ULTRASONIC MEASUREMENTS IN THE 1-(*TRANS*-4-HEXYLCYCLOHEXYL)-4-ISOTHIOCYANATOBENZENE NEAR THE NEMATIC-ISOTROPIC TRANSITION

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The absorption and velocity of ultrasonic longitudinal waves in the nematic liquid crystal 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT) have been measured as a function of temperature between 24°C and 55°C at 5.2 MHz. The temperature dependence of ultrasonic absorption has a sharp maximum, whereas that dependence of velocity shows a local minimum in the region of the nematic-isotropic (N-I) phase transition. Additional temperature measurements of density have been done to calculate the thermal coefficient of expansion and the temperature coefficient of adiabatic compressibility. Both these parameters exhibit critical behaviour at the transition which has been analysed. The values of the exponent determining the growth of the order fluctuations have been calculated and compared with references.

Key words: ultrasonic measurements, ultrasonic velocity and absorption, nematic-isotropic transition, adiabatic compressibility, thermal expansion.

1. Introduction

In the substances called liquid crystals, the transition from crystal solid state into isotropic liquid during temperature increase goes through some intermediate states – mesophases – that characterise different degrees of molecular order. For the temperature far from the temperature of phase transition, the phases are stable. However, when the temperature becomes close to the temperature of phase transition many anomalies of physicochemical parameters occur, among them the velocity and absorption of ultrasonic waves as well as coefficients of the thermal expansion and adiabatic compressibility.

This work presents results of temperature measurements of velocity and absorption of longitudinal ultrasonic waves for nematic liquid crystal 1-(*trans*-4-hexylcyclohexyl)-

4-isothiocyanatobenzene (6CHBT). The molecule of this liquid crystal contains the aromatic (benzene) and cycloaliphatic (cyclohexyl) rings instead of two aromatic rings, as it takes place in the molecules of the most nematic liquid crystals. 6CHBT has a good chemical and physical stability, that will allow to obtain reliable ultrasonic data. According to known references, there are no ultrasonic measurements of 6CHBT up to this moment. Additional measurements of the density are related. The temperature dependences of the coefficient of thermal expansion and the temperature coefficient of adiabatic compressibility for this substance are also presented.

2. Theoretical part

Anomalies of physicochemical properties of liquid crystals near the nematic – isotropic transition are explained by means of density fluctuations governed by the order fluctuations [1–5]. These density fluctuations change with temperature as [6]:

$$(\Delta\rho)^2 \sim (T - T^*)^{-\gamma}, \tag{1}$$

where T^* is the temperature of phase transition, γ is the exponent determining the growth of the order fluctuations. The density fluctuations cause an increase of the coefficient of thermal expansion, α_T, according to Eq. (2):

$$\alpha_T = \alpha_0 + A(T - T^*)^{-\gamma} \tag{2}$$

and the temperature coefficient of adiabatic compression (3):

$$\beta_T = \beta_0 + B(T - T^*)^{-(\gamma+1)}, \tag{3}$$

where α_0 and β_0 denote the coefficient of thermal expansion and the temperature coefficient of adiabatic compressibility at temperature far from the temperature of phase transition, respectively. A and B are constants.

The coefficient of thermal expansion is defined as:

$$\alpha_T = \frac{1}{v_0}\frac{dv}{dT}, \tag{4}$$

where v is the specific volume (equal to the reciprocal of density ρ), and v_0 is the specific volume taken at the middle point of the specific volume curve when it rises near the phase transition.

The temperature coefficient of adiabatic compressibility is given by formula (5):

$$\beta_T = \frac{1}{\beta_{ad}^0}\frac{d\beta_{ad}}{dT}, \tag{5}$$

where β_{ad} denotes the adiabatic compressibility near the transition and β_{ad}^0 is the maximum value of the adiabatic compressibility.

3. Experimental part

The velocity was measured using the ultrasonic setup (Matec, USA) configured to the echo-overlap method [7]. The ultrasonic absorption was determined by measuring the amplitudes of the received pulse for two different distances of ultrasonic probes, i.e. by the pulse method. These measurements were done at frequency 5.2 MHz. The densitometer MG-2 (Unilab, Poland), which operates on the principle of frequency measurement of a U-shaped capillary pipe containing the tested liquid, was used for density measurements of the liquid crystal. Temperature of the 6CHBT sample was kept by thermostated bath with the accuracy $\pm 0.01^\circ$C. The velocity, v, absorption coefficient, α/f^2, and density, ρ, have been measured with accuracy of 0.5 m/s, $2 \cdot 10^{-13}$ Np·s^2/m and $5 \cdot 10^{-5}$ g/cm^3, respectively.

