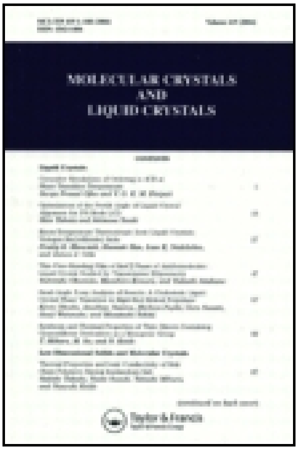

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TEMPERATURE DEPENDENCE OF ACOUSTICAL RELAXATION TIMES INVOLVING THE VICINITY OF N-I PHASE TRANSITION POINT IN 5CB LIQUID CRYSTAL

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Temperature Dependence of Acoustical Relaxation Times Involving the Vicinity of N-I Phase Transition Point in 5CB Liquid Crystal

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Acoustical properties of nematic liquid crystal 4-pentyl 4′-cyanobiphenyl (5CB) were investigated in temperature interval from 298 to 333 K involving the vicinity of nematic phase – isotropic phase transition temperature. Measurements of the velocity of sound propagation in liquid 5CB have been staged by pulse – phase method at frequencies 2.5; 5.0; 10; 15; 35; 50, and 500 MHz. Amplitude coefficient of sound attenuation α has been determined by pulse method in the frequency interval from 2.5 to 1800 MHz. Acoustic spectra of 5CB consist of two relaxation areas. The low-frequency region of acoustical relaxation in the vicinity of N-I phase transition is connected with order parameter fluctuations. Relaxation time of low-frequency region tends to infinity according to low $\tau \sim |t|^{-1/2}$. The high-frequency region cause by processes of hydrogen bonds rupture and formation between molecules of 5CB. Main contribution to sound attenuation in 5CB being made by volume effects. It was shown that, within limits of experimental error, relaxation times of shear and bulk viscosity are indistinguishable.

Keywords: 5CB; acoustical spectroscopy; sound attenuation; bulk viscosity

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1. INTRODUCTION

Different methods for investigation of molecular dynamics and molecular interactions in liquid crystals (LC), such as NMR, neutron scattering, dielectric relaxation, light scattering, etc., have made it possible to establish the existence of different types of non-oriented movements both of separate molecules and whole complexes with similar molecular orientation. Obtained by these methods the relaxation times differs by several decimal orders. So, using method of quasi-elastic neutron scattering, relaxation times of the order $\tau \sim 10^{-12}$ s have been obtained [1,2]. Similar values of relaxation times have been obtained also by means of IR-spectroscopy. Relaxation times, determined by NMR and dielectric spectroscopy, correspond to relaxation processes having $\tau \sim 10^{-8} \div 10^{-12}$ s. Experiments with light scattering on fluctuations of molecular orientation in liquid crystal isotropic phase in the vicinity of clearing point have given relaxation times of the order $\tau \sim 10^{-7}$ s, which correspond to orientation relaxation of correlated regions having magnitude of up to 20 nm [3].

In order to establish the mechanisms of non-equilibrium processes, taking place in liquid crystals during thermal motion, method of acoustic spectroscopy has been used widely [1-3]. The main attention has been turned upon studies of LC behavior in the vicinity of phase transition temperature. These studies have shown that at low frequencies ($f < 1$ MHz) speed of sound propagation in nematic phase is independent of the direction of propagation and is determined by coefficient of volume compressibility. As to coefficient of sound attenuation α, its temperature and frequency dependencies in most cases is well defined using one relaxation time τ.

At higher frequencies in the region of 2 - 60 MHz, in the region of N - I phase transition temperature the behavior of sound speed and attenuation is changed. Coefficient of attenuation attains maximal, and speed - minimal value, change of these values on withdrawal from the transition temperature being insignificant.

In all cases, branch of the curve on the high-temperature side is more steep, than the low-temperature one. Asymmetry of the curves is probably due to different mechanisms of relaxation. At still higher frequencies ($f > 100$ MHz) no anomalies in temperature dependence of the coefficient of sound attenuation is observed.

Thus, in the frequency region of $f > 100$ MHz sound speed and attenuation exhibit no singularities in the vicinity of T_{tr}.

We would like to note that analysis of works dedicated to studies in mechanisms of non-equilibrium processes in LC, especially in the vicinity of T_{tr}, gives no clarity. It is still hard to obtain strictly valid quantitative and even qualitative conclusions.

As it was noted already, utilization of the acoustic methods in studies of LC in the region of phase transitions is especially productive. The fact is, that many known experimental groups, using calorimetric and optical data, searched for the region of strongly developed fluctuations, i.e. scaling laws for the phase transition of NLC - isotropic fluid [1-9]. However, there were obtained no reliable results, which could be explained within the limits of self-consistent field theory. Besides, there are no grounds to reckon that they will be governed by simple power laws, interrelated with one another by universal correlation, as it is in case of the second-order phase transition.

