ARCHIVES OF ACOUSTICS
6, 2, 163-172 (1981)

THE INVESTIGATION OF RELAXATION PROCESSES IN CHOSEN LIQUID CRYSTALS BY ULTRASONIC AND DIELECTRIC METHODS

ADAM DRZYMAŁA

The Technical University of Rzeszów, The Institute of Mathematics and Physics
(35-959 Rzeszów, ul. W. Pola 2)

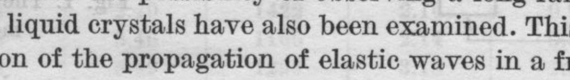
Relaxation processes have been found to occur in 4-*n*-methoxybenzoated-4-*n*-pentylphenylene and 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate. The findings are based on ultrasonic and dielectric investigations. Both chemical compounds exhibit two regions of relaxation in the range of frequencies investigated. A comparison has been made of the values of the activation energy derived from the dielectric and acoustic investigations.

1. Introduction

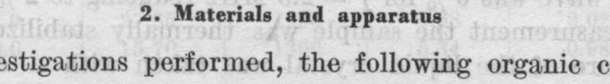
In the last few years there has been particular interest in acoustic methods of investigating liquid crystals [1,3-5, 8, 9]. One of the reasons for this is the unique physical properties of liquid crystals which combine the properties of liquids, such as fluidity, with the properties of solid bodies, such as anisotropic physical properties and the possibility of observing a long-range order. Critical phenomena [7] in liquid crystals have also been examined. This paper is devoted to the investigation of the propagation of elastic waves in a frequency range of 2.5-60 MHz in samples of two chosen nematic materials.

2. Materials and apparatus

In the investigations performed, the following organic compounds were used: 4-*n*-methoxybenzoate-4-*n*-pentylphenylene produced in the Institute of



Basic Chemical Sciences of the Medical Academy in Łódź; and 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate received from The Institute of Chemistry of the



M. Luther University in Halle.

The substances in question reveal, under a microscope, the properties of nematic crystals. Transition phase temperatures obtained by the DSC method for 4-*n*-methoxybenzoate-4-*n*-pentylphenylene are: solid state→29.1 °C nematic phase →41.6 °C isotropic liquid, while for 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate the temperatures are: solid state→51.6 °C nematic phase→83.1 °C isotropic liquid. The measurements of the transition phase temperatures were performed in the University in Halle using a DSC apparatus made by Perkin-Elmer. The measurements of the coefficient of absorption and the velocity of propagation of the ultrasonic waves were performed with an ultrasonic set of high frequency, the US-6, and an ultrasonic interferometer, the UI-15, both made by IPPT of Warsaw (Fig. 1).

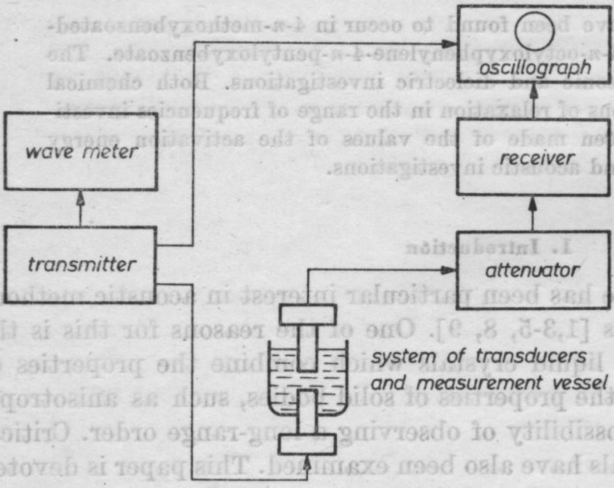


Fig. 1. The block diagram of the measuring set

The relative error in determining the value of the absorption coefficient o the ultrasonic wave was 6 % for $f = 2.5$ MHz reducing to 2 % for $f = 60$ MHz.

Before measurement the sample was thermally stabilized for two hours. The temperature of the liquid crystal was taken with a copper-constantan thermocouple and a digital voltmeter V-534.

