

Preliminary Studies on the Dielectric Permittivity in the Isotropic and Mesophase of Cholesteryl Oleyl Carbonate

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Z. Naturforsch. **57 a**, 126–128 (2002); received December 11, 2001

The phase detection in cholesteryl oleyl carbonate was studied over a broad temperature range by dielectric spectroscopy. Tests were conducted in the static and the low frequency ionic regions. They point to the possibility of relatively simple detection of phase transition. Some manifestations of pretransitional behaviours were also found. – Pacs: 64.70Md, 77.22Ch, 64.30+t

Key words: Static Dielectric Permittivity; Dielectric Spectroscopy; Liquid Crystal Blue Phase; Ionic Impurities; Critical Fluctuations.

1. Introduction

The blue phase of liquid crystalline materials displays ordering typical for solids to a much larger extent than the majority of other liquid crystal phases. In blue phases, mass centres of molecules do not exhibit positional ordering, and the preferred direction of orientation adopts a helical structure which is quite different from the structure present in the chiral nematic phases. Furthermore, a collection of defect lines (disclinations) forms a dense network throughout the phase. Such disclinations can be observed as three different structures or phases [1 - 3]. In two of the blue phases (BP I and BP II), they form a simple cubic or body centred network, while the third blue phase (BP III) gives an amorphous structure. Hence, some authors suggest that BP III is a second isotropic phase [4, 5]. Moreover they suggest an isotropic - to - BP III phase transition, analogous to the liquid - gas transition [4].

One of the classical BP materials is cholesteryl oleyl carbonate (COC), for which the blue phases are placed between the isotropic (I) and the chiral nematic phase (N*). Studies on COC and blue phases have been performed with fluctuation sensitive susceptibility-related methods like Kerr KE effect, light - scattering I, nonlinear dielectric effect NDE, and optical activity [6 - 14]. From these measurements it can be seen that the temperature dependence on approaching the I - BP transition resembles the behaviour of the

isotropic phase of nematogens in the vicinity of the I-N transition [14], i. e. $KE, I, NDE \propto 1/(T - T^*)$. The latter dependence remains valid also for the I-BP transition [13, 14]. It is worth noting that the temperature discontinuity of the transition I-BP is $\Delta T_{I-BP} \cong 0.5$ K, while the discontinuity of I-N is $\Delta T_{I-N} \cong 1 \div 2$ K for all nematogens with permanent dipole moment parallel, *n*-cyanobiphenyl (*n*CB), and perpendicular, *n*-*p*-methoxybenzylidene-*p*'-butylaniline (MBBA), to the principal axis of the molecule [15, 16].

Unlike fluctuation sensitive methods, the static dielectric permittivity registers the averaged polarizability of the sample. In this method the measuring electric field does not induce distortions in the diagram of the mesophases. To the best of the authors knowledge there have been no attempts to portray the temperature evolution of the static dielectric permittivity at lower frequencies in COC. The aim of this paper was to test the application of the static dielectric permittivity for the detection of mesophases in COC. The study also covers the ionic dominant frequency range hardly explored up to now in liquid crystalline materials.

2. Experimental

The sample was prepared by use of the procedures described in [17]. Prior to measurement the sample was carefully degassed. The sample was placed in a measurement capacitor made of Invar: the gap of the

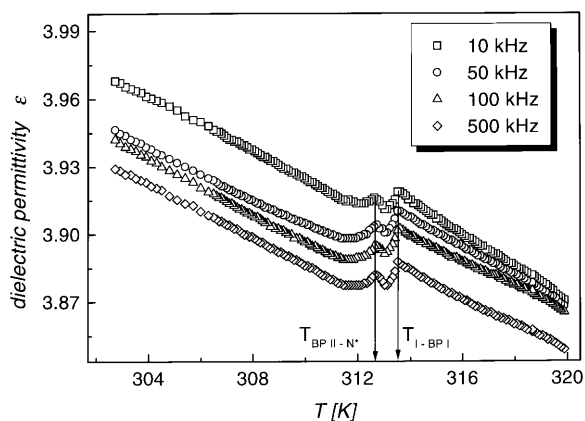


Fig. 1. Results of dielectric permittivity measurements with four frequencies in COC.

capacitor was $d = 0.24$ mm, diameter $2r = 20$ mm. A quartz ring was used as the spacer. Hence, the sample was only in contact with Invar, quartz, and Teflon. The tested compound, cholesteryl oleyl carbonate COC, was in contact only with stainless steel, teflon and quartz. The details of the capacitor assembly are described in [18]. The capacitor was placed into a thermostated jacket fed from Julabo FP45 HD thermostat with external circulation. The temperature was changed in steps of 0.1 K, and at each temperature the control was ± 0.01 by means of a miniature platinum resistor (DIN 43 260) placed in one of the covers of the capacitor, and a Keithley 195A multimeter. Such fine adjustment and control of temperature are significant for the present measurements. The dielectric permittivity and conductivity were measured using the impedance analyser HP 4192 A. The measuring voltage was 1 V. Data were analyzed by means of Origin 6.1 software (Microcal Inc.). All errors are given as three standard deviation errors.

