

Premelting Phenomena in *n*-Alcohols from Nonanol to Dodecanol

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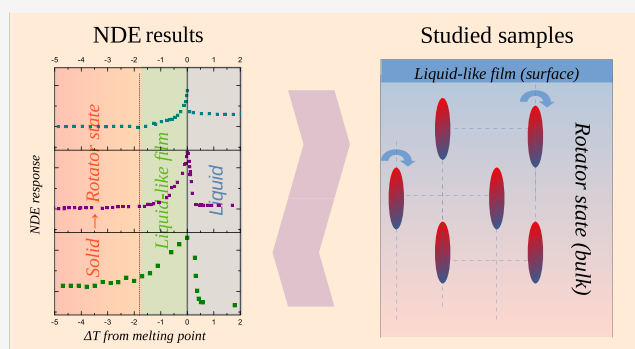
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ABSTRACT: The nonlinear dielectric effect (NDE) measurements of nonanol, undecanol, and dodecanol in the vicinity of the melting point were performed to examine and to develop the hypothesis on pretransition phenomena in decanol (Pocheć et al., *J. Phys. Chem. C* 2019, 123, 16929–16933). The results show that the anomalous increase of the nonlinear dielectric effect in the immediate vicinity of the melting point is uniform for each of the studied compounds. We link the observed anomaly with the formation of a liquidlike film on the surface of the solid. The scaling function describing these anomalies was proposed and tested. We proved the feasibility of NDE studies in the examination of premelting phenomena.



INTRODUCTION

Nonlinear dielectric measurements of solid–liquid phase transition in medium-chain, aliphatic alcohols were inspired by the previous study of 1-decanol conducted by the authors.¹ In the mentioned paper, the authors have shown that in the vicinity of the melting point the nonlinear dielectric effect (NDE) increases considerably. This increase was attributed to the emergence of the rotator state, followed by surface premelting. This concept needed verification in other alcohols.

Nonlinear dielectric effect measurements are based on the study of the difference between low- and high-field dielectric permittivity. In general, the electric permittivity can be described by the following function of electric field intensity (E)

$$\epsilon'_E = \epsilon' + \epsilon'_3 E^2 + \epsilon'_5 E^4 + \dots \quad (1)$$

where ϵ' is the low-field dielectric permittivity, ϵ'_i are the parameters of expansion according to E , and i denotes the order of expansion of polarization according to E . In simple dipolar liquids, only the first and the second terms are detectable.^{2,3} A double-field NDE method, as in the case of experiments presented in this paper, provides an increment in NDE, which is the difference between the high- and low-field dielectric permittivity $\Delta\epsilon_{\text{NDE}} = \epsilon'_E - \epsilon'$. The ratio of the NDE increment and a square of polarizing field intensity E is called the Piekara factor, approximated as

$$\Delta\epsilon_{\text{NDE}}/E^2 \cong \epsilon'_3 \quad (2)$$

In liquids consisting of simple, rigid, dipolar, and non-interacting molecules, the Piekara factor is negative and usually of the order from 10^{-16} to 10^{-18} m² V⁻². If the electric field can change the dipole moment (either by changing the geometry

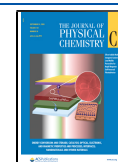
of the molecules⁴ or affecting the equilibrium between high- and low-dipole-moment associates⁵), an anomalous, positive NDE can be observed. Critical phenomena can also result in high, positive NDE values^{6–10} as well as pretransitional effects, as seen in liquid crystals.¹¹

Nonlinear dielectric measurements in solids are very rare and are difficult to perform. Only a few attempts have been published so far.^{12,13} In this study, we conducted nonlinear dielectric experiments for three alcohols: nonanol, undecanol, and dodecanol. Because the results obtained previously for decanol were unique, it was interesting to compare them with those of its close “neighbors” from the homologous series. As expected, they exhibited a similar increase in NDE response in the vicinity of the melting point. We believe that the reason for this is the uniform nature of the surface premelting. In the case of previously investigated decanol, symptoms of the existence of a rotator state were also found. In the present experiments, symptoms of the rotator phase could only be postulated for nonanol; however, this is not the case for undecanol and dodecanol despite their similarities to each other. This distinction between close neighbors, however, has been observed for other compounds as well.^{14–16} With the extension of measurements to many alcohols, we were able to propose a scaling function describing anomalous changes of the NDE in the premelting area.

