using 30 kg ballast. The electrode assembly including the sample was placed in the oil bath in a climatic chamber at a temperature stabilized to an accuracy of ± 0.1 K. The measurements were performed using a 6517A Keithley meter under $E = 10$ kV/m electric field strength.
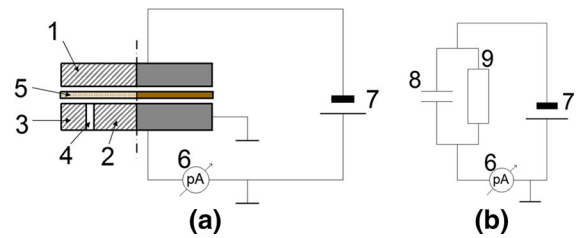
Fig. 1 Three-electrode measurement system (**a**). *1* Voltage electrode; *2* measuring electrode; *3* protective electrode; *4* insulator; *5* examined pressboard; *6* Keithley 6517A piko-ammeter; *7* DC voltage source (Keithley 6517A); parallel equivalent circuit of the measurement system (**b**). *8* Capacitor with ideal dielectric with relative permittivity ε_r; *9* resistor with DC conductivity σ

The measurement system, presented in Fig. [1]a, has two electrodes with large surfaces (about 200 cm²). A sample of moist pressboard impregnated with insulating oil was placed between these electrodes using a parallel-plate capacitor. The dielectric in this capacitor has relative permittivity ε_r and DC conductivity σ. The equivalent circuit of this system is parallel (Fig. [1]b). After the DC voltage U has been connected to the measuring system in the dielectric, two parallel phenomena take place—capacitor charging and conduction current. As time passes, the capacitor voltage increases and the capacitor charging current intensity decreases, as is shown in Fig. [2]. When the capacitor voltage reaches the supply voltage value U, the charging current falls to zero and the conduction current I_0 starts flowing through the measurement system, which is only related to the nonzero conductivity value of the pressboard. These current values stay constant, as can be seen for large time values in
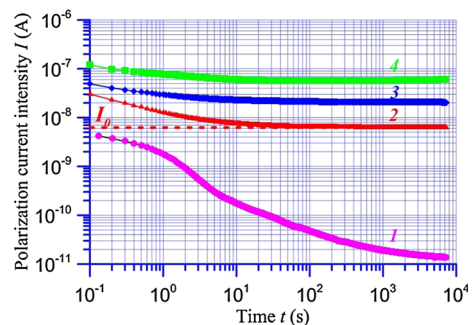
Fig. 2 Measurement results of the polarization current intensity versus time for the pressboard samples measured at $T = 318$ K of moisture *1* 1.8 wt%, *2* 3.2 wt%, *3* 4.0 wt% and *4* 5.1 wt%

Fig. 2. Determination of the I_0 value from the time charts allows calculating the DC conductivity value of the pressboard using formula (1).

Figure 2 shows the relationship between the current intensity running through the pressboard and the time measured at the temperature 318 K for different moisture levels (1.8–5.1 wt%). Similar relationships were obtained for the temperature 297 K, and conductivity of the samples was calculated by the following equation:

$$\sigma = \frac{I_0}{SE}, \qquad (1)$$

where I_0 is the fixed value of the current intensity, E is the electric field intensity, and S is the area of the measuring electrode.

The method for determining the I_0 value is shown in Fig. 1 for one of the attempts.

Result analysis of the DC conductivity measurements

As is shown in this article (Żukowski et al. 2014), in moist pressboard impregnated with transformer insulating oil, the DC conductivity dependence on the moisture content is much stronger than on the linear function, and the temperature dependence on conductivity is exponential.

As follows from the study by Shklovsky and Efros (1984), only in the case of tunneling of electrons between the nearest potential wells does this occur very strongly, i.e., exponential dependence of the conductivity on the concentration of potential wells N_o. For analysis of the temperature dependence on conductivity and charges and potential wells concentrations in the case of electron tunneling, the dependence given in the paper by Ravich and Nemov (2002) should be used:

$$\sigma(r, T = \text{const}) = \sigma_0 \exp\left(-\frac{\beta \cdot r}{R_0} - \frac{\Delta E}{k \cdot T}\right), \qquad (2)$$

where r is the average distance between potential wells; R_0 is a position radius of a wave function of a hopping electron; β is a numeric factor ranging $\approx (1.75 \pm 0.05)$ (Shklovsky and Efros 1984), ΔE is an activation energy of conductivity, and k is the Boltzmann constant.

Initially, it was assumed (Żukowski et al. 2014) that the potential wells were randomly arranged for single

water molecules with an average distance of r_1 separating the water molecules and concentration of N_0, i.e.,

$$r_1 \cong N_0^{-\frac{1}{3}} = \left(\frac{X \cdot \rho}{100 \cdot u \cdot M_{\text{H}_2\text{O}}}\right)^{-\frac{1}{3}}, \qquad (3)$$

where $\rho \approx 1{,}000$ kg/m³ is the pressboard density, $M_{\text{H}_2\text{O}} = 18$ is the water molecular mass, $u = 1.67 \times 10^{-27}$ kg is the atomic mass unit, and X is the moisture, wt%.