The measurement results of velocity, absorption and density are shown in Figs. 1–3. The dependences of the ultrasonic velocity (Fig. 1) and the coefficient of absorption, α/f^2, (Fig. 2) on temperature have local minimum and maximum in the vicinity of phase transition temperature, respectively. In the region of phase transition the curve of density has a characteristic inflection (Fig. 3).
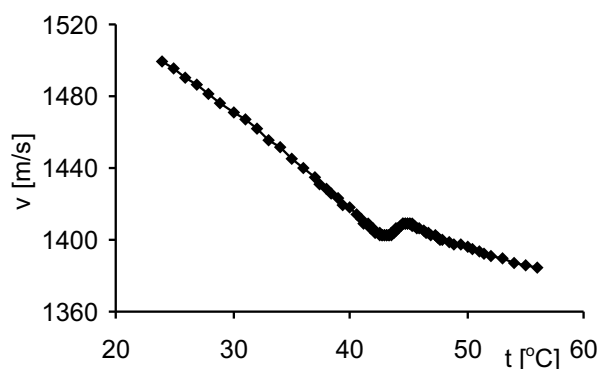

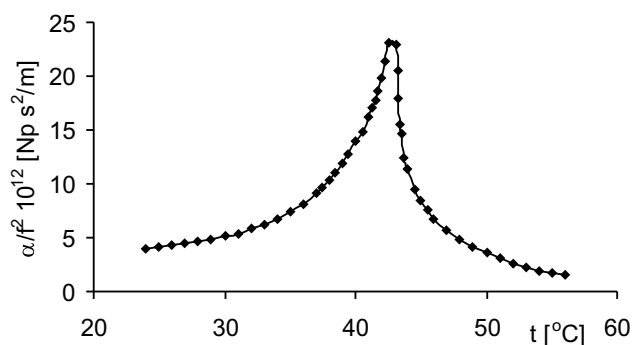Fig. 1. Plot of the ultrasonic velocity vs. temperature for 6CHBT.

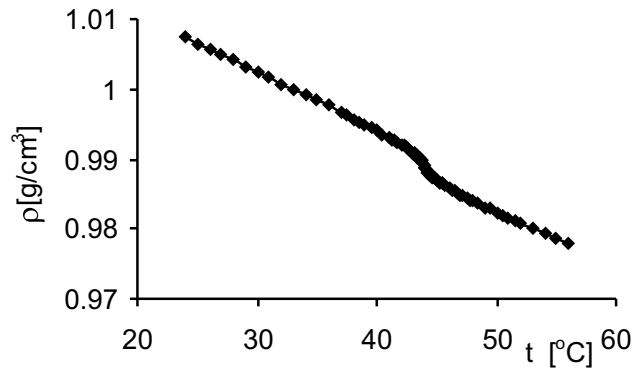Fig. 2. Plot of the ultrasonic absorption vs. temperature for 6CHBT.

Fig. 3. Plot of the density vs. temperature for 6CHBT.

The adiabatic compression has been calculated according to Eq. (6):

$$\beta_{\mathrm{ad}} = \frac{1}{\rho v^2} \tag{6}$$

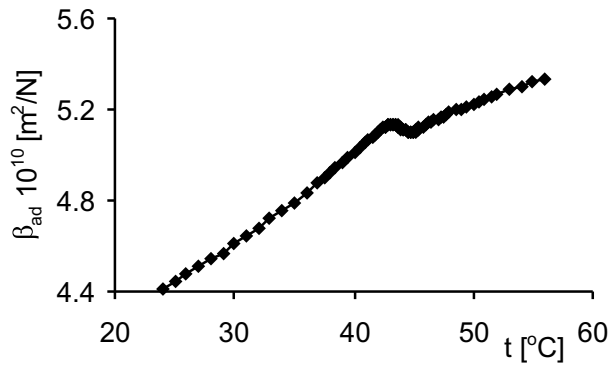and its dependence on temperature is presented in Fig. 4.

Fig. 4. Plot of the adiabatic compressibility vs. temperature for 6CHBT.

Applying Eqs. (4) and (5), the values of the coefficient of thermal expansion, α_T, and the temperature coefficient of adiabatic compressibility, β_T have been calculated, respectively. The dependences of these coefficients on temperature are shown in Figs. 5 and 6. Solid lines denote the values calculated from Eqs. (2) and (3) with the values of parameters adjusted by the non-linear regression method. The values of these parameters are placed in Tables 1 and 2.