The question arises if the canonical properties in the vicinity of nematic - isotropic fluid can be described in universal manner, and if so, what is the nature of this universality. Since relaxation time τ is natural scaling factor for canonical coefficients, and its conjugate second variable is frequency ω, then the most informative from this point of view are investigations of acoustic relaxation [3].

In [3], the nature of critical dynamics for N - I transition has been established experimentally. Two compounds - MBBA and BMOAB - have been studied in the frequency range of 0,9 ÷ 26,5 MHz, and temperature interval of 293 ÷ 373 T. In order to calculate the excessive absorption coefficient (α'), the regular part, related to shear viscosity and non-critical portion of bulk viscosity, has been substracted from the experimental data. It was shown that dispersion of speed and excessive sound absorption are homogeneous functions of temperature and frequency. Besides, these functions have turned out to be the same for the two compounds studied, though different for isotropic and nematic phases.

The universal nature of critical dynamics in NLC, as well as the shape of asymptotic of the universal functions obtained, have made it possible for the authors to propose new considerations as to the nature of nematic - isotropic transition. These are as follows. Tensorial nature of the order parameter and nature of N - I transition, which it is related to, constitute main reason of the problems arising when attempting to describe it within the self-consistent field approach, despite the relatively small values of Ginsburg criterion obtained when neglecting the cubic invariant in Landau expansion.

Critical attenuation and dispersion in the nematic phase are determined, as minimum by two mechanisms: relaxation of the order parameter Q_{ij} and relaxation of correlation function of order parameter fluctuations $\left(\left\langle Q_{ij}Q_{ji}\right\rangle\right)$. The existence of the cubic invariant destroys universal correlation between temperature dependencies of physical parameters anomalies. Use of the relaxation times as scaling factor restores this universality. The universal picture restored is characterized with field-mean critical indices.

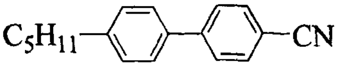
In our opinion, use of relaxation times as scaling factor is artificial, because it is necessary in the beginning to establish nature of the relaxation process observed, to determine correctly temperature dependence of the relaxation time, and to calculate correctly excessive sound attenuation.

Absence of satisfactory theory for propagation of sound in LC is due not only to limited nature of our notions on thermal motion and molecular interactions, but also to lack of reliable experimental results in the wide region of frequencies and thermodynamical parameters.

There are certain works of authors, which have conducted measurements of sound attenuation and speed in the wide region of frequencies and temperatures. Thus, in [10] measurements of sound attenuation and speed in liquid crystal (5CB) were for the first time performed in the frequency range of 2.5 to 1800 MHz, and temperature interval 298 ÷ 333 T. It was established that for the 5CB studied and disperse systems on its basis two regions of relaxation have been observed. However, no analysis of acoustic spectra in the region of phase transition has been attempted. In this paper, we will analyze acoustical spectra of the 5CB.

2. EXPERIMENTAL PROCEDURES

A nematic liquid crystal of 4-pentyl 4'-cyanobiphenyl (5CB) has been used for experiments, whose structural formula is given below:



and transition temperature ($T_{N\text{-}I}$) nematic phase - isotropic phase (clearing point $T_{cl} = T_{N\text{-}I}$) equal to 307,8 K.

Measurements in 5CB have been conducted in temperature interval of 298 - 333 T.

Measurements of the velocity of sound propagation in liquid 5CB have been staged by pulse - phase method at frequencies 2.5; 5.0; 10; 15; 35; 50, and 500 MHz. The accuracy of the experimental velocity measurements is better than ± 0.1%.

Amplitude coefficient of sound attenuation α has been determined by pulse method in the frequency interval from 2.5 to 1800 MHz with 2-5% error.

The corresponding density and viscosity data, necessary for analyzing the ultrasonic relaxation spectra, have been previously reported by us [11].

3. RESULTS AND DISCUSSION

Temperature dependence of the velocity of sound propagation in 5CB at frequencies of 2.5 and 500 MHz is shown in Fig.1.

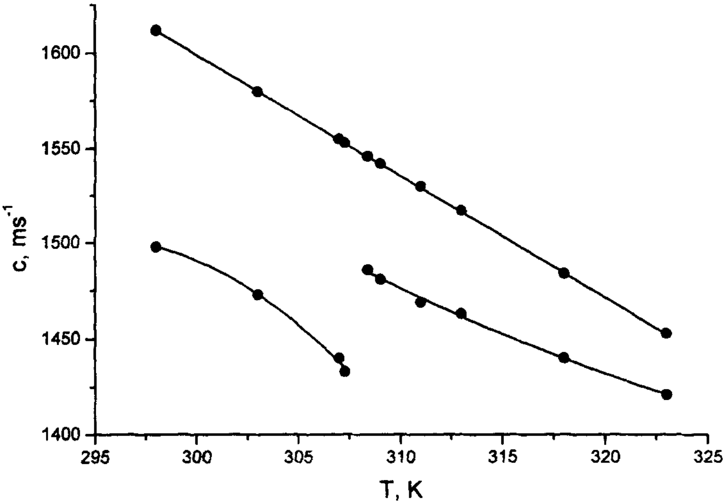


FIGURE 1 Temperature dependence of the speed of sound propagation in 5CB at frequencies of 2.5 and 500 MHz.

