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Application of Non-Linear Dielectric Effect for Estimation of Conductivity in Strong Electric Field[*]

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The high-field, constant-current electric conductivity was estimated from the Joule heating effect observed in non-linear dielectric (NDE) experiments. Quality of the obtained data and applicability of NDE method for estimation of σ_E was discussed for ethanol + tetramethylammonium chloride mixtures.

Key words: non-linear dielectric effect (NDE), conductivity, Wien effect

Non-linear dielectric effect (NDE) consists in measurements of the change of electric permittivity caused by application of a strong electric field. The NDE increment is defined as $\Delta\varepsilon_{NDE} = \varepsilon_E - \varepsilon_{E\to 0}$, where ε_E is the permittivity measured at strong electric field, $\varepsilon_{E\to 0}$ is the permittivity measured at a low electric field strength. The sample is subjected to the influence of two parallel fields; the measuring one – of high frequency and low amplitude, and the polarizing one – of high amplitude, usually applied as rectangular short pulses. The investigated sample is placed in a capacitor, which is a part of LC circuit. The change of properties of the LC circuit (resonance frequency and/or quality factor) allows to observe the influence of strong electric field on permittivity. In simple liquids, even for the strongest possible electric fields, Debye-Langevin function can be approximated by two initial terms of the expansion series. For rigid, non-interacting molecules the NDE increment is negative and proportional to the fourth power of the dipole moment and to the square of the electric field strength. Applicability of the NDE method is usually limited to liquids of low conductivity. In typical NDE experiments the conductivity is an undesirable effect and experimentalists reduce it by suitable selection of the investigated materials and careful purification. However, NDE method can also be used for measurements of electric conductivity at strong electric field. This idea was explored already by Jones and Krupkowski [1] and by Nackaerts, De Maeyer and Hellemans [2]. The former group investigated pure liquids: acetone and higher alcohols. In case of alcohols, the obtained conductivity is similar to that measured by classical methods, but in the case of acetone the "NDE conductivity" was much higher. Experiments of Nackaerts *et al.* [2] were performed in diluted solutions of tetra-n-butylammonium picrate in benzene.

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

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A considerable increase of conductivity in strong electric field consistent with Onsager theory [3] was found.

The influence of a strong electric field on a electrolytic conductivity was originally predicted and measured by Wien [4,5]. Conductivity was found to increase, when electric field of high intensity was applied. In the case of strong electrolytes, the relative increase of conductivity $(\sigma_E - \sigma_0)/\sigma_0$ is only a few percent (the first Wien effect), but in weak electrolytes conductivity may increase even several times (the second Wien effect). In NDE experiments it has been often observed, that the electric conductivity of pure liquids decreases under influence of electric field. This phenomenon was described and explained by Małecki and co-workers [6] as a result of competition between creation and annihilation of ions. If the annihilation process (mainly in electrode reaction) prevails, the resulting conductivity decreases under influence of strong electric field. It is apparently inconsistent with the Wien effects. However, the Wien effects are characteristic for liquids containing considerable amount of ions or molecules able to dissociate, whereas the effect described by Małecki *et al.* is expected for liquids with very low conductivity. It seems interesting to evaluate the applicability of NDE equipment to measure the electric conductivity in strong electric field. Experimental conditions of NDE measurement are still in progress and it is possible now to perform accurate measurements in mixtures of relatively high conductivity. In the presented measurements we demonstrate the influence of a strong electric field on electrolytic conductivity in ethanol + tetramethyl-ammonium chloride (TMAC). Different constructions of the capacitor containing sample were tested. The time dependence of electrolytic conductivity was also analysed.

EXPERIMENTAL

The scheme of the NDE equipment is presented in Fig. 1. The experimental set-up is similar to that used already by Orzechowski [7] in investigations of critical systems. The liquid capacitor c_x was connected in series with the blocking capacitor c_B ($c_B >> c_x$) and parallel to the inductance (L). Capacitors and the inducting coil are a part of the Colpitt's-type oscillator. The resonance frequency of LC circuit ($f \approx 5$ MHz) was measured using a HP 53310A Modulation Domain Analyser. The frequency is a function of the relative permittivity (ε), geometric capacitance (c_o), stray capacitance (c_s) and inductance (L):

