

RELAXATION PHENOMENA IN THE NEMATIC PHASE OF LIQUID CRYSTAL NEAR PHASE TRANSITION

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Absorption of ultrasonic longitudinal waves in the nematic liquid crystal 1-(trans-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT) was measured in the temperature (24-56°C) and frequency (3.2-100 MHz) ranges. In the region of the phase transition the anomalous absorption has been observed. This absorption rapidly increases when the frequency of the ultrasonic wave decreases. The experimental results for the nematic phase were analysed and two relaxation processes have been found. Relaxation parameters for both processes were calculated. The process with the longer relaxation time is connected with the order parameter changes. The isomeric changes in the hexyl chain of the 6CHBT molecule is the origin of the process characterized by the shorter relaxation time.

Keywords: nematic-isotropic transition, ultrasonic absorption, relaxation

1. INTRODUCTION

Many anomalies of physicochemical parameters have been observed in the region of the phase transition of a liquid crystal [1]. One of them is an ultrasonic absorption. Ultrasonic spectroscopy, i.e. measurements of the ultrasonic absorption as a function of the ultrasonic wave frequency, is applied as a tool for investigation of non-equilibrium processes in liquid crystals. Main attention is directed to the region of the phase transition. However, it is still hard to obtain unequivocal quantitative and even qualitative conclusions [2].

This work presents results of measurements of the absorption of longitudinal ultrasonic waves in the nematic liquid crystal 1-(trans-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT) in the wide temperature and frequency ranges. From an analysis of these results for the nematic phase, the existence of two relaxation processes has been established and the

origins of these processes have been found. The analysis of the experimental results for the isotropic phase will be presented in the next work.

2. RESULTS OF MEASUREMENTS AND THEIR ANALYSIS

The ultrasonic absorption was determined by the pulse method, i.e. by measuring the amplitudes of the received pulse, which passed through the 6CHBT layer, for two different distances of ultrasonic probes. The measurements were done for frequency from 3.2 to 100 MHz at temperature 24÷56°C. The Matec (USA) and constructed in IFTR PAS set-ups were used. The temperature of the liquid crystal sample was kept by a thermostated bath with accuracy $\pm 0,01^\circ\text{C}$. The absorption coefficient α/f^2 has been measured with accuracy better than $2 \cdot 10^{-13} \text{ Np s}^2 \text{ m}^{-1}$

The results of the ultrasonic absorption measurements at different temperature and frequencies are presented in Fig.1.

In the vicinity of the nematic-isotropic (N-I) transition, values of the absorption coefficient α/f^2 grow very fast and achieve their maximum at the transition temperature t_c . These values and maximum of α/f^2 decrease when the frequency of the ultrasonic wave increases. For 100 MHz the absorption exhibit no singularities in the vicinity of t_c . The dependence of the absorption coefficient on temperature is not symmetrical – the increase of this coefficient is different for the nematic and isotropic phases.

The representative plot of the dependencies of the absorption coefficient on the frequency in the nematic phase is shown in Fig.2. A course of the dependencies is characteristic for liquids, where the relaxation phenomenon is induced by the ultrasonic wave propagation. The obtained results of the measurements can be well described with the help of the equation with two relaxation times for liquids with the velocity dispersion:

$$\frac{\alpha}{f^2} = \frac{2\pi^2 c}{c_0^2} \left[\frac{b_1 \tau_1}{1 + (\omega \tau_1)^2} + \frac{b_2 \tau_2}{1 + (\omega \tau_2)^2} \right] + B \quad (1)$$

where c is the speed of sound for the measurement frequency, c_0 - the speed of sound for $f \rightarrow 0$. b and τ denote the relaxation strength and time, respectively. B is the contribution to the ultrasonic absorption from any other processes that may occur at higher frequencies beyond the frequency range measured. ω is the angular frequency ($\omega = 2\pi f$). Subscripts “1” and “2” denote the parameters for the first and second processes.

For the liquid crystal near the phase transition the sound speed dispersion takes place, that can be easily noticed in Fig.3.