As it was stated repeatedly in literature [1-3], sound propagation in LC has peculiarity of the sound velocity decreasing at first linearly with temperature. The linear character of the speed changes keeps true for all frequencies up to temperature (1 ÷ 1,5) T below the clearing point. On approaching to the temperature of clearing the speed of sound decreases, reaching minimum value in the clearing point. In isotropic phase near the point of N - I transition, speed of the sound propagation first increases with temperature, and then, at approximately (2 - 3) T from the clearing point, begins to decrease linearly. Anomalous behavior of the speed of sound in nematic phase can be explained on basis of hypothesis about sound interactions with order parameter fluctuations. This interaction becomes appreciable in the vicinity of N - I transition temperature and causes the speed anomaly. In hypersonic frequency range (above 300 MHz) these fluctuations, obviously, are nonessential, and, correspondingly, temperature dependence of the speed of sound has regular trend.

Both in nematic and isotropic phases frequency dependence of the speed of sound propagation is observed. Frequency dependence of c value follows equation

$$\left(\frac{c_0}{c}\right)^2 = 1 - \frac{b_1\left(ff_{r1}^{-1}\right)^2}{1+\left(ff_{r1}^{-1}\right)^2} - \frac{b_2\left(ff_{r2}^{-1}\right)^2}{1+\left(ff_{r2}^{-1}\right)^2}, \qquad (1)$$

where b_1 and b_2 denote relaxation strength for first and second regions of dispersion; f_{r1} and f_{r2} are relaxation frequencies; c_0 denote value of the speed of sound propagation at frequencies $ff_{r1}^{-1} << 1$; and c represent speed of sound at a frequency f.

Temperature dependence of the speed of sound propagation at frequencies above 50 MHz is of regular character, i.e. there is no temperature anomaly observed. Regular character is observed both for nematic and isotropic phases of LC.

Fig.2 represents temperature dependence of the sound attenuation value αf^{-2} in LC at frequencies of 2.5 MHz; 10 MHz; and 90 MHz. At phase transition temperature $T_{N\text{-}I}$ in the frequency range of 2.5 - 35 MHz attenuation goes through maximum, whose value is a function of the frequency. The temperature dependencies of αf^{-2} values we have obtained coincide qualitatively with those listed in [2]. Both in nematic and isotropic phases far from the point of phase transition sound attenuation changes insignificantly with temperature. But on approaching the $T_{N\text{-}I}$ temperature from the low-frequency side its value increases more steeply than from the high-frequency side.

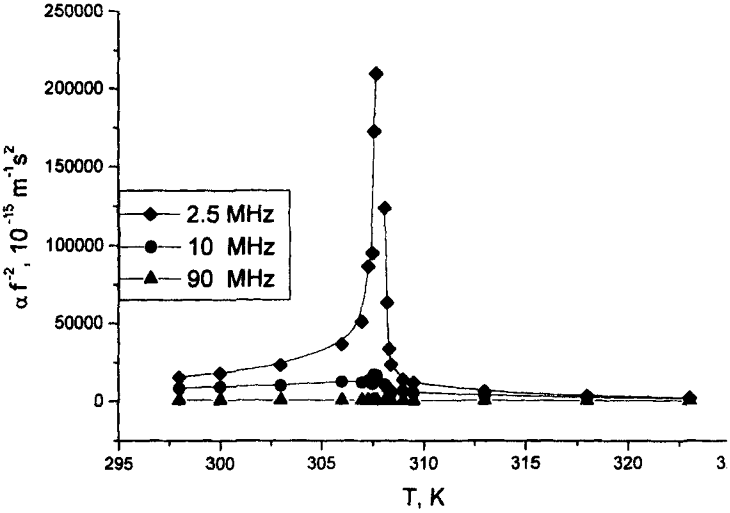


FIGURE 2 Temperature dependence of the sound attenuation in 5CB.

The investigations staged have shown that frequency dependence of the sound attenuation, i.e. acoustic relaxation, is observed in 5CB. Within limits of experimental error, frequency dependence of the sound attenuation αf^{-2} is described by equation with two relaxation times.