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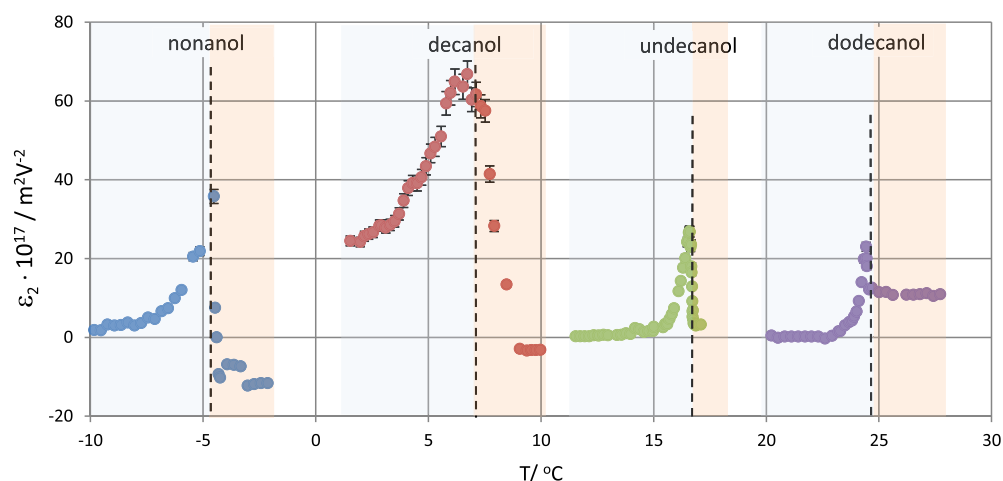


Figure 1. Temperature dependence of the Piekara factor in the studied alcohols. The blue area depicts the solid phase and the pink area depicts the liquid phase. Melting temperatures are presented as dotted lines.

EXPERIMENT

The NDE experiment used in the reported measurements was a double-field method, in which a low-amplitude, high-frequency measuring field (approx. 4 MHz, 1 V pp) and a high-amplitude, quasi-rectangular field (HV), with intensities up to 6.25×10^6 V/m for liquids and up to 6.25×10^5 V/m for solids, were applied. The decrease in the applied voltage when samples were solid was aimed at protecting against electrical breakdowns. The capacitor was a part of the parallel resonant LC circuit. Change in permittivity, caused by the application of a strong electric field, results in the alteration of resonance frequency of the circuit, measured by a fast counter. A capacitor of a parallel-plate configuration was made of stainless-steel electrodes with a diameter of 19 mm and a separation of 0.32 mm. The capacitor was filled with liquid alcohols and mounted in an air/liquid bath thermostat. A detailed description of the experimental setup can be found in the method-related paper.¹⁷ The polarizing field was applied in impulses lasting from 1 to 8 ms. The procedure used in this measurement was identical to that of the previous study.¹ Data were acquired in the temperature range of $-5 \text{ K} < T - T_m < +2 \text{ K}$, where T_m is the melting temperature, and in increments of 0.1–0.2 K. Prior to each measurement, the sample was thermostated for approx. 10 min to suppress the temperature gradient. The resolution of NDE measurements was 5%, with a precision of 15% in liquids and 20% in solids.

Alcohols were of >95% purity, and were dried on A3 molecular sieves and degassed prior to the experiment.

RESULTS

The results of NDE measurements for nonanol, undecanol, and dodecanol, supplemented by the results of the previous decanol study, are presented in Figure 1.

The results suggest that NDE behavior in decanol was not accidental. A similar increase in NDE in the vicinity of the melting point can be observed in all tested alcohols. In undecanol and dodecanol at 2 K below the melting point, the NDE is still not visible. In nonanol, even 5 K below the melting point, the NDE is considerably above zero, somewhat resembling the results obtained for decanol.¹ It seems that in the analyzed homologous series of alcohols, decanol is somehow unique. As the temperature approaches the melting point, the NDE increases sharply and reaches its maximum

value at the melting temperature, or just before melting temperature.