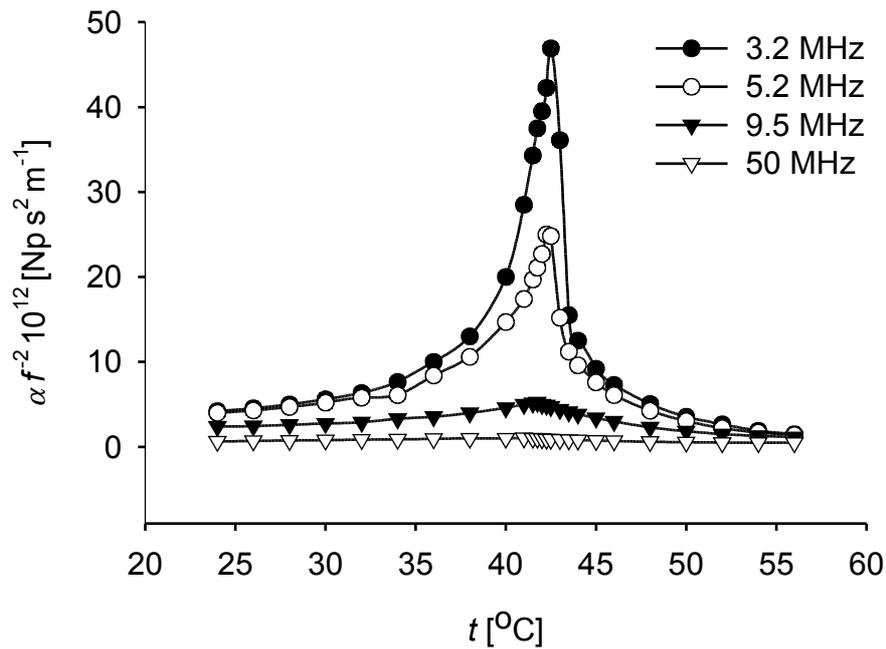


Fig.1. Plot of the absorption coefficient α/f^2 vs. temperature t for some frequencies.

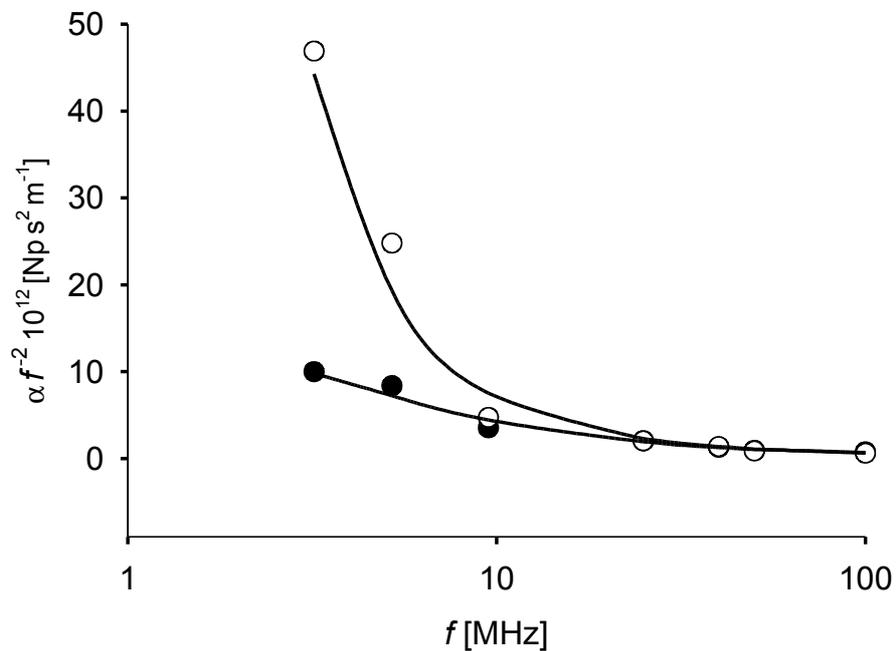


Fig.2. Plot of the absorption coefficient α/f^2 vs. frequency f for two values of temperature.

The parameters of Eq.1 were calculated by means of a non-linear regression and their values are placed in Tab.1.