Frequency dependence of the sound attenuation αf^{-2} follows equation

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

Interpretation of acoustic spectra has been made as follows. At the beginning, empirical equation has been used to describe αf^{-2} values

$$\alpha f^{-2} = \frac{A_1}{1+(\omega\tau_1)^2} + \frac{A_2}{1+(\omega\tau_2)^2} + B, \tag{3}$$

where A_1, A_2, and B denote frequency-independent constants, and τ is relaxation time.

However, equation (3) makes no account of the sound speed dispersion, leading sometimes to significant errors in calculations of the acoustic relaxation parameters [13]. As it was stated above, dispersion of the speed takes place in the systems studied.

Calculations of relaxation strengths and adjusted relaxation frequencies have been carried out using iteration procedure until such values of all the parameters required will be obtained, that correspond to minimal deviations of calculated αf^{-2} values from the experimental ones in the frequency range studied.

Fig.3 shows logarithmic frequency and temperature dependencies of αf^{-2} for 5CB. Solid curves represent calculated dependencies of αf^{-2}, and geometrical symbols denote experimental values of αf^{-2}. As it is seen in the figure, departure of experimental values from those calculated theoretically doesn't exceed experimental error.

Results of calculations of relaxation parameters values A_i, B, and f_i are listed in Table. Index i = 1 relates to the first low-frequency region of dispersion, and 2 - to the second high-frequency region of dispersion. Also listed are calculation results of values of relaxation strengths b_{ps}, made in accordance with formula

$$b_{ps} = \frac{A_i c_{0i} f_{ri}}{\pi}. \tag{4}$$

Also listed in Table are calculations results of sound attenuation $\alpha_{cl} f^{-2}$, stipulated by shear viscosity, made using data on kinematic viscosity and speed of sound by equation

$$\alpha_{cl} f^{-2} = 26{,}3\frac{\nu_0}{c_o^3}, \tag{5}$$

v_0 denote coefficient of kinematic viscosity, and c_0 - speed of sound at $\omega\tau_1 << 1$.

Calculations have shown that parameters A_1, A_2, f_1, f_2, b_1, and b_2 for the objects studied depend on temperature. Temperature dependencies for low-frequency parameters in nematic and isotropic phases differ. In the nematic phase amplitude A_1 of low-frequency process and relaxation time $\tau_1 = (2\pi f_{r1})^{-1}$ increase with temperature, while for the second relaxation processes A_2 and τ_2 decrease with temperature. In isotropic phase A_1 and τ_1 decrease with temperature.

It follows also from the data presented in Table that, since $A_1 >> A_2$, principal contribution to the dispersion of αf^{-2} values both in nematic and isotropic phase is made by the first, low-frequency, region of acoustic relaxation.

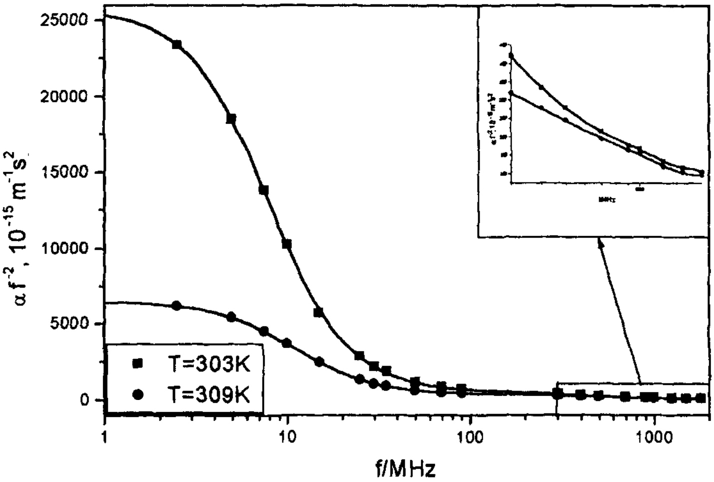


FIGURE 3. Frequency dependencies of the sound attenuation in 5CB for different temperatures.

TABLE Temperature dependensies of relaxation and physics parameters of 5CB.