3. The results of the measurements

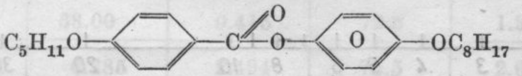
Measurements of the absorption coefficient and the velocity of propagation of the ultrasonic wave at various temperatures which included the nematic mesophase and the isotropic liquid were carried out for 4-*n*-methoxybenzoate-4-*n*-pentylphenylene and 4-*n*-octyloxyphenylene-4-*n*-pentylexybenzoate. The results of the measurements of the absorption coefficient and the velocity at different frequencies, for given temperatures can be used to establish the experimental dependencies

$$\frac{\alpha}{f^2} = F(f), \qquad \alpha\lambda = F(f),$$

where α denotes the absorption coefficient, f the frequency, $\alpha\lambda$ the absorption coefficient in relation to the length of the wave.

Some of the measurements obtained on 4-n-methoxybenzoate-4-n-pentylphenylene have been presented previously [2]. For 4-n-octyloxyphenylene-4-n-pentyloxybenzoate, Table 1 shows, as an example, typical results of the measurements of the absorption coefficient and the velocity of the ultrasonic wave (at a temperature of 58 °C).

Table 1. The measurements and calculations for



at 58 °C

f [MHz]	α [cm^{-1}]	v [m·s^{-1}]	$\alpha\lambda\cdot 10^2$	$\frac{\alpha}{f^2}\cdot 10^{-14}$ [cm$^{-1}\cdot$s^2]
2.5	1.03	1405	5.79	16.48
5.0	1.12	1400	3.14	4.48
7.5	1.08	1410	2.04	1.93
9.6	1.84	1402	2.69	1.99
11.0	1.82	1452	2.40	1.50
13.6	2.23	1442	2.36	1.21
15.8	2.40	1422	2.16	0.96
18.8	3.46	1166	2.14	0.98
22.3	5.49	1293	3.18	1.10
27.0	9.34	1350	4.07	1.28
34.4	24.69	1307	9.38	2.09
35.0	25.60	1260	9.22	2.09
37.0	27.65	1295	9.68	2.02
40.0	15.70	1360	5.34	0.98

4. An interpretation of the results

While interpreting the results, it was found that the function $\alpha\lambda = F(f)$ is a complicated one, possibly containing information about more than one relaxation time. Based on the data given in Table 1, Fig. 2 shows the dependence as a function of frequency. From Fig. 2 we can determine the value of the frequency of relaxation for the region containing the maximum, but the lack of experimental points for frequencies below 2.5 MHz does not allow us to state the second frequency of relaxation.