$$f = \left[2\Pi\sqrt{L(\varepsilon \cdot c_o + c_s)}\right]^{-1} \qquad (1)$$

Parameters L, c_s were found in a calibration, geometric capacitance was calculated as $\varepsilon_o \cdot S/d$ (where ε_o is the permittivity of the vacuum, S and d are the area of and distance between electrodes). The high field pulses (amplitude up to 2500 V, duration time 0.2–0.5 ms) were applied to the parallel-plate capacitor. Ethanol was obtained by purification of the 99% material. It was dried using magnesium activated by iodine and then distilled in inert gas atmosphere. Tetramethylammonium chloride (analytical grade) was dried in vacuum desiccator over P_2O_5. The final content of water was controlled by the Carl Fisher method. Low field conductivity was measured by Radelkis conductometer type OK-102/1. All operations were made in dry nitrogen atmosphere at room temperature (20±2°C).

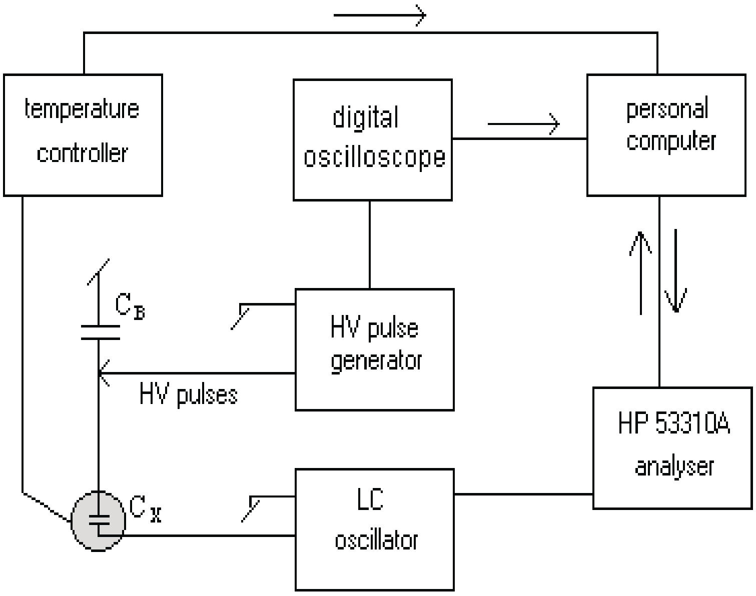

Figure 1. The scheme of the experimental set-up.

In the measurements, two different types of capacitors made of stainless steel and glass were used. Details of their construction are presented in Figs 2a and 2b. In the capacitor depicted as "a", almost all the investigated liquid is placed in high electric field area, whereas in the capacitor "b" only a small portion of the sample is subjected to the electric field of high intensity. The diameter of electrodes was 10 and 2.5 mm in capacitors "a" and "b" respectively, the distance between electrodes was varied between 0.3 and 0.8 mm.

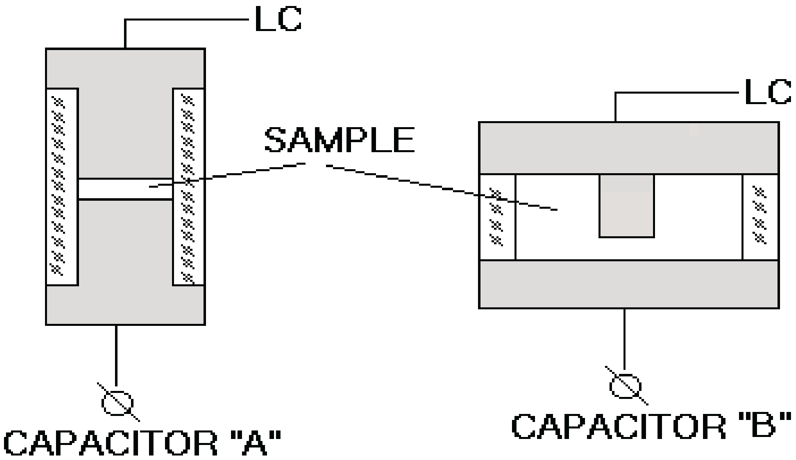

Figure 2. Construction of capacitors used.