	298 K	303 K	307 K	309 K	313 K	318 K
$A_1\cdot10^{15}$, $m^{-1}s^2$	16000	25000	65100	14500	6500	3400
$A_2\cdot10^{15}$, $m^{-1}s^2$	550	480	395	350	310	260
$B\cdot10^{15}$, $m^{-1}s^2$	95	80	75	73	70	68
$\alpha_{cl}f^{-2}\cdot10^{15}$, $m^{-1}s^2$	121	107	101	142.2	120	97.7
f_1, MHz	9.7	8.0	4.7	8.6	11.0	14.2
f_2, MHz	400	430	475	520	570	640
c_0, m/s	1496	1467	1412	1478	1462	1440
$c_{\infty 1}$, m/s	1553	1541	1530	1522	1487	1456
c_∞, m/s	1655	1634	1612	1598	1555	1516
$b_1\cdot10^{-2}$	7.4	9.3	13.7	5.9	3.3	2.2
$b_2\cdot10^{-2}$	10.9	10.1	8.4	8.6	8.4	7.4
$\eta_s\cdot10^{-3}$, Pa·s	15.8	13.4	11.3	17.4	14.5	11.7
$\eta_{v1}\cdot10^{-3}$, Pa·s	2875	4250	9766	2411.5	1089	581.5
$\eta_{v2}\cdot10^{-3}$, Pa·s	90	75.6	55	45.6	41.9	36.9
$K_0\cdot10^{-10}$, Dyn/sm^2	2.5	2.45	2.4	2.37	2.25	2.15
$K_\infty\cdot10^{-10}$, Dyn/sm^2	2.84	2.75	2.66	2.62	2.46	2.33
$K_r\cdot10^{-10}$, Dyn/sm^2	34	30	26	25	27	18
$G_\infty\cdot10^{-10}$, Dyn/sm^2	4	3.6	3.4	5.7	5.2	4.7

In accordance with universally adopted classification, temperature dependencies of A_1 and τ_1 in nematic phase allow us to attribute the first relaxation region to relaxation of the order parameter fluctuations [1-3] or to collective processes [12].

It has to be noted, that amplitude of the second region of acoustical relaxation $A_2 + B$ exceeds the attenuation $\alpha_{cl} f^{-2}$, attributed to shear viscosity. The ratio of $B/\alpha_{cl} f^{-2}$ is less than unity and but weakly depends on temperature. Inequality $B < \alpha_{cl} f^{-2}$ testifies to the relaxation of bulk viscosity η_{v2} being accompanied by relaxation of shear viscosity. Since frequency dependence of αf^{-2} is described by equation with one relaxation time

$$\alpha f^{-2} = \frac{A_2}{1+\omega^2\tau^2} + B, \qquad (6)$$

then relaxation times for bulk η_{v2} and shear η_s viscosity could not be distinguished within the limits of experimental error.

The inequality $B < \alpha_{cl} f^{-2}$ and weak temperature dependence of the $B/\alpha_{cl} f^{-2}$ ratio are characteristic for structural relaxation [12-14].

As it was noted above, phase transitions in liquid crystals are characterized with extraordinary diversity. However, closeness of transition from nematic phase to isotropic to the second order phase transition constitutes a characteristic feature of the most LC known. Nature of critical phenomena in LC is determined by variety of the symmetry types for different phases and reciprocal influence of these phases on one another.

Absence of the strict theory often compels scientists to interpret the results obtained only within the mean field approximation. Specific problem of experiments interpretation is concerned also with asymmetry of temperature interval of approximation due to different causes.

Steep increase of αf^{-2} value in the vicinity of $T_{N\text{-}I}$ transition constitutes direct proof of the presence of spatial inhomogeneities of fluctuation nature. Analysis of the temperature dependence of αf^{-2} value testifies also to their asymmetry in relation to phase transition temperature $T_{N\text{-}I}$ in the frequency range 2.5 - 50 MHz. At frequencies above 50 MHz no steep increase of sound attenuation is observed at $T_{N\text{-}I}$. Value of αf^{-2} is only decreasing with temperature as in ordinary liquids.

Fig.4 shows temperature dependence of reciprocal attenuation value $\left(\alpha f^{-2}\right)^{-1}$ for a series of sound frequencies. Analysis of these data demonstrates that for frequencies from 2.5 to 50 MHz maximal value of the sound attenuation both in nematic and isotropic phases corresponds to the temperature $T_{N\text{-}I}$ = 307,8 K. On withdrawal from this temperature both into nematic and isotropic phases $\left(\alpha f^{-2}\right)^{-1}$ value increases linearly with a value of $|\Delta T| = |T_{N-I} - T|$. It also follows from the Figure 4 that for frequencies 2.5-50 MHz in the point of phase transition sound attenuation in the nematic phase exceeds value of αf^{-2} in isotropic phase.

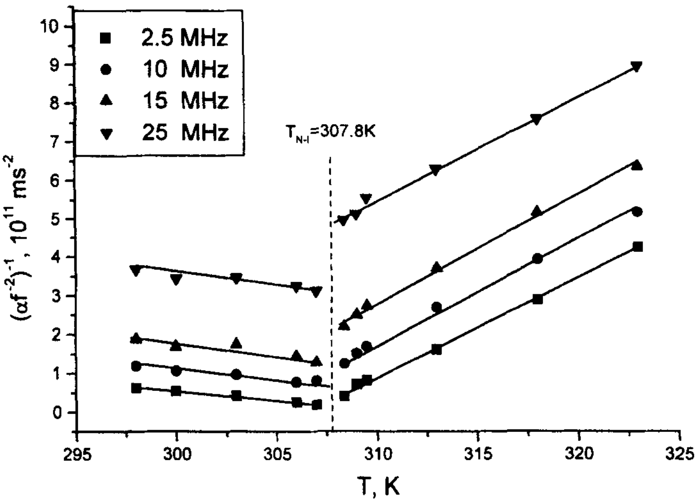


FIGURE 4 Temperature dependence of reciprocal attenuation value

On basis of the data obtained value of sound attenuation in the vicinity of phase transition temperature can be written as