Verification of the relationship in Eq. (2) is a sufficient condition for the occurrence of hopping (tunneling) of electrons between the nearest potential wells in the examined sample. The verification of Eq. (2) first of all takes place in checking the constancy of the activation energy ΔE value for the whole spectrum of changes in the presence of impurities (in this study, moisture). Based on measurements of DC conductivity for the impregnated pressboard at temperatures of 297 and 318 K, the dependence of the activation energy on the moisture was estimated by the Eq. (2), as shown in Fig. 3 (Żukowski et al. 2014). The figure shows that the activation energy value $\Delta E \approx (0.853 \pm 0.071)$ eV is relatively independent of the moisture concentration.

Using the experimental results that determined the independence of the activation energy from moisture (distance between water molecules), Eq. (2), in the case of $T = \text{const.}$, it can be transformed into:

$$\log \sigma(r_1, T = \text{const}) = \left[\log \sigma_0 - \frac{\Delta E}{kT}\right] - \frac{\beta}{R_0} r_1$$
$$= -\frac{\beta}{R_0} r_1 + C, \qquad (4)$$

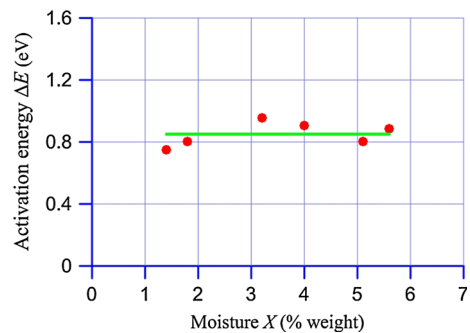where $C = \left[\log \sigma_0 - \frac{\Delta E}{kT}\right]$.

Fig. 3 Calculated results of the activation energy of the pressboard conductivity versus moisture concentration X

Then the experimental values of conductivity using $\{\log \sigma, r_1\}$ were plotted in Fig. 3. In a semi-logarithmic coordinate system, the dependence (4) appears to be a decreasing linear function.

Figure 3 shows the experimental results of DC conductivity of the pressboard versus the distance between water molecules at the temperatures of 297 and 318 K. The figure also shows the results of approximation of the experimental values by the least squares method.

Figure 3 shows that the average value of the slopes $\beta/R_0 \approx (15.651 \pm 0.015)$, the dependence of $\log \sigma$ on r_1, for both measured temperatures are diminishing linear functions of equal slopes (i.e., slopes $\beta/R_0 \approx 15.666 \pm 0.015$ and 15.635 ± 0.015 for 297 and 318 K, respectively; the uncertainty limit is <0.1 %). The coefficients of determination of R^2 approximation using the least squares method are close to the unit value, i.e., 0.979 and 0.994 for 297 and 318 K, respectively, which shows a very high accuracy of approximation.

The study by Shklovsky and Efros (1984) reported that $\beta \approx (1.75 \pm 0.05)$, as was assumed in this article, where the potential wells representing a single water molecule were determined from the waveforms shown in Fig. 4. The experimental value of the position radius of the wave function of a hopping electron is $R_0 \approx (0.112 \pm 0.003)$ nm. When single water molecules are present, then electron tunneling can take place between the doubly and negatively charged oxygen ions, and the ionic radius determined by X-ray is $R_r = 0.135$ nm (Van Vlack 1972). The position radius of the outer-shell electron of the ion
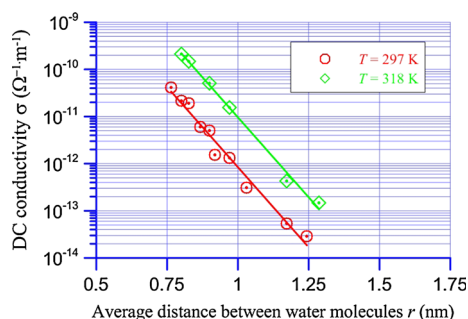
Fig. 4 Measurement results of DC conductivity of the pressboard versus the average distance between water molecules r_1 at temperatures of 297 and 318 K. The figure also shows the results of approximation of the experimental values by the least squares method

placed in a dielectric medium (Shklovsky and Efros 1984) should be larger than R_r, i.e.,

$$R_0 > R_r. \tag{5}$$

Comparing the experimental results achieved in this study, i.e., $R_0 \approx (0.112 \pm 0.003)$ nm and the radius determined by X-ray $R_r = 0.135$ nm, revealed the opposite inequality compared to Eq. (5). This can be explained by considering water molecules forming nanodrops that contain on average n water molecules. This caused a decrease in the number of drops in comparison with the number of water molecules and an increase in the distance between the drops as a result. The radius R_0^* of an electron located at the surface of a nanodrop in the pressboard, in the first approximation, can be written as (Shklovsky and Efros 1984):

$$R_0^* \approx \varepsilon_r \cdot R_r, \tag{6}$$

where ε_r is the dielectric permittivity of the pressboard impregnated with oil at high frequencies, and $R_r = 0.135$ nm is the radius of the oxygen ion determined by X-ray.