The calculated values of parameters α_0 and β_0 are the values of the coefficient of thermal expansion and the temperature coefficient of adiabatic compression for nematic and isotropic mesophases at a temperature far from the temperature of phase transition [6].

Table 1. Values of the parameters of Eq. (2).

mesophase	α_0 [10^{-4} K^{-1}]	A [10^{-4}]	γ
nematic	7.9 ± 0.7	4.2 ± 0.4	0.90 ± 0.07
isotropic	7.8 ± 0.8	3.8 ± 0.3	0.89 ± 0.07

Table 2. Values of the parameters of Eq. (3).

mesophase	β_0 [10^{-3} K^{-1}]	B [10^{-4}]	γ
nematic	-8.0 ± 1.0	4.2 ± 0.5	0.91 ± 0.06
isotropic	-5.5 ± 0.8	15.7 ± 1.9	0.82 ± 0.07
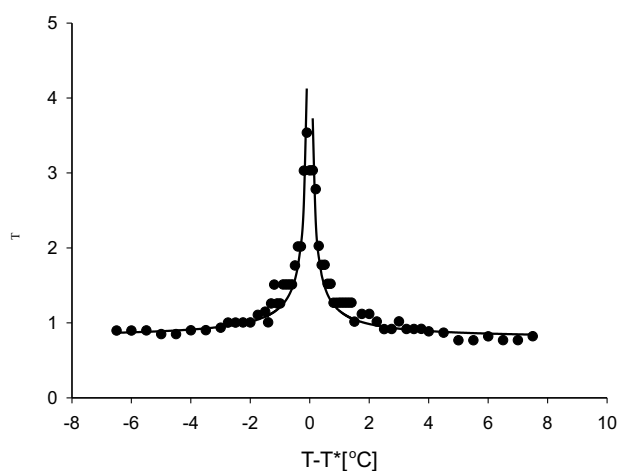
Fig. 5. Plot of the coefficient of thermal expansion, α_T, vs. temperature for 6CHBT.
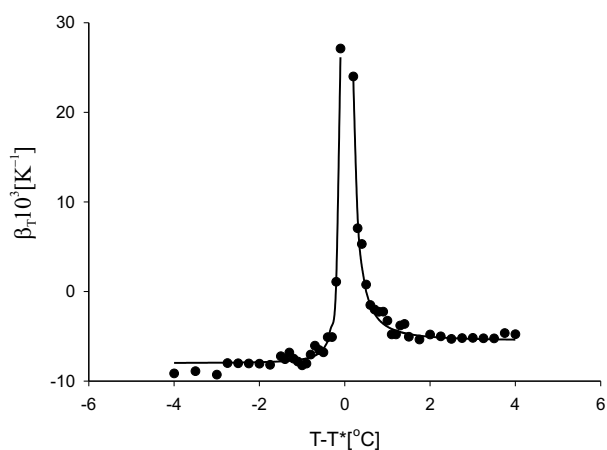
Fig. 6. Plot of the temperature coefficient of adiabatic compression, β_T, vs. temperature for 6CHBT.

The values of α_0 for both phases are close. The value of β_0 for isotropic phase is higher than that for the nematic one. The coefficients A and B behave similarly as α_0 and β_0, but the value of B for isotropic phase of 6CHBT is almost four times greater than that for the nematic one. Thus the influence of order fluctuations on the coefficient of thermal expansion in both phases is nearly identical, whereas that influence on the temperature coefficient of adiabatic compression is more distinct for isotropic than nematic phases.

The values of parameter γ determined from the dependences of the coefficient of thermal expansion, α_T, and temperature coefficient of adiabatic compression, β_T, on temperature, are relatively close to unity. This is in accordance with references, e.g. [1, 8].

4. Conclusions

As a result of ultrasonic measurements in liquid crystal 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT), the dependences of velocity and absorption of ultrasonic waves on temperature have been obtained. In the vicinity of the temperature of nematic – isotropic liquid transition the absorption reaches a maximum, whereas the velocity – a local minimum.

The calculated values of the coefficient of thermal expansion, α_T, and the temperature coefficient of adiabatic compression, β_T, follow the power relations (2) and (3) suggested by the fluctuation theory, i.e. these values rapidly grow near the temperature of phase transition. The values of γ parameter determined by the non-linear regression method are close to unity, which is consistent with the theoretical predictions and experimental investigations.

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