$$\alpha_{N,I}^{-1}\left[\left(T < T_{N-I}\right)_N, \left(T > T_{N-I}\right)_I\right] = C_{N,I} + A_{N,I}^{0} f^{-2} |t|, \tag{7}$$

where $C_N = \alpha_N^{-1}\left(T = T_{N-I}\right)$, $C_I = \alpha_I^{-1}\left(T = T_{N-I}\right)$, and $C_N/C_I \approx 1{,}5$ denote reciprocal values of coefficients of sound attenuation for nematic and isotropic phase in phase transition points, correspondingly, A_{N-I}^0 is a constant coefficient, and It has to be noted that value of coefficients ratio A_I/A_N coincides with value of the liquid compressibility amplitudes ratio Γ_1/Γ_2 in the direction of critical isochore $\beta_1 = \Gamma_1|t|^{-\gamma}$ and phase interface $\beta_2 = \Gamma_2|t|^{-\gamma}$ for dielectric liquids [15]. The results obtained testify to the sound attenuation in the vicinity of nematic liquid crystal - isotropic fluid phase transition point occurring on fluctuations of order parameter $\langle\Delta\eta^2\rangle$, which are directly related to susceptibility $\chi_s \sim \langle\Delta\eta^2\rangle$ of the liquid studied. $\left(A_I/A_N \approx 5\right)$, $t = \left(T - T_{N-I}\right)T_{N-I}^{-1}$.

Experimental results have shown that in the vicinity of the transition temperature in the frequency range 2.5 - 50 MHz both in nematic and isotropic phases frequency dependence of αf^{-2} value is written by equation

$$\alpha f^{-2} = \frac{A_1}{1+\left(\omega\tau_1\right)^2} + B_1, \tag{8}$$

where A_1 and $B_1 = A_2 + B$ denote low-frequency $\left(\omega\tau_1 << 1\right)$ and high-frequency $\left(\omega\tau_1 >> 1\right)$ limits of αf^{-2} value; and τ_1 is relaxation time for low-frequency region.

Values of A_1, B_1 and τ_1, which define low-frequency dispersion region of αf^{-2} values, are listed in Table.

In the nematic phase, as distinguished from the isotropic one, where A_{1I} and τ_{1I} are changing monotonously on temperature decreasing, parameters A_{1N} and τ_{1N} are increasing. Steep increase of A_{1N} and τ_{1N} in the vicinity of N - I transition temperature constitutes direct proof of existence of the spatial inhomogeneities of fluctuation structure in the nematic phase [1-3].

In order to analyze temperature dependencies of the relaxation times and A_{1N} parameter, let's write equation (8) as

$$\alpha f^{-2} - B_1 = \frac{A}{1+\left(\omega\tau_{1N}\right)^2} = \alpha^{\bullet} f^{-2} \tag{9}$$

for nematic phase

$$\left(\alpha^{\bullet}\right)_N^{-1} = \left(\alpha_N f^2\right)^{-1} + \frac{\omega^2\tau_N^2}{\alpha f^2}. \tag{10}$$

Reciprocal values of the attenuation coefficients may be written for nematic and isotropic phases as

$$\left.\begin{aligned}\left(\alpha'\right)_N^{-1} &= C_N + A_N^0 f^{-2}|t| \\ \left(\alpha'\right)_I^{-1} &= C_I + A_I^0 f^{-2}|t|\end{aligned}\right\} \tag{11}$$

It was demonstrated above that $C_N/C_I \approx 1{,}5$.

It follows from comparison of (10) and (11) that parameter

$$A_{1N} = \left(A_{N,I}^0\right)^{-1}|t|^{-1} \tag{12}$$

on approaching to the critical temperature tends to infinity $A_{1N} \sim |t|^{-1}$. Value of attenuation coefficient in the critical point is also found from equations (9), (10) and (11)

$$\left(\alpha'\right)_{NI}^{-1} = \frac{\omega^2\tau^2}{A_{1N} f^2} = (2\pi)^2\,\tau_{N,I}^2 A_{N,I}^0\,|t| = C_{N,I}. \tag{13}$$

On basis of this relationship, temperature dependence of relaxation time is defined in nematic phase

$$\tau_N(t) = \frac{1}{2\pi}\left(\frac{C_N}{A_N^0}\right)^{1/2}|t|^{-1/2} = 3{,}4\cdot10^{-9}|t|^{-1/2}\ [\text{c}]. \tag{14}$$

and in isotropic phase

$$\tau_I(t) = \frac{1}{2\pi}\left(\frac{C_I}{A_I^0}\right)^{1/2}|t|^{-1/2} = 1{,}7\cdot10^{-9}|t|^{-1/2}\ [\text{c}]. \tag{15}$$

Thus, it follows from the relationships (10), (14), and (15), that the time of low-frequency region tends to infinity at t → 0 for 5CB studied in nematic and isotropic phases. Temperature dependence of experimental low-frequency relaxation time is shown in Fig.5.

