Apparent non-linear dielectric effect in liquids containing ions

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Abstract

Addition of ions into ethanol + *p*-xylene mixtures lead to an apparent, negative non-linear dielectric increments (a difference between an electric permittivity obtained at strong and at weak electric fields). The electrode polarisation phenomena were supposed to be responsible for the observed effect.
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1. Introduction

According to the Debye–Langevine theory, in fluids, an electric permittivity is a non-linear function of strength of an electric field [1]

$$\varepsilon_E = \varepsilon_0 + \varepsilon_1 E^2 + \varepsilon_2 E^4 + \cdots. \tag{1}$$

Succeeding terms of the series decreases quickly and the ratio $\varepsilon_1/\varepsilon_0$ rarely exceeds 10^{-18}–10^{-17} m^2/V^2. Hence in common dielectric experiments an electric permittivity is approximated by the first term only. To observe next terms of the series, very strong electric field, up to 10^8 V/m, in a specially designed experimental set-up, has to be applied. An increment of non-linear dielectric effect (NDE) is defined as a difference between an electric permittivity obtained at strong (ε_E) and at weak (ε_0) electric fields

$$\Delta\varepsilon_{NDE} = \varepsilon_E - \varepsilon_0. \tag{2}$$

Assuming that only two first terms of the series (1) are important, the NDE increment could be approximated as $\Delta\varepsilon_{NDE} \cong \varepsilon_1 E^2$. When the system contains rigid, non-interacting molecules, for Onsager local field, the NDE increment could be presented as (see for example [2]):

$$\Delta\varepsilon_{NDE} = -\frac{\varepsilon^4(n^2+2)^4}{(2\varepsilon^2+n^4)(2\varepsilon+n^2)}\frac{N_A\bar{M}}{\rho}\frac{\mu_s^4}{45\varepsilon_v k^3 T^3}E^2, \tag{3}$$

where ε is the electric permittivity, n is the refractive index, N_A is the Avogadro number, M is the mean molar mass, ρ is the mass density, μ_s is the dipole moment of polar molecules, ε_v is the vacuum electric permittivity, k is the Boltzmann constant, T is the temperature, and E is the electric field strength. Following the above equation the ratio $\Delta\varepsilon_{NDE}/E^2$ should be negative and would be calculated using simple quantities. It is often observed that the experimental NDE increments and that calculated using Eq. (3) are different. In some systems the experimental NDE increment is even positive, what is not possible in frame of Deby'e–Langevin theory. The reason of that is an influence of a strong external field on molecules and favouritism of much polar structures. Non-linear dielectric increment is very sensitive to association [3–6], tautomeric equilibriums [7–9], critical and pre-critical phenomena in liquids [10–12], liquid crystals [13] and solids [14]. It is a reason why the NDE method is helpful in understanding of molecular structure, conformation, dynamics, intermolecular interactions, structure of liquids and liquid crystals.

Applicability of the NDE method is usually limited to liquids of low conductivity and experimentalists try to reduce it by suitable selection of the investigated materials and careful purification. However, in many interesting systems the conductivity is an inherent property of the material. The knowledge of the effect of ions on the NDE increment seems to be important both from theoretical and practical reasons.

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In measurements presented in this Letter, a small amounts of tetramethylamonium chloride (TMAC) was dissolved in a mixed solvent ethanol + *p*-xylene. Selection of the materials was aimed to providing a sufficient solubility of ionic salt in relatively simple non-aqueous solvent.

2. Experimental

Measurements of non-linear dielectric effect, consists in detection of small permittivity changes of a material after application of strong electric field. The capacitor filled by the investigated liquid is a part of LC circuit. Application of strong electric field changes electric permittivity of the material what influences resonant frequency and quality factor of the LC circuit. In measurements, described in this Letter, the capacitor (parallel-plate configuration, diameter and distance between electrodes 10 and 0.3 mm, respectively), was a part of the Colpitt's oscillator with large feed back. High field was applied as rectangular pulses (duration time 0.2–0.4 ms, strength up to 10^7 V/m). The resonant frequency was approximately 5.5 MHz but in some experiments it was shifted to 3.7 MHz by replacing of inducting coil in the LC circuit. The frequency was read in function of time by fast counter (Modulation Domain Analyser HP 53310A). The scheme of experimental set-up is presented in Fig. 1.

The change of the resonant frequency is a result of the non-linear dielectric effect, and the Joule heating in strong electric field. Analysis of time dependence of the resonant frequency allows obtaining the required NDE increment. An example of time dependence of resonant frequency in a conducting system is presented in (Fig. 2).