RESULTS AND DISCUSSION

The change of the electric permittivity of a material placed between high field electrodes is caused by two effects: a) the change of permittivity of a dipolar liquid in a strong electric field (the non-linear dielectric effect) and b) the increase of temperature, being a result of the Joule heating in a conducting system. If the permittivity is measured in function of time, the effects can be resolved. Figure 3 presents an example of ε(t) dependence, where the non-linear dielectric effect is negative and heating is observed. Assuming the adiabatic heating, the permittivity could be presented as follows:

$$\varepsilon = \varepsilon^{o} + \Delta\varepsilon_{NDE} \cdot E^{2} + (\partial\varepsilon/\partial T) \cdot \rho^{-1} c_{p}^{-1} \sigma_{E} E^{2} \cdot t \tag{2}$$

where ε^{o} is the permittivity in the absence of strong electric field, $\Delta\varepsilon_{NDE}$ is the non-linear dielectric increment, T is temperature, ρ is density, c_p is heat capacity, σ_E is electrolytic conductivity at field E, t is time (measured from the beginning of HV pulse). Taking into account the above, the electric conductivity in a strong electric field can be obtained from the slope of $\varepsilon(t)$ dependence, if density, heat capacity and the temperature dependence of electric permittivity are known. To analyse the dependence of the electric conductivity *versus* field strength, it is much more convenient to use the differentiated form of (2):

$$\left(\frac{\partial\varepsilon}{\partial t}\right) = \frac{1}{\rho \cdot c_p}\left(\frac{\partial\varepsilon}{\partial T}\right) \cdot \sigma_E E^2 = A\sigma_E E^2, \qquad \text{where} \qquad A = \frac{1}{\rho \cdot c_p}\left(\frac{\partial\varepsilon}{\partial T}\right) \tag{3}$$

If the conductivity is field independent, the dependence ($\partial\varepsilon/\partial t$) *versus* E^2 should be linear. Figures 4a and 4b present the mentioned dependences for ethanol + TMAC mixtures. Experiments were performed in capacitors indicated as "a" and "b", respectively. The dependences have negative curvatures – this means that in the presence of a strong electric field the electric conductivity increases in comparison with the low field values. In our experiments, an interesting but not fully understood effect was observed. To check stability of the investigated mixture, we measured (by Radelkis conductometer) the electric conductivity just before and after NDE experiments. We found that these two values of the conductivity were different (the differences 5–10%). In the case of capacitor "a", conductivity after NDE was lower than before it, and it did not change considerably in time. In the case of capacitor "b", conductivity after NDE experiment was larger than before it, and during 30 minutes it was attaining the initial value. The change of conductivity was observed especially for low concentrations of TMAC, at higher concentrations the effect was negligible. The observed decrease of conductivity in the capacitor "a" can be explained by Małecki's model, where annihilation of ions (in the electrode reaction) prevails creation and consequently, the conductivity decreases. In the case of capacitor "b", the increase of

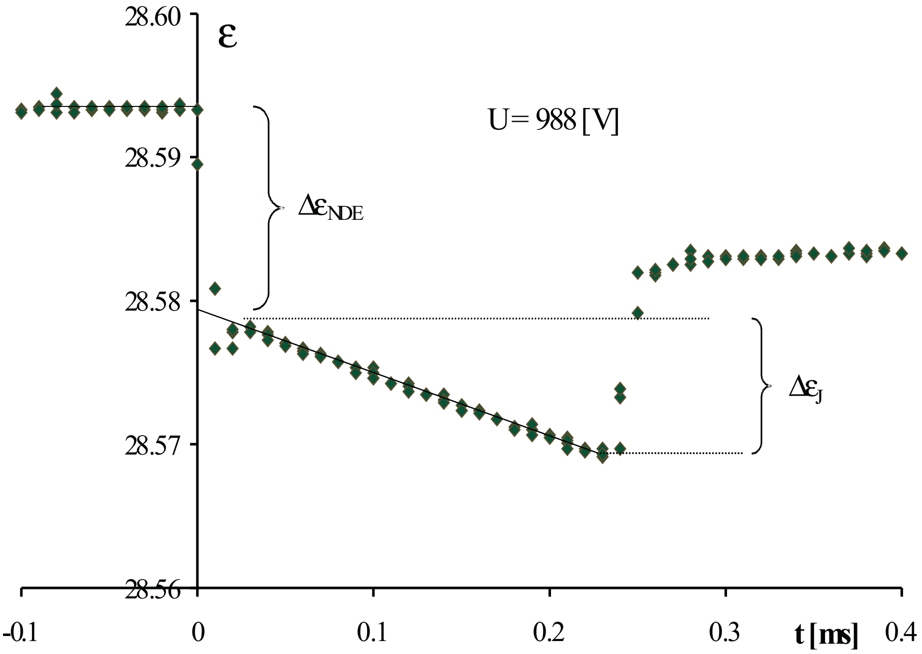

Figure 3. An example of $\varepsilon(t)$ dependence, where the non-linear dielectric effect is negative and heating is observed ($c_s = 2\cdot10^{-5}$ mol/dm^3).

