Non-linear dielectric response for menthol solutions

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Introduction

The non-linear dielectric effect **(NDE)** is determined by measuring the difference in electric permittivity at strong and weak electric fields. [1] This difference is called the NDE increment (**$\Delta\varepsilon_{NDE}$**). NDE measurements are typically performed for liquids, while measurements for solids are difficult and therefore very rare. [2]

According to the Debye–Langevin theory, in dipolar liquids the NDE increment should be negative and proportional to the square of the electric field strength. However, a strong electric field can sometimes modify the dipole moments of molecules, complexes, or compounds. This leads to the appearance of a positive, so-called anomalous NDE increment. Such an anomalous increment may result from the influence of a strong electric field on conformational changes, intermolecular interactions, critical fluctuations, and equilibrium phenomena. [2, 3]

Alcohols can form linear and cyclic associations. The strong electric field shifts equilibrium toward open associates of large dipole moments, that may result in anomalous NDE increment. [3, 4]

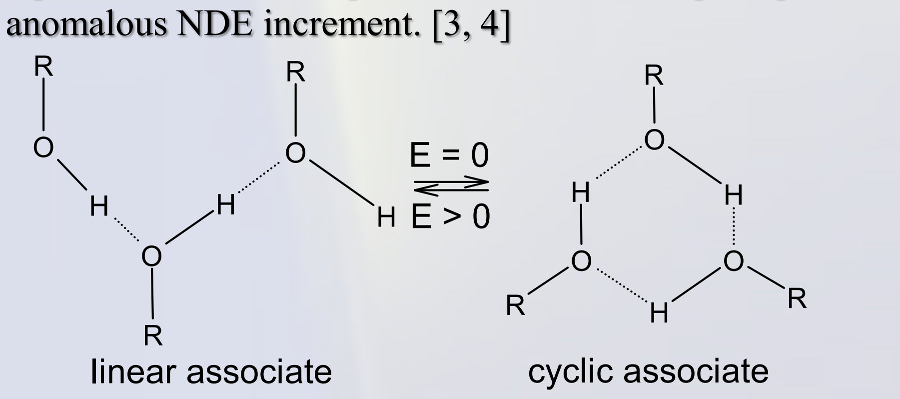


Figure 1. Formations of associations in alcohols by hydrogen bonds.

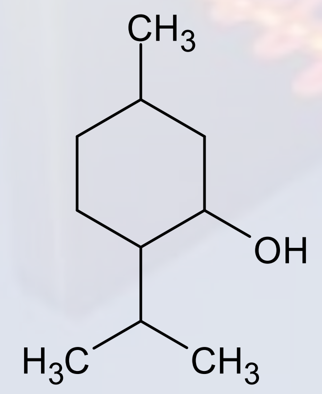


Figure 2. Structure of menthol.

In this study we present dielectric measurements in a menthol-p-xylene mixture. The NDE measurements were supplemented with electric permivitty, density and refractive index data. In the course of interpretation, we compare the experimental NDE with calculated one in the frame of Onsager's local field model.

Methods

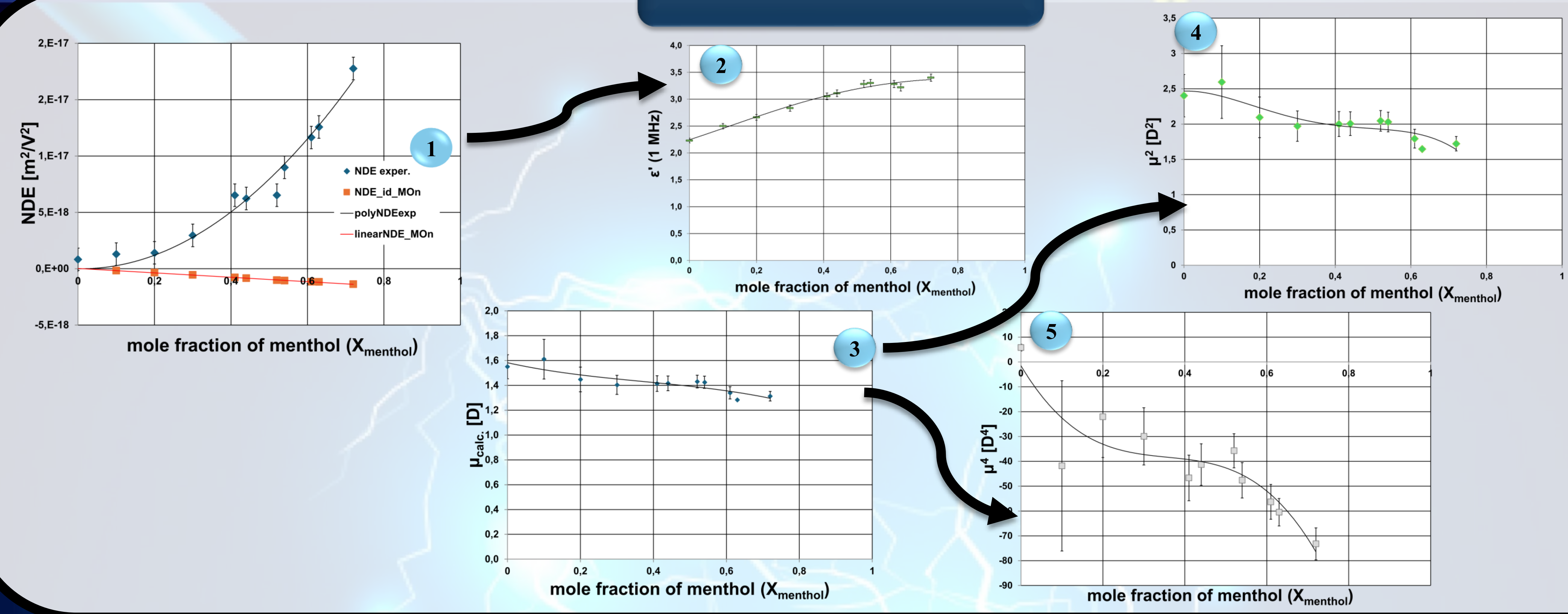
Experiment of non-linear dielectric measurements