The NDE increment was calculated using the equation:

$$\Delta\varepsilon_{\text{NDE}} = C\left(\frac{1}{f_{\text{E}}^2} - \frac{1}{f_0^2}\right), \tag{4}$$

where C is the constant obtained in a calibration procedure, f_{E} and f_0 are defined in Fig. 2. The absolute precision of measurements of the NDE increment was ±10%, resolution ±3%, the high field strength was
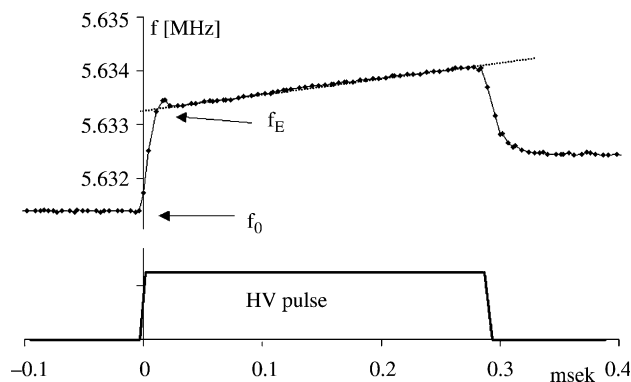
Fig. 2. A resonant frequency of LC oscillator in function of time in conducting liquid.

measured with the precision 2%. The alcohol was dried by using magnesium activated by iodine and then distilled in inert gas atmosphere. TMAC was dried in vacuum essicator over P_2O_5. *p*-Xylene (analytical grade) was used without additional purification. All operation were made at 25 ± 2 °C under dry nitrogen atmosphere.

3. Results and discussion

According to the data presented in Fig. 3 the NDE increment in the ethanol + *p*-xylene + TMAC mixture is proportional to the square of an electric field strength. It is similar to that observed in simple dipolar liquids and consistent with Debye–Langevive theory. However, the obtained increments are larger than that expected and observed in the pure system (Figs. 4 and 5). We found that ions lead to large negative NDE increments, independently on a sign of the increment in the pure mixture. For example, the addition to the mixture containing 0.67 mole fraction of ethanol of only 10^{-5} mol/dm^3 of tetramethylammonium chloride decreases the NDE increment (increases its absolute value) twenty times. When in a pure mixture the NDE increment is positive, the addition of ions decreases the increment, at some salt concentration it passes zero and finally attained large negative values. The NDE (presented as $\Delta\varepsilon_{\text{NDE}}/E^2$ ratio) was found to be a linear function of the salt concentration.

As it was mentioned before, the NDE increment in doped mixtures is a linear function of E^2. However, in order to obtain such dependence, a single, short HV pulses have to be applied. For the longer pulses applied repeatable (as in common NDE experiments) non-linearity depending on the repetition frequency of HV pulses and the geometry of the capacitor was observed. The possible reasons of this observation seem to be similar to those described previously in measurements of the conductivity in strong electric field [15]. Application of repetitive HV pulses results in a movement of ions
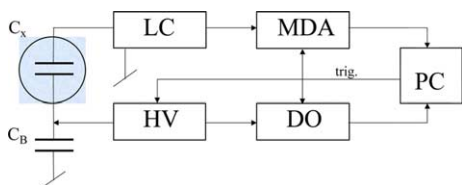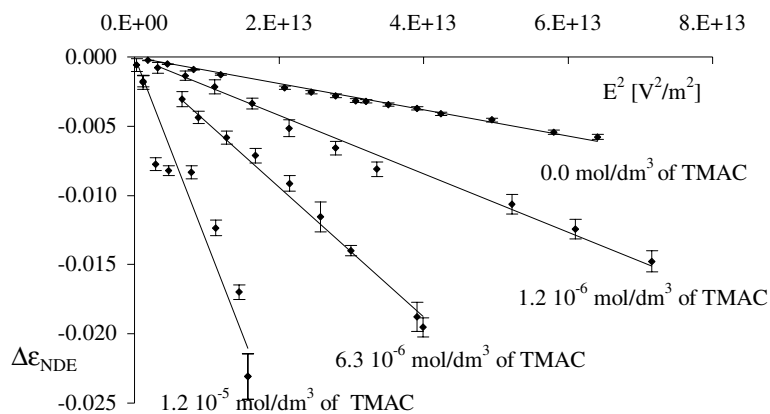

Fig. 1. Scheme of the experimental set-up: LC, Colpitt's oscillator; MDA, modulation domain analyser; HV, high voltage pulse generator; DO, digital oscilloscope; PC, personal computer; C_x is the measuring capacitor, C_B is the blocking capacitor ($C_B \gg C_x$).