conductivity could be a result of "sucking" of ions in the area of high field strength (between electrodes). When the high field is switched off, concentration of ions returns, by diffusion, to the initial value. Similar observation (the change of conductivity before and after application of HV field) were announced already by Maed and Fuoss [8,9]. Consequently, the question arises, if the discussed phenomena influence the measured σ_E. To test this, σ_E was measured repeatedly, with HV pulses of constant amplitude and frequency of 4 Hz applied continuously. The results of these experiments are presented in Fig. 5. In the capacitor "a" the obtained relative conductivity was slightly decreasing as function of time, whereas in the capacitor "b" the change of conductivity was smaller than the precision of the obtained values. Conseqently for the short single pulse the effect is negligible. Another proof of the importance of the discussed effect could be obtained on the basis of the analysis of $(\partial\varepsilon/\partial t)$ *versus* E^2 dependences in both types of capacitors. If the change of concentration of ions between electrodes determine the obtained data, one will observe the positive curvature of $(\partial\varepsilon/\partial t)$ *versus* E^2 in the case of capacitor "a" (decrease of concentration of ions and hence decrease of conductivity), and the negative curvature in the case of capacitor "b" (increase of concentration of ions). Similar dependences observed in both types of capacitors (Figs. 4a, 4b) seem to prove that the discussed change of concentration is less important than the inherent change of conductivity. Assuming that the observed non-linearity is caused mainly by the increase of electrolytic conductivity, and that $\sigma_E = \sigma_o + \sigma_1 E^2$ one obtains:

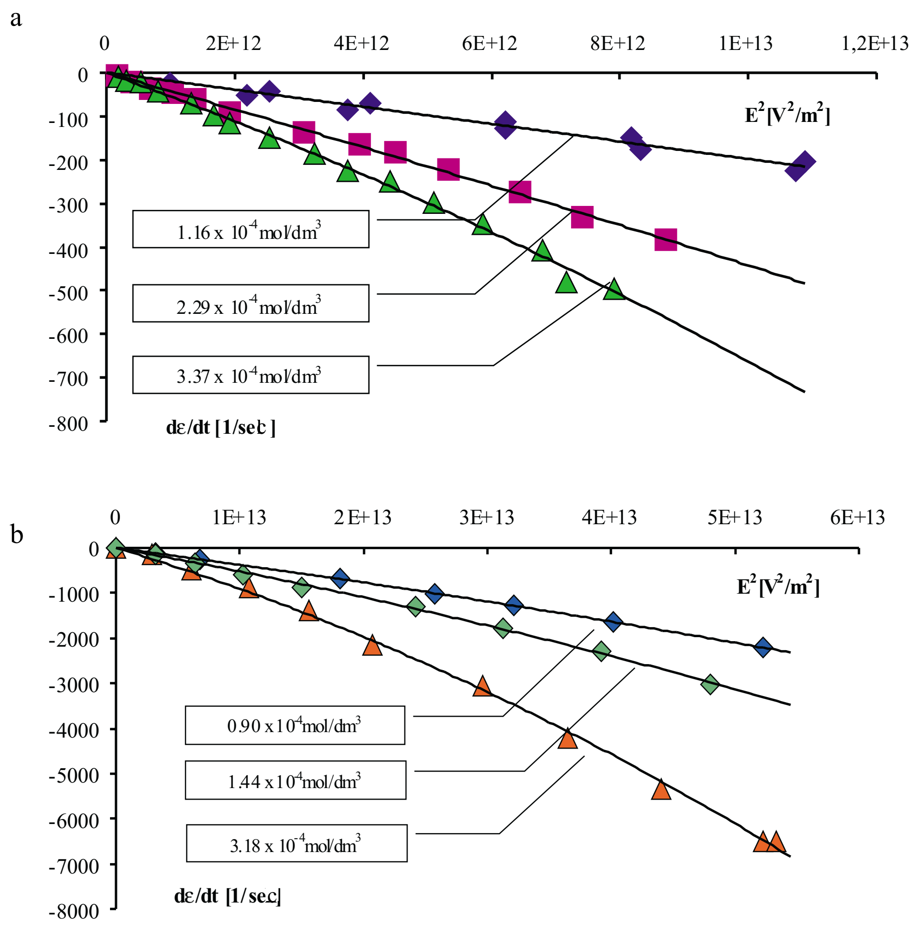

Figure 4. The $d\varepsilon/dt = f(E^2)$ dependence for ethanol + TMAC mixtures. Experiments were performed in capacitors indicated as "a" and "b", respectively.