The NDE response to an increase in the electric field exhibits a delay in relation to the polarizing impulse. An example of the time dependence of the electric permittivity of undecanol is presented in Figure 2. A similar dependence was also observed in other solid alcohols studied.

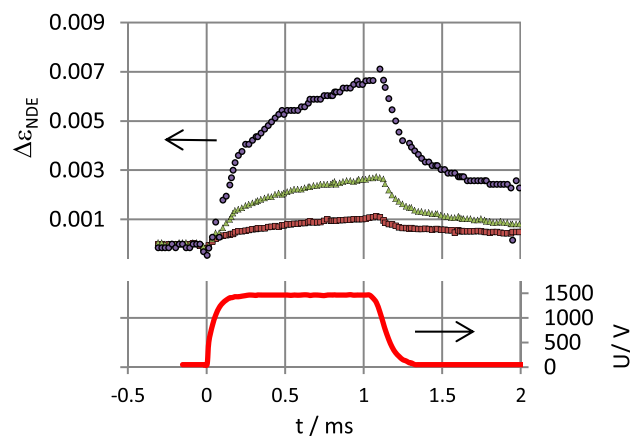


Figure 2. Time dependence of applied polarizing impulse (below) and NDE response for temperatures (from lowest to highest: 15.5, 16, and 16.5 °C) in undecanol.

In measurements of decanol,¹ the time dependence of the NDE increment was described by the stretched-exponential relaxation function^{18,19}

$$\epsilon'_3 = \epsilon'_{3,0} E^2 [1 - e^{-(t/\tau)^\beta}] \quad (3)$$

where $\epsilon'_{3,0}$ is the “static” value of the NDE increment, τ is the relaxation time for the NDE response, and β is the stretch parameter for the relaxation time. Equation 3 is not the only equation that can be used to describe the NDE increment evolution as a function of time. In liquids, where charge migration is possible while subjected to the strong-field pulse, a term containing the integral $\int (tE^2) dt$ is usually added to describe the Joule heating under adiabatic conditions.²⁰ However, in the case of the tested alcohols, even in their liquid state, the heating effect is very small and we decided to

exclude it in the function describing the NDE response. Analyzing the shape of the $\Delta\epsilon(t)$ response, shown in Figure 2, we can see that the baseline of NDE increment before and after the strong-field pulse differs significantly. It is possible that the NDE response hides additional processes, especially those with long relaxation times. To solve this problem, it is necessary to carry out NDE measurements for prolonged HV pulses, with a long recording time. The equipment that we currently use, however, does not provide such possibilities. We decided to apply the same function to fit the NDE increment that we used previously,¹ bearing in mind that future research may verify the precision of the equation used.

Equation 3 was fitted to the results of the NDE experiment presented in Figure 1. We found, contrary to the fitting performed in decanol,¹ that the β parameter was close to 1. In undecanol, similar to the previously studied decanol, it was observed that further from the melting point, the relaxation time was shortening with the decrease of the temperature. This change could be described using the Arrhenius equation (logarithm of the relaxation time is proportional to the inverse of temperature—straight line in Figure 3).

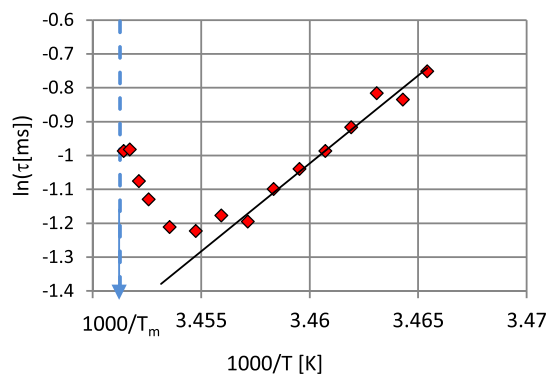


Figure 3. $1000/T$ dependence of logarithm of relaxation time in undecanol.

In the vicinity of the melting point, an increase in relaxation time while approaching the phase transition temperature (an increase in relaxation time with an increase of temperature) was observed. An increase in relaxation time in the vicinity of phase transition has already been observed, a phenomenon known as “critical slowing down”.^{21–23} In the case of nonanol and dodecanol, relaxation times were obtained with larger error, making such an analysis impossible.