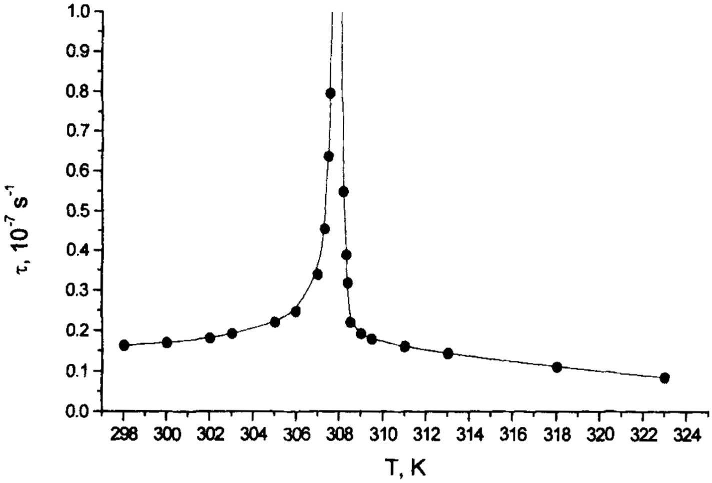


FIGURE 5 Temperature dependence of the experimental low-frequency relaxation time.

It follows also from equations (14) and (15) that relaxation time in nematic phase τ_N exceeds τ_I value for isotropic phase. At the same time, values of critical parameter coincide for nematic and isotropic phases. Really, amplitude ratio

$$\frac{\tau_{0N}}{\tau_{0I}} = \left(\frac{C_N A_I^0}{C_I A_N^0} \right)^{1/2} \approx 2. \tag{16}$$

It has to be noted that value of this relationship coincide with relaxation times ratio for dielectrics liquid systems in the vicinity of liquid-vapor critical point [15].

$$\frac{\tau(t>0)}{\tau(t<0)}=\frac{R_0(t>0)}{R_0(t<0)}\approx 2. \qquad (17)$$

Here $R_0(t>0)$ and $R_0(t<0)$ denote correspondingly correlation radii of liquid system in the direction of critical isochore $(t>0)$ and phase interface $(t<0)$.

The result we obtained testifies to fluctuation mechanism of low-frequency relaxation processes in the vicinity of nematic liquid crystal - isotropic fluid phase transition point. Value of parameter $y = 1/2$ in equation (16) corresponds to fluctuation being considered in gaussian approach, while it is important here that effective critical indices for heat capacity ($\alpha < 0{,}5$) and relaxation time ($\varepsilon < 1$) do not agree with self-consistent field approach ($\alpha = 0{,}5$ and $\varepsilon = 1$).

Scaling approach to the description of acoustic relaxation seems attractive, at least because it allows to avoid use of great number of fitting constants in expanding density of thermodynamical potential in module of order parameter [3].

It was demonstrated previously, that high-frequency dispersion region of αf^{-2} value in the objects studied is due to structural relaxation. Now consider mechanism of structural relaxation.

In order to study structural relaxation in 5CB we will use model proposed by M.I.Shakhparonov [13]. Any microscopic volume of liquid 5CB during period of structural relaxation time ($t \sim \tau_2$) is considered as dynamic three-dimensional collective system (quasimolecule, supermolecule), in which separate fragments (molecules, associates) are connected with bonds of the type C - H ... C, C - H ... N, C ≡ N ... H, etc.

The sound wave on passing through liquid crystal produces in it compression and rarefaction, i.e. local deviations from dynamic equilibrium. Then deviations can be described by means of reaction equation [13]

$$\mathrm{M}_i \overset{K_1}{\underset{K_2}{\rightleftarrows}} \mathrm{M}_j, \tag{18}$$

where K_1 and K_2 denote reaction constants for hydrogen bonds rupture and formation. Elemental events of reaction (18) proceed as follows. In liquid quasimolecule M_i, with structure we have no need to define in the given case, rupture of molecular bond(s) takes place and displacement of the parts of M_i, connected with these bonds. The shift is great enough to make restoration of the molecular bonds impossible. As a result of intermolecular bonds rupture and displacement of quasimolecule M_i parts, its structure will be changed to some extent, transforming it to quasimolecule M_j. M_i differs from M_j during period of structural relaxation τ_2 in number of intermolecular bonds.