Exchanging the radius R_0 in Eq. (2) with R_0^*, determined in Eq. (6), should cause an increase of $\beta \cdot r_1$ to a value of $\beta \cdot r^*$, so that

$$\frac{\beta \cdot r^*}{R_0^*} \approx \frac{\beta \cdot r^*}{\varepsilon_r R_r} = \frac{\beta \cdot r_1}{R_0} = 15.651 \cdot r_1. \tag{7}$$

The result of Eq. (7) shows that if water is present in a pressboard, nanodrops will be created at the average distance between them (r^*), which is higher in comparison with the distance between single water molecules r_1 because:
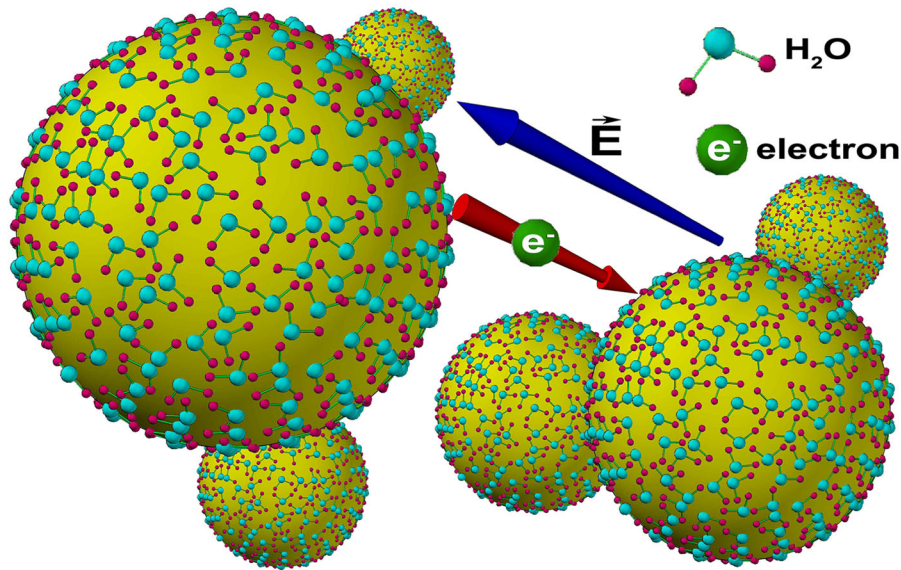
$$r^* \cong \frac{15.651 \cdot r_1 \cdot \varepsilon_r \cdot R_r}{\beta}. \tag{8}$$

Considering the value of r^*, defined in Eq. (8), and transforming Eq. (3) allowed the concentration of water nanodrops N_n in a pressboard to be calculated:

$$N_n \cong (r^*)^{-3} \cong \left(\frac{\beta}{15.651 \cdot r_1 \cdot \varepsilon_r \cdot R_r}\right)^3. \tag{9}$$

Resulting from Eq. (3), when single water molecules appear, their concentration is connected with the average distance between them and described by equation:

$$N_0 \cong r_1^{-3}. \tag{10}$$

Fig. 5 Nanodrops of water and electron hopping between them

Assuming the number of water molecules in a nanodrop is n, and the number of nanodrops, as follows from formula (9), is N_n, the total number of water molecules:

$$N_0 = n \cdot N_n. \tag{11}$$

From Eqs. (9), (10) and (11), we can state that the average number of water molecules in a nanodrop can be calculated as:

$$n \cong \frac{N_0}{N_n} = \left(\frac{15.651 \cdot \varepsilon_r \cdot R_r}{\beta} \right)^3. \tag{12}$$

The determined high-frequency permittivity ε_r (Ekanayake et al. 2006) used in Eqs. (6)–(12) was almost independent on moisture in a pressboard impregnated with insulating oil of $\varepsilon_r \approx 5.0$ value. Substituting the values of ε_r, R_r and β in Eq. (12), the average number of water molecules in a nanodrop can be calculated, and it equals $n \approx 220$. The average diameter of these nanodrops is around 2.32 nm. Figure 5 shows water nanodrops and a hopping electron between them.

The presented experiments reveal that for a device of cellulose impregnated with insulating oil, water created nanodimensional clusters, i.e., nanodrops, related to the fact that water virtually does not dissolve in oil. Below the temperature of 373 K, water does not form chemical compounds with oil. The maximum level of water dissolved in oil does not exceed 200 ppm (0.02 %) (Oommen 1983), and the remaining water should precipitate in a second phase form. Large differences between the free surface energy of water and oil (respectively 70 and 30 mN/m at 293 K temperature) caused the water to create spherical clusters of nanometer dimensions (Pogrebnjak and Beresnev 2012).

Conclusion

The DC conductivity dependence on a moist pressboard impregnated with insulating oil at various moisture and sample temperature levels is presented in this article. The study verified that the conductivity appeared because of electron hopping (tunneling) between the nearest potential wells created by water nanodrops in a cellulose structure. Results of computations and their analysis were discovered and determined in water nanodrops, which were created in the pressboard impregnated with insulating oil structure with an approximate number of 220 water molecules. The average dimension of the nanodrops was around 2.32 nm.

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