$$\left(\frac{\partial\varepsilon}{\partial t}\right) = A\sigma_o E^2 + A\sigma_1 E^4 \qquad (4)$$

Fitting the double square dependence to the obtained experimentally $(\partial\varepsilon/\partial t)$ *versus* E^2 data allows to obtain both the low field conductivity and its electric field dependent part. For these calculations density, heat capacity and $d\varepsilon/dT$ are necessary. It can be assumed, that the required parameters are close to those of pure ethanol (ρ = 788 kg/m^3, c_p = 2412 J/K·kg, $d\varepsilon/dT = -0.167$). The results of estimations of conductivity by NDE method and that measured conductometrically are presented in Table 1. The low field conductivity (σ_o) was found to be a monotonic function of concentration. However, the differences in σ_o obtained in capacitors "a" and "b" are higher than

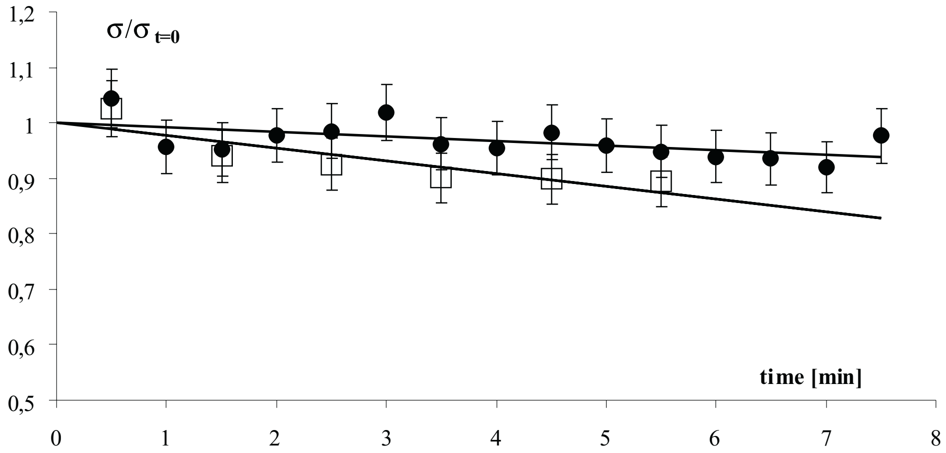

Figure 5. The ratio σ_E/σ_o measured in function of time, when HV pulses of constant amplitude were applied with the frequency of 4 Hz ($c_s = 2\cdot 10^{-5}$ mol/dm^3, HV = 15 kV/cm).

the error of fitting. The main problem in determining the precise absolute value of σ_o consists in a proper estimation of c_o of capacitors used in NDE experiments. In the case of the capacitor "a", the electric field is almost homogeneous and c_o is close to $\varepsilon_o\cdot S/d$. In the case of capacitor "b", the field is strongly inhomogeneous (especially at the border) and the application of the same expression may result in an apparent decrease of the calculated value of σ_o.

Table 1. The results of fitting of Eq. (4) to the experimental data. The A parameter was calculated assuming that density, heat capacity and $d\varepsilon/dT$ of diluted mixtures are those of pure ethanol.