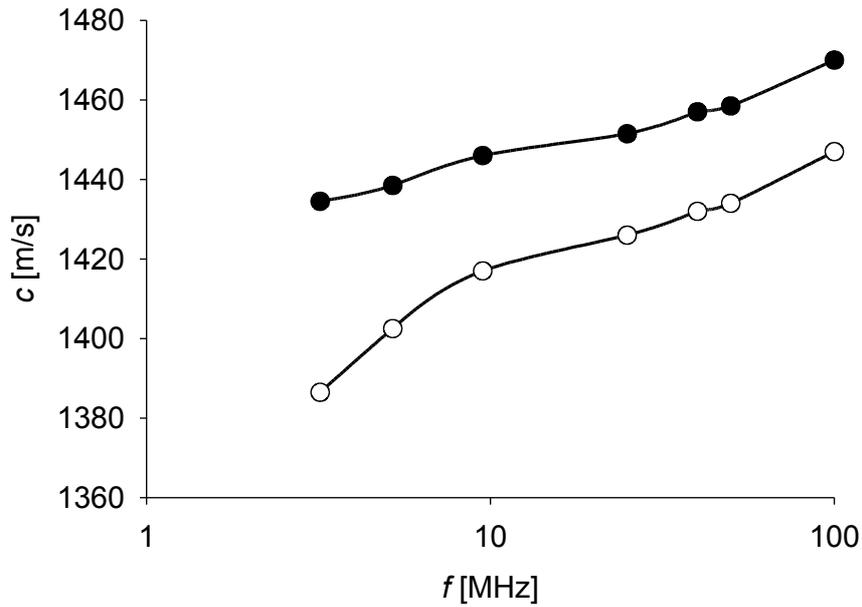


Fig.3. Plot of the speed of sound c vs. frequency f for two values of temperature.

Tab. 1. Values of the relaxation parameters for 6CHBT.

t [°C]	c_0 [m/s]	$\tau_1 \cdot 10^8$ [s]	$b_1 \cdot 10^2$	$\tau_2 \cdot 10^9$ [s]	$b_2 \cdot 10^2$	$B \cdot 10^{15}$ [s ² m ⁻¹]
36	1431	3.19	2.80	6.83	2.36	570
38	1417	4.45	3.79	6.60	2.32	535
40	1399	5.92	6.40	6.39	2.30	501
41	1382	7.80	7.70	6.29	2.29	484
42	1361	15.0	11.9	6.19	2.27	465
42.5	1373	16.2	20.7	6.14	2.27	456

For the sake of a strong dependence of the relaxation parameters (relaxation time τ_1 and relaxation strength b_1) on temperature, the process with the longer relaxation time is connected with the N-I phase transition. The dependencies of the relaxation parameters of this process on difference between temperature of the N-I transition for 6CHBT ($t_c=42.8^\circ\text{C}$) and temperature of the sample t are presented in Figs.4 and 5. It is considered that the anomalous absorption near the phase transition of the liquid crystal is caused by two mechanisms: fluctuations and relaxation of the order parameters. The first one results from the fluctuations of the order parameter produced by the temperature changes of the liquid crystal when the ultrasonic wave propagates. These fluctuations near the transition temperature have strong spatial correlation and the equilibrium correlation function cannot follow the temperature variations induced by the ultrasonic wave.

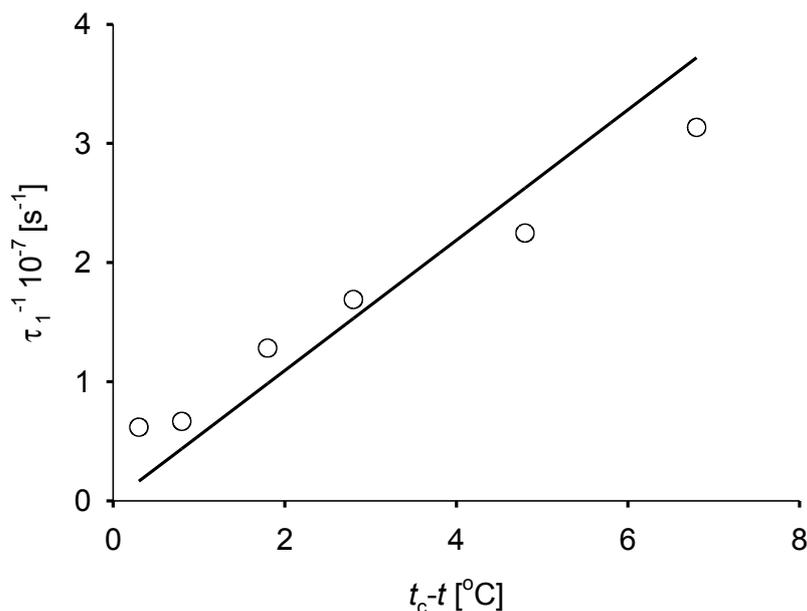


Fig.4. Plot of reciprocity of the relaxation time τ_1 vs. temperature difference $t_c - t$.