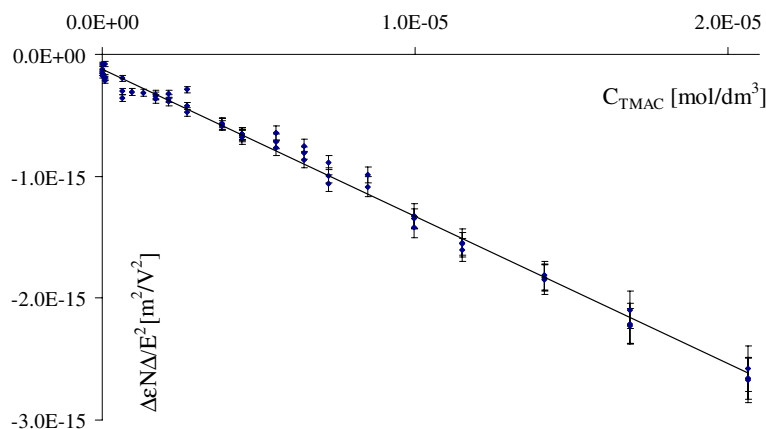Fig. 3. The NDE increment versus square of electric field strength in ethanol + *p*-xylene + TMAC mixture.

Fig. 4. The dependence of $\Delta\varepsilon_{NDE}/E^2$ versus concentration of TMAC. Mole fraction of EtOH = 0.67.
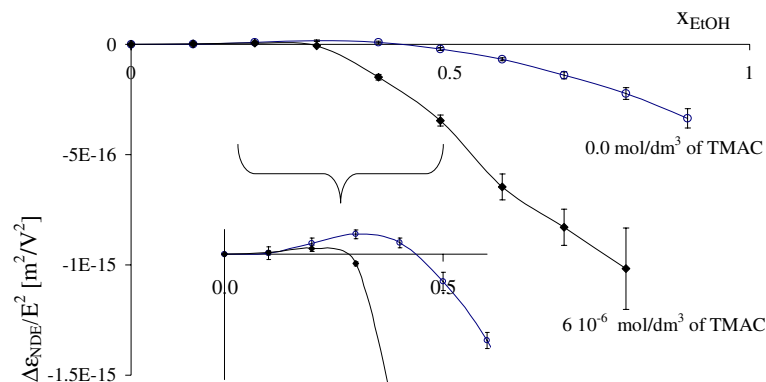

Fig. 5. NDE in the pure and in the doped mixture versus alcohol concentration.

toward electrodes and, as a consequence, in inhomogeneous distribution of the carriers inside capacitor. This effect was considerably reduced when short, single (or rarely repeatable) HV pulses were applied.

Any system containing ions, subjected to the influence of an electric field of sufficient intensity, has to undergo electrochemical red–ox reactions. It is also the

case of the investigated mixtures. However, we found that in the succeeding measurements (performed in the same sample) the results were repeatable. It proves that the obtained NDE increments were not disturbed significantly by the red–ox reactions.

In explanation of the presented data we propose to consider a role of electrode polarisation in NDE

experiments. Polarisation of electrodes appears as a result of accumulation of ions close to charged surfaces and formation of a so-called 'double layers'. The effect of electrode polarisation considerably disturbs low frequency dielectric measurements leading to strong increase of the experimental permittivity. In NDE measurements two fields influence the investigated sample: a low amplitude, high frequency measuring field ($E = 10^3$ V/m, $f = 3$–6 MHz), and high amplitude (up to 10^7 V/m) DC pulses of polarising field. In the interpretation of the non-linear dielectric experiments it is convenient to consider the differential definition of electric permittivity ($\varepsilon - 1 = \varepsilon_v^{-1}(\partial P/\partial E)$, where P is electric polarisation, ε_v is the permittivity of a vacuum). The definition relates the permittivity with a change of polarisation under influence of the measuring field. The NDE increment compares permittivity measured in the absence of strong electric field and in the presence of it. In the absence of a strong field, electric permittivity of the systems with ions is influenced both by distortion polarisation (dipolar, atomic, electronic) and by electrode polarisation. When a strong DC field is applied ions in double layer became almost 'frozen' and the high frequency low amplitude measuring field cannot disturb considerably the electrode polarisation. It means that, under influence of a strong electric field, some decrease of the measured permittivity is expected. Following this picture it seems that the electrode polarisation phenomena should lead to the negative component of the NDE increment ($\varepsilon_E < \varepsilon_0$). The experimental NDE is a sum of a 'bulk' effect related to the NDE of dipolar molecules in the interior of liquid and a 'surface' effect related to the electrode polarisation. Consequently, the experimental NDE increment could be presented as follows:

$$\Delta\varepsilon_{NDE} = (\Delta\varepsilon_{NDE})_{bulk} + (\Delta\varepsilon_{NDE})_{surface}, \tag{5}$$

where the second term is related to the electrode polarisation phenomena.

As it was presented in the Introduction, the NDE increment in simple dipolar liquids is proportional to the square of the electric field strength. According to the Fig. 3, similar dependence seems to be correct in a system doped by ions.