DISCUSSION

We have attributed the observed increase in the positive NDE effect to premelting phenomena when approaching solid–liquid phase transition. We suggest treating phenomena in the vicinity of the melting point as a double process: premelting promoted a rotational state for the larger distance from the melting point, and surface premelting. Surface premelting occurs in the closest vicinity of the melting point and consists of the formation of a thin liquidlike layer on the surface of solids.²⁴ A premelting-promoted rotator state can be observed in a larger temperature distance before the melting point and is a result of the loosening of the structure of solids, allowing the molecules to have some freedom of movement that resembles the rotator phase.^{14–16} Following that reasoning, while approaching the melting point, we consider the initial increase

in the NDE effect as a premelting-promoted rotational state, and in the immediate vicinity of the melting point as a surface premelting.

An anomalous increase was not shown in the NDE only. In Figure 4, the dependence of electric permittivity on temper-

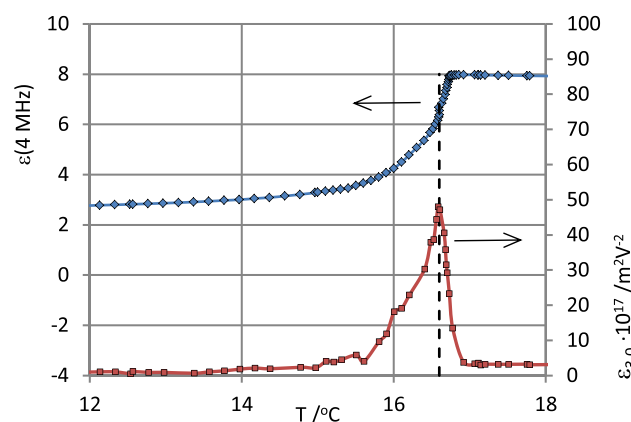


Figure 4. Temperature dependence of electric permittivity ϵ' (above) and NDE increment (below) in undecanol.

ature together with the NDE effect in undecanol is presented. The increase of permittivity from approx. 2.5 to 8 is visible, starting at 4 K before the melting point. The increase in permittivity is consistent with the concept of gaining the freedom of molecular movement by dipolar molecules. However, this does not explain why the NDE effect is positive. The Debye–Herweg theory predicts that a strong electric field should suppress electric permittivity and, therefore, it is anticipated that the NDE effect in liquids will be negative.²⁵ A positive NDE effect can be observed if a strong electric field affects the dipole moment of molecules or molecular complexes.²⁶ A positive NDE effect was also obtained in the vicinity of the critical point in binary liquid mixtures.^{5–10} In the latter case, the positive NDE increment was explained as a result of deformation of concentration fluctuations caused by the strong electric field. It is not possible to directly apply the same model in the vicinity of a solid–liquid phase transition. To explain the reason for the positive NDE effect in the vicinity of the melting point, we consider the influence of a strong electric field on melting. The free energy of materials containing polar or polarizable ingredients (polar molecules, polar or polarizable domains, fluctuation) decreases in the presence of the electric field. The liquid phase formed by dipole particles typically has higher permittivity than the solid phase. This is due to the increased freedom of rotation after transition to the liquid phase. The free energy of dielectrics decreases according to the electric permittivity and the electric field square. It is possible to presume that in the vicinity of the melting point when a solid is almost “ready” to transform into a liquid, a strong electric field enhances premelting. This can happen because premelting “produces” a local (volume or surface) increase in permittivity; therefore, it is favorable in a strong electric field and results in a positive NDE effect. A potent increase in the NDE effect in the immediate vicinity of the melting point can be attributed to the Maxwell–Wagner effect.^{27–29} A liquid layer appearing on the surface of solids allows the movement of charges (possibly from auto-ionization, as well as ionic impurities), and results in the formation of macrodipoles, hence a considerable increase in

electric permittivity. This process is time-consuming and therefore an increase in NDE relaxation time in the immediate vicinity of the melting point was observed (Figure 3).