In the NDE measurements we used the double-field method. The experiment is based on comparison of the value of electric permittivity measured at high and at low electric field strength. Capacitor, which contained the investigated liquid was a part of LC circuit. Resonance frequency allows to calculate the permittivity with a resolution up to 10^{-5}. LC circuit was operated at frequency of 4 MHz and low-amplitude of 1 V. For a short time (of 1 ms) a high voltage pulse was applied (500-3000 V) and the change of the resonance frequency of LC circuit caused by the change of electric permittivity was measured. This allowed to calculate the NDE effect expressed as **$\Delta\varepsilon_{NDE}/E^2$**, where $\Delta\varepsilon_{NDE}$ is a difference between electric permittivity obtained at high electric field strength and at low electric field strength. Details of experimental setup can be found in paper. [5]

Electric permivitty measurements

Measurements of electric permittivity were performed using HP 4284A Precision LCR Meter in a frequency range 100 Hz - 1 MHz. Capacitor had coaxial configuration. Geometry capacity and load capacity was obtained using liquids of known permittivity (air, 1,2-dichloroethane). Geometry capacity was found of 5 pF. Temperature was stabilized by water thermostat at 25 ± 0.1°C.

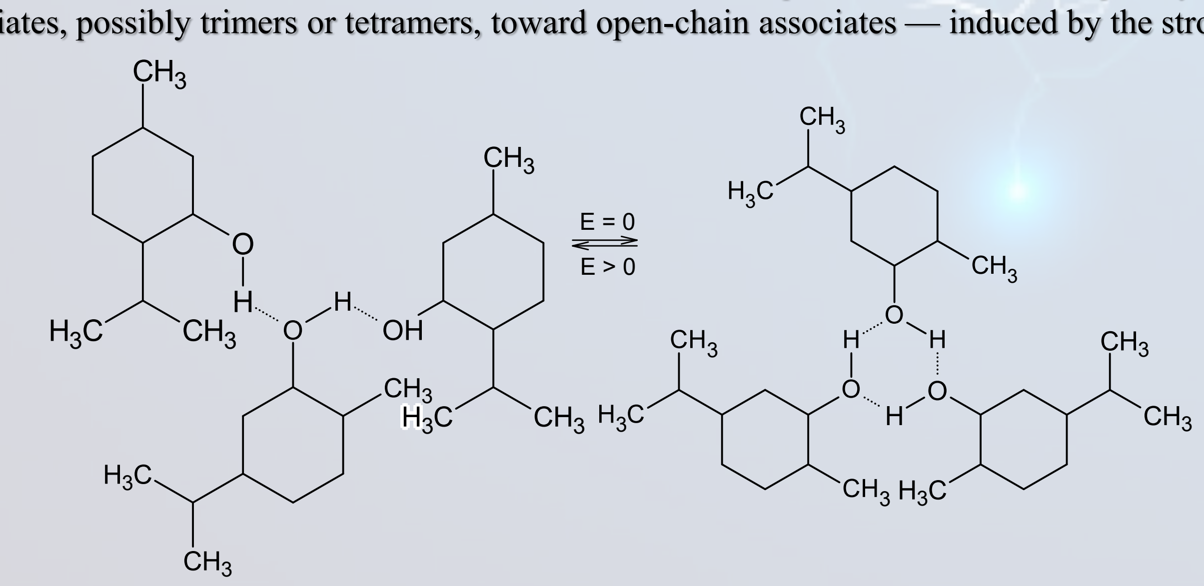
Results



Discussion and conclusions

A characteristic feature of the menthol–p-xylene mixture is the presence of a positive (anomalous) NDE effect across the entire concentration range, with the NDE value increasing as the menthol concentration rises. This behavior is similar to that observed in NDE measurements for aliphatic alcohols with long hydrocarbon chains [3, 4].

The mean dipole moment, calculated from electric permittivity, density, and refractive index, decreases with increasing menthol concentration. This suggests that high menthol content promotes the formation of molecular associates with low dipole moments. Consequently, the anomalous NDE effect can be attributed to a shift in equilibrium — from cyclic menthol associates, possibly trimers or tetramers, toward open-chain associates — induced by the strong electric field.



Literature

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