The influence of electrode polarisation on the electric permittivity is very large at low frequencies. In high frequencies when the space charge near the dielectric–electrode interface will not have time to be established, the role of the electrode polarisation is lightened. According to the model presented by Johnson and Cole [16] the experimental permittivity could be presented as

$$\varepsilon_{expt.} = \varepsilon + G^2/4\pi^2 f^2 C_0(C_{el})_0, \tag{6}$$

where C_0 is the air capacitance, G is the conductance factor, f is the measuring frequency, $(C_{el})_0$ is the capacitance of a double layer (F/m^2). The second term

(related to the electrode polarisation) is proportional to $(G/f)^2$. It could be assumed, that 'surface' component of NDE should obey similar dependence. Taking into account the above it could be proposed that

$$\frac{(\Delta\varepsilon_{NDE}(f_1))_{surface}}{(\Delta\varepsilon_{NDE}(f_2))_{surface}} = \frac{\left(\frac{G(f_1)}{f_1^2}\right)}{\left(\frac{G(f_2)}{f_2^2}\right)}. \tag{7}$$

The NDE increment is proportional to the E^2 what motivate presentation of the experimental data as a ratio $\Delta\varepsilon_{NDE}/E^2$. Assuming that the conductivity factor G is independent on frequency one obtains

$$\frac{(\Delta\varepsilon_{NDE}(f_2))_{surface}}{(\Delta\varepsilon_{NDE}(f_1))_{surface}} = \frac{\left(\frac{\Delta\varepsilon_{NDE}(f_2)}{E^2}\right)_{surface}}{\left(\frac{\Delta\varepsilon_{NDE}(f_1)}{E^2}\right)_{surface}} \simeq \frac{f_1^2}{f_2^2}. \tag{8}$$

To check this property the measurements were repeated for two frequencies: 5.96 and 3.59 MHz. In the measurements we used ethanol + p-xylene (0.45 mole fraction of EtOH) mixture doped by TMAC (4×10^{-6} mol/dm^3). The pure mixture has negligible NDE increment what allows to suppose that $(\Delta\varepsilon_{NDE}/E^2) \cong -((\Delta\varepsilon_{NDE}/E^2)_{surface}$. The results are summarised in Table 1. The ratio of the non-linear dielectric increments (2.3 ± 0.3) is a bit smaller than the square ratio of the frequencies (2.7). In the estimations it was supposed that the conductivity factor is independent on frequency. In reality, the conductivity increases with the increase of frequency and hence, the ratio of NDE increments could be smaller than $(f_1/f_2)^2$.

It is interesting to consider an influence of ion pairs on the NDE increment. In diluted aqueous mixtures formation of ion pairs is prevented by strong hydration of ions and large permittivity of the solvent. However, in liquids of low or moderate permittivity formation of ion pairs is possible. Evidences of that were given by the measurements of conductivity of electrolytes dissolved in non-aqueous solvents [17]. Ion-pairs have very large dipole moments. For example, two elementary charges separated by 1 nm gives the dipole moment $\mu = 48$ D. Non-linear dielectric increment is proportional to the fourth power of μ what results in extraordinary sensitivity of the NDE on an existence of ingredients with large dipole moments. It is possible that the formation of ion pairs could influence the obtained NDE

Table 1
NDE effects measured at two different frequencies

	$(\Delta\varepsilon_{NDE}/E^2)$
$f_1 = 5.96$ MHz	$-28(\pm3)\times10^{-17}$ m^2/V^2
$f_2 = 3.59$ MHz	$-66(\pm7)\times10^{-17}$ m^2/V^2
$(\Delta\varepsilon_{NDE}(f_2)/E^2)/(\Delta\varepsilon_{NDE}(f_1)/E^2)$	2.3 ± 0.3
$(f_1/f_2)^2$	2.7

Mole fraction of EtOH = 0.45, concentration of TMAC = 4×10^{-6} mol/dm^3.

increments in ion-doped solutions. However, it is impossible to resolve on the base of the presented data the electrode polarisation effect and that related to formation of ion pairs.

4. Conclusions

The main result of the presented measurements is the conclusion that the non-linear dielectric increment attains large negative values in presence of even small amounts of ions capable to migrate in an external field. It is an apparent effect and the experimental NDE increment has to be presented as a sum of the 'bulk' (property of a material) and the 'surface' effects: $\Delta\varepsilon_{\mathrm{NDE}} = (\Delta\varepsilon_{\mathrm{NDE}})_{\mathrm{bulk}} + (\Delta\varepsilon_{\mathrm{NDE}})_{\mathrm{surface}}$. The surface effect was found to be proportional to square of electric field strength ($E < 10^7$ V/m) and inversely proportional to square of frequency of the measuring field. It seems that the electrode polarisation is responsible for the discussed phenomena. Formation of ion pairs in the investigated non-aqueous mixture was also considered.

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