This absorption occurs both above and below the transition. According to Imura and Okano theory for the isotropic phase [3], subsequently extended to the nematic phase by Nagai, Martinoty and Candau [4], the excess absorption per wavelength and therefore the relaxation strength b_1 is proportional to $(t_c - t)^{-1/2}$, and a reciprocity of the relaxation time τ_1 – to $(t_c - t)$. However, the fluctuations of the order parameter in the nematic phase are relatively small, in contrast to the isotropic phase [5].

The second mechanism is explained by Landau and Khalatnikov theory [6], first time applied to a superfluid helium. It is assumed that the equilibrium value of the order parameter is disturbed by the ultrasonic wave and then relaxes in a finite time to a local equilibrium value determined by the temperature and pressure. Near the transition the order parameter cannot follow the pressure variations induced by the ultrasonic wave and this leads to anomalous absorption. In contrast to the fluctuation of the order parameter, this effect occurs only in the ordered phase, where the value of the order parameter is not zero. This theory predicts the same dependencies of the relaxation time and strength on $(t - t_c)$ as previous one. There were attempts to separate the contributions from these two mechanism, e.g. [7], but they are very questionable. The straight lines in Figs.4 and 5 represent the dependencies predicted by the theories mentioned above. One can notice the good agreement between the experimental data and the theories.

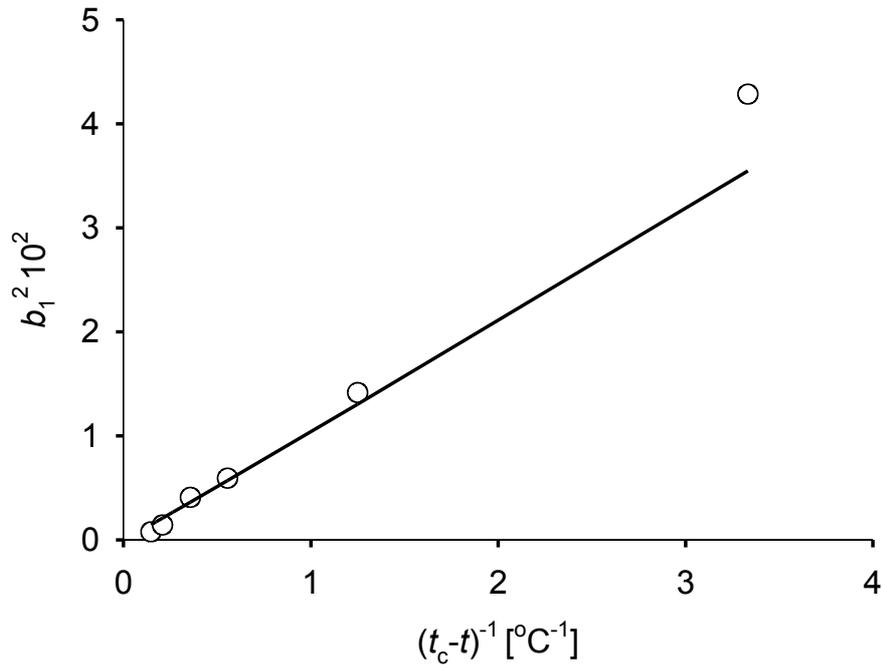


Fig.4. Plot of square of the relaxation strength b_1 vs reciprocity of temperature difference $t_c - t$.

The dependence of the relaxation parameters of the second relaxation process is small and the relaxation time τ_2 is shorter than τ_1 by one order. These facts suggest that this relaxation process is rather not connected with the phase transition. Assuming this process is caused by a first-order reaction and applying the procedure presented in [8] the value of the reaction enthalpy, 3.9 kJ/mole, and the value of the opposite reaction enthalpy, 10.1 kJ/mole, have been calculated. These values are close to those for N-(4-methoxybenzylidene)-4-butylaniline (MBBA), where the isomeric transformation of the butyl chain was found [9]. Thus, one can conclude that the second relaxation process in 6CHBT is originated by isomerism of the hexyl chain in the molecule of this liquid crystal.

3. SUMMARY

As a result of the measurements of the ultrasonic absorption in 6CHBT and analysis of the experimental data for nematic phase, two relaxation processes have been established. The process with the longer relaxation time is connected with the order parameter changes. The process characterised by the shorter relaxation time is caused by the isomeric changes in the hexyl chain of the 6CHBT molecule.

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