3. Results and Discussion

Figure 1 shows the temperature dependence of the real part of the complex dielectric permittivity $\varepsilon(T)$ for three chosen frequencies. On cooling, a linear dependence of $\varepsilon(T)$ can be observed up to the I-BP transition, without a pretransitional anomaly. The dielectric experiments register the total polarizability contribution from all molecular structures in the sample. In the isotropic phase it is the sum of contributions from the liquid-like “background” and fluctuations with premesomorphic ordering. In nCB the perma-

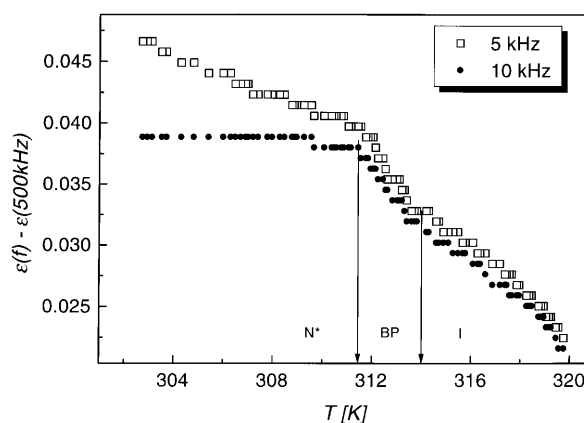


Fig. 2. Behaviour of low frequency ionic contribution: $\Delta\varepsilon = \varepsilon - \varepsilon(500 \text{ kHz})$. The constancy of $\Delta\varepsilon$ in the N^* phase for $f = 10 \text{ kHz}$ suggests that this phase it is still in the static frequency region.

nent dipole moment is positioned along the main axis. This results in the cancellation of permanent dipole moments positioned in the antiparallel way. Hence, dielectric permittivities of fluctuations and their surrounding differ significantly. This is the molecular origin of the pretransitional behaviour of $\varepsilon(T)$ in nCB , where a contrast factor between the “background” and the fluctuations exists. This mechanism is absent for instance in MBBA, where the permanent dipole moments are almost perpendicular to the main axis of the molecule. In this case there is no manifestation of pretransitional fluctuations [16], and $\varepsilon(T)$ is a linear function of temperature up to the clearing point. The same temperature behaviour occurs in the isotropic phase of COC.

A clearly visible change of the temperature evolution of $\varepsilon(T)$ occurs at $T_I = 313.52$ and $T_{II} = 313.12$, which may point to BP II and BP I phase transitions, respectively. Our set-up allows us to change the temperature by 0.1 K, which complies with the width of BP III phase [8].

The phase transition from isotropic to BP II is discontinuous, and for BP II to BP I it is continuous. Noteworthy is the phase transition from chiral nematic N^* to BP I, known as an almost continuous transition [1]. In the chiral nematic phase N^* , on approaching the blue phase the pretransitional anomaly of $\varepsilon(T)$ is clearly visible. This resembles the behaviour found in the isotropic phase of some nematogens and smectogens evoked by pretransitional fluctuations [15, 16]. This similarity may suggest a pretransitional origin of the $\varepsilon(T)$ behaviour in the N^* phase. At low tem-

peratures in the cholesteryl nematic phase the static dielectric permittivity increases linearly with decreasing temperature.

The behaviour of the dielectric permittivity of liquid crystalline materials in the ionic dominated, low-frequency region is a puzzling problem. The decrease of the measurement-frequency boosts the value of $\varepsilon(T)$. The effect of the possible influence of ionic impurities on the low frequency data in the isotropic phase of some liquid crystalline materials was previously presented in [16]. In this paper the same procedure for the isotropic and mesophase is applied. The temperature dependence of $\Delta\varepsilon(T) = \varepsilon(T) - \varepsilon(500 \text{ KHz})$ is presented in Figure 2. Data for $f = 500 \text{ kHz}$ are taken as a ‘non-ionic’ reference background [16]. As in [16], $\Delta\varepsilon(T)$ is a linear functions. It was suggested in [16] that in the fluctuation-dominated region $\Delta\varepsilon(T)$ is a linear function of temperature. This is caused by the fact that residual ionic impurities are caught within fluctuations. Such behaviour is visible in Fig. 2 both in the isotropic phase and in the mesophase. The value of $\Delta\varepsilon(T)$ increases linearly in the isotropic liquid and in the mesophases, with slopes different for each phase. It is also noteworthy

that the temperature range of the BP region of $\Delta\varepsilon(T)$ is slightly wider than the range for the static dielectric permittivity dependence. One may put forward the hypothesis that on approaching the phase transition, ionic impurities are caught in the quasi-critical, pre-BP fluctuations and polarise them. This phenomenon takes place both in the isotropic and the chiral nematic phases.

The experimental detection of the transitions between mesophases in liquid crystalline materials exhibiting blue phases poses a serious challenge [8, 9]. Concluding, the results presented show that relatively simple static dielectric measurements may be an effective research tool for phase detection. When the low frequency region is included, additional information concerning regions dominated by blue phase fluctuations is available.

Acknowledgements

The authors wish to thank the Polish State Committee for Science Research (KBN) for financial support: grant 5PO3B 022 20. We are also very grateful to Prof. E. S. R. Gopal for discussions and help in the preparation of the paper.

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