If reaction (18) is a non-collective one, then acoustic relaxation time is defined as [12]

$$\tau_2^{-1} = K_1 + K_2 = K_1\left(1 + \frac{n_1}{n_2}\right), \tag{19}$$

where n_1 denote number of molecular bonds, and n_2 - number of ruptured bonds.

Since on small departures from the dynamic equilibrium $K_1 n_1 \approx K_2 n_2$ and $n_1 >> n_2$, then $K_2 >> K_1$. Taking into account the fact of the resulting rate for consecutive processes being determined by stage having the least reaction rate constant, equation (19) may be rewritten as follows

$$\tau_2^{-1} = K_1. \tag{20}$$

After that, using expression

$$K_1 = \frac{kT}{h}\exp\left(\frac{\Delta S^*}{T}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \tag{21}$$

enthalpy value has been calculated $\Delta H^* = 16.0$ kJ/mole.

It follows from the experimental data (see Table) that high-frequency limit of the attenuation value B in 5CB is less than $\alpha_{cl} f^{-2}$ values. Inequality $\alpha_{cl} f^{-2} < B$ indicates to relaxation of bulk viscosity η_{v2} being accompanied by relaxation of shear viscosity, because frequency dependence of αf^{-2} value for high-frequency region is described by equation with single relaxation time. Thus, within limits of experimental error, relaxation times for bulk and shear viscosity are indistinguishable $(\tau_r \approx \tau_s \approx \tau_{v2})$.

The dispersion expression describing relaxation of bulk η_{v2} and shear viscosity is written as [14]

$$\alpha f^{-2} = \frac{2\pi^2}{\rho c^3}\left(\frac{4}{3}\frac{G_\infty \tau_s}{1+\omega^2\tau_s^2} + \frac{K_r \tau_{v2}}{1+\omega^2\tau_{v2}^2}\right), \tag{22}$$

where c denotes speed of sound at frequency f; G_∞ is high-frequency shear modulus; τ_s and τ_{v2} represent relaxation times for shear and bulk viscosity; K_r is difference between high-frequency G_∞ and low-frequency K_0 elasticity module.

At low frequencies, $\omega\tau_s << 1$ and $\omega\tau_{v2} << 1$, so the expression (4.16) has a look of

$$\alpha f^{-2} = \frac{2\pi^2}{\rho c_{02}^3}\left(\frac{4}{3}\eta_s + \eta_{v2}\right), \tag{23}$$

where $\eta_s = G_\infty \tau_s$; and $\eta_{v2} = K_r \tau_{v2}$.

Values of elasticity and shear module were calculated using expressions $K_0 = \rho c_{02}^2$; $K_\infty = \rho c_{\infty 2}^2$; and $G_\infty = \eta_s / \tau_r$. Results of calculations are listed in Table. Values of elasticity and shear module we have obtained coincide in the order of magnitude with similar values for liquids having hydrogen bonds and other liquid crystals [1-3, 16].

Results of measurements indicate to the greatest contribution to sound attenuation in 5CB being made by volume effects. Values of the bulk viscosity we have obtained exceed significantly values of shear viscosity.

Using G_∞, K_0, K_∞, and K_r values obtained, frequency dependence of the speed of sound has been determined according to equation [12]

$$c^2 = \frac{1}{\rho}\left[K_0 + \frac{K_r\omega^2\tau_{v2}^2}{1+\omega^2\tau_{v2}^2} + \frac{4}{3}\frac{G_\infty\omega^2\tau_s^2}{1+\omega^2\tau_s^2}\right] \qquad (24)$$

Within the limits of experimental error, the calculated and experimental values coincide. For example, experimental value of the speed of sound at frequency 500 MHz and T = 298 K equals to 1612 m/s, while the calculated one is 1611 m/s. Coincidence of calculated c_{calc} and experimental c_{exp} values bears out the model we have adopted, being consistent with $\tau_s \approx \tau_{v2}$.

4. CONCLUSIONS

Acoustical properties of nematic liquid crystal 4-pentyl 4'-cyanobiphenyl (5CB) were investigated in temperature interval from 298 to 333 K involving the vicinity of nematic phase - isotropic phase transition temperature. Acoustic spectra of 5CB consist of two relaxation areas. The low-frequency region of acoustical relaxation in the vicinity of N-I phase transition is connected with order parameter fluctuations. Relaxation time of low-frequency region tends to infinity according to low $\tau \sim |t|^{-1/2}$. The high-frequency region cause by processes of hydrogen bonds rupture and formation between molecules of 5CB. Main contribution to sound attenuation in 5CB being made by volume effects. It was shown that, within limits of experimental error, relaxation times of shear and bulk viscosity are indistinguishable.

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