C (TMAC) [mol/dm^3]	σ_o [S/m]	σ_1 [Sm^3/V^4]	σ_1/σ_o [m^2/V^2]	$\sigma_{cond.}$ [S/m]
capacitor "a"				
$1.16\cdot 10^{-4}$	$0.23\cdot 10^{-3}$	$0.2\cdot 10^{-18}$	$1\cdot 10^{-15}$	$0.65\cdot 10^{-3}$
$2.29\cdot 10^{-4}$	$0.48\cdot 10^{-3}$	$2.8\cdot 10^{-18}$	$6\cdot 10^{-15}$	$1.09\cdot 10^{-3}$
$3.37\cdot 10^{-4}$	$0.60\cdot 10^{-3}$	$15\cdot 10^{-18}$	$24\cdot 10^{-15}$	$1.51\cdot 10^{-3}$
capacitor "b"				
$0.90\cdot 10^{-4}$	$0.41\cdot 10^{-3}$	$1.5\cdot 10^{-18}$	$3.6\cdot 10^{-15}$	$0.55\cdot 10^{-3}$
$1.44\cdot 10^{-4}$	$0.56\cdot 10^{-3}$	$2.9\cdot 10^{-18}$	$5.2\cdot 10^{-15}$	$0.76\cdot 10^{-3}$
$3.18\cdot 10^{-4}$	$0.94\cdot 10^{-3}$	$8.9\cdot 10^{-18}$	$9.4\cdot 10^{-15}$	$1.44\cdot 10^{-3}$

Comparison of the conductivity obtained in NDE experiments (σ_o) and that measured conductometrically ($\sigma_{con.}$) shows that $\sigma_o < \sigma_{con.}$. The reason of this seems to be clear if separation of ions in a strong electric field and randomisation of ions in the absence of HV is considered. The strong electric field in our experiments was applied as short rectangular pulses. Ions migrate toward electrodes, when the pulse is applied.

Switching off the HV field allows randomisation. However, the randomisation is controlled by diffusion and hence it is much more time consuming than migration in a strong electric field. Repeatedly applicated electric field pulses causes partial separation of positive and negative ions, resulting in a non-uniform spreading of ions between electrodes – an increase of concentration of ions close to electrodes and a decrease far from them. Competition between migration and diffusion decreases the Joule heating effect (related to the amount of ions capable to move), and hence a decrease of the NDE conductivity is observed. Consequently, the σ_o is lower than that measured conductometrically.

Figure 6 presents the molar conductivity (measured conductometrically) *versus* the square root of concentration. Non-linearity of the obtained dependence means, that the investigated systems belong to relatively weak electrolytes. According to Onsager theory, the relative increase of conductivity $(\sigma_E - \sigma_o)/\sigma_o$ should be independent of concentration of the solute. In our case the relative increase of conductivity is equal to the ratio σ_1/σ_o. Unfortunately, this quantity strongly depends on concentration, especially in the capacitor "a", what is inconsistent with Onsager theory.

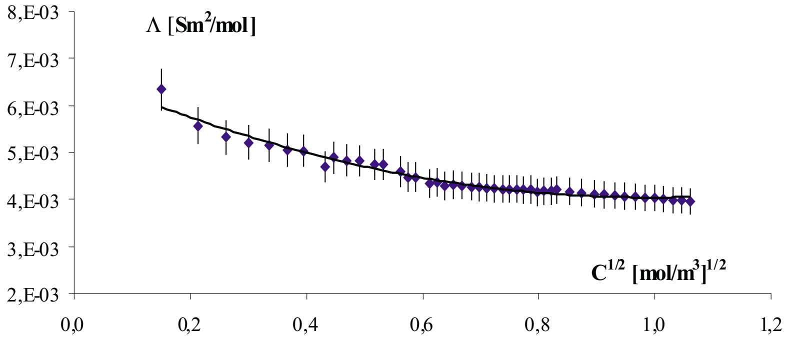

Figure 6. The molar conductivity (measured conductometrically) *versus* the square root of concentration.

CONCLUSIONS

a) The NDE method allows to obtain the "static" conductivity on the base of analysis of the Joule heating effect and the change of permittivity resulting from the increase of temperature during a HV pulse. However, the absolute precision of the obtained values is low and the data obtained in this way can be used only in examinations of relative changes of conductivity.

b) To obtain the low field conductivity and the field dependent part, the analysis of $(\partial\varepsilon/\partial t)$ *versus* E^2 is necessary.

c) The σ_o conductivity, deduced from the NDE experiments, is lower than that obtained by classical methods.

d) The NDE method allows to observe an increase of conductivity in a strong electric field. However, the field-dependent part of conductivity was found to be inconsistent with the Onsager theory, what probably reflects additional effects not considered in the theory.

e) Conductivity before the NDE experiments was different from that after it.

The shift relates probably to changes of concentration of ions between the electrodes and depends on the construction of capacitors. To reduce this effect, short, single HV pulses should be applied.

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