Figure 1 shows that in all studied alcohols, the NDE in the vicinity of the melting point behaves similarly. We were interested in a function that could describe the observed increase in NDE. The changes are somewhat similar to those observed in the vicinity of the critical point.⁶ We have to take into account, however, that melting is a discontinuous phase transition and the direct application of theories and methods used to describe critical phenomena is not substantiated. When searching for the function describing changes of $\epsilon'_{3,0}$, we have noted that the temperature range of those “anomalies” is different for different alcohols. This means that the function describing the temperature dependence of NDE should include both the range and the amplitude of those changes, likely varying for every compound. Although melting is a discontinuous phase transition as we previously noted, we propose considering the description of the pretransitional anomaly using the same functions as those used to describe the critical anomalies. The power function, the argument of which is the distance from the characteristic temperature, in our case melting point, gives the opportunity to describe an anomaly, even when the measured value implies a tendency to be discontinuous at the characteristic temperature. The technique based on the power function, amplitudes, and critical exponents has already been used to describe pseudo-critical anomalies in NDE research.⁵ The performed fittings have demonstrated that the description of the temperature dependence of NDE in the vicinity of the melting point could be approximated using the following function

$$\epsilon'_{3,0} = \epsilon'_{3,bg} + b(T_m - T)^\vartheta \quad (4)$$

where $\epsilon'_{3,bg}$ is the background, T_m is the melting temperature, and b , ϑ are parameters. Table 1 shows the results of fittings, and Figure 5 presents the experimental results for all alcohols in a normalized scale.

Table 1. Parameters of Equation 4 Fitted for NDE Data of the Investigated Alcohols

	nonanol	decanol	undecanol	dodecanol
$\epsilon'_{3,bg} \cdot 10^{17}$ [m ² V ⁻²]	-0.9 ± 1	31.3 ± 5	1 ± 1	0 ± 1
$b \cdot 10^{17}$ [m ² V ⁻² K ^{-ϑ}]	23.9 ± 1	17.9 ± 1	9.9 ± 0.5	3.7 ± 0.1
T_m [°C]	-4.8 ± 0.2	-5 ± 0.2	16.6 ± 0.2	24.5 ± 0.2
ϑ	-1 ± 0.1	-1 ± 0.1	-1 ± 0.1	-1 ± 0.1

From the fitting, it is evident that all of the experimental points follow the same curve. The value of the “ b ” parameter, describing the temperature range and the amplitude for the anomaly, is decreasing from nonanol to dodecanol. The background for nonanol, undecanol, and dodecanol is negligible but has a large value for decanol. A large background term in the case of decanol and a large value of the b parameter in the case of nonanol and decanol are explained by the emergence of the rotator state caused by premelting. In the case of other alcohols, no signs of the rotator state were detected.

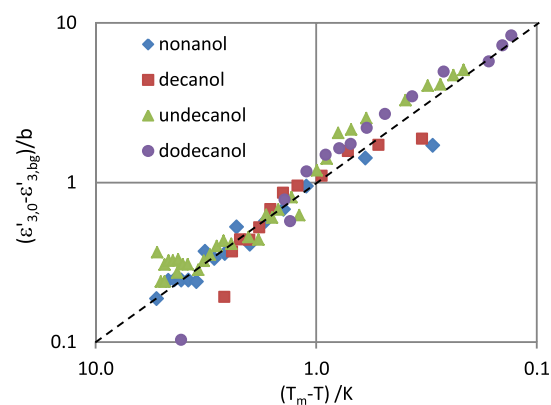


Figure 5. Pretransition increase of the NDE effect on a normalized scale for (◇) nonanol, (□) decanol, (Δ) undecanol, and (○) dodecanol. The dotted line presents the equations with $\vartheta = -1$.

CONCLUSIONS

The nonlinear dielectric effect (NDE) measurements in nonanol, undecanol, and dodecanol have confirmed the uniform nature of a large increase in NDE in close vicinity of the melting point observed previously in decanol.¹ We have linked the increase of the NDE effect and the electric permittivity before melting to the premelting phenomena. The positive NDE effect was explained as an enhancement of the volume and/or surface premelting in a strong electric field. We found that the NDE anomaly in the vicinity of the melting temperature could be described by the universal function proportional to the inverted temperature distance from the melting point.

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Notes

The authors declare no competing financial interest.

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