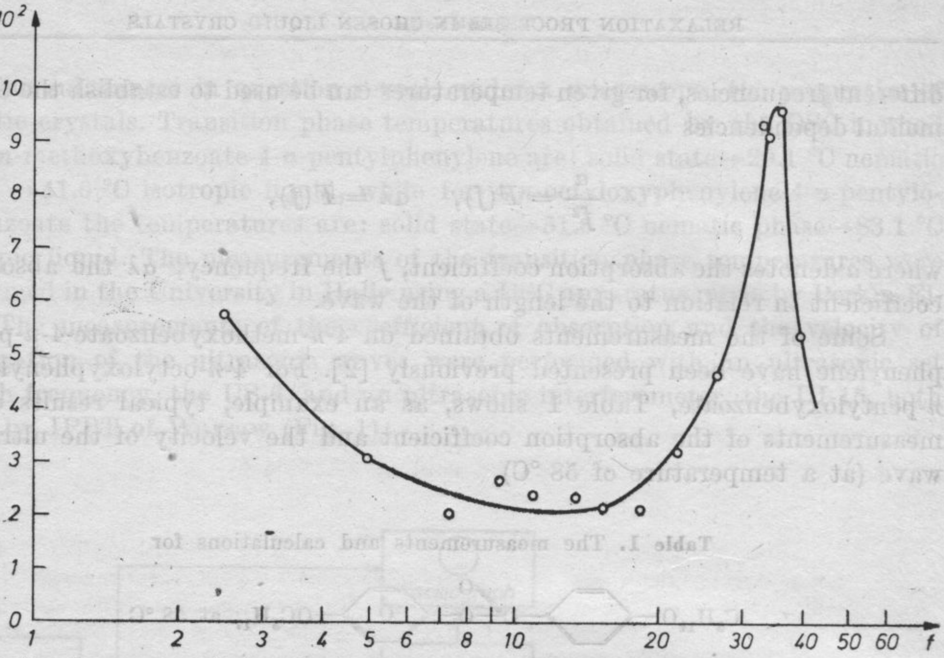


Fig. 2. The dependence of $\alpha\lambda$ on the frequency of 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate at 58 °C

$t = 58.0$ °C, $f_R = 36.2$ MHz

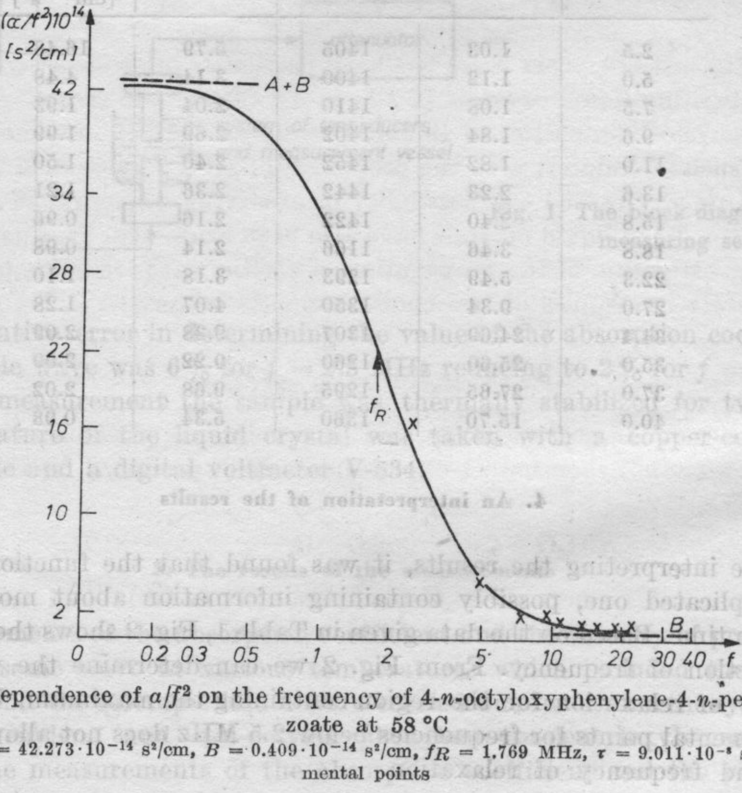
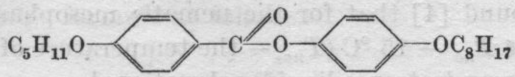


Fig. 3. The dependence of α/f^2 on the frequency of 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate at 58 °C

$t = 58.0$ °C, $A = 42.273\cdot10^{-14}$ s²/cm, $B = 0.409\cdot10^{-14}$ s²/cm, $f_R = 1.769$ MHz, $\tau = 9.011\cdot10^{-8}$ s, x – experimental points

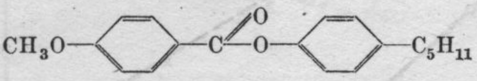
Table 2. Measurements and calculations of the frequency and the time of relaxation for



Acoustic			Dielectric*		
T [°C]	f_R [MHz]	$\tau_R\cdot 10^{-8}$[s]	T [°C]	f_R [MHz]	$\tau_R\cdot 10^{-8}$[s]
55.4	1.506 35.00	10.568 0.455	53.5	0.222	71.691
58.0	1.769 36.20	8.997 0.439	61.2	0.475	33.506
67.1	3.340 37.00	4.765 0.430	66.5	0.763	20.859
75.6	38.00	0.415	72.5	1.350	11.789
77.0	6.385	2.494	78.5	2.630	6.052
80.3	7.857	2.026			

* unpublished information received from Dr. H. KRESSE of the M. Luther University in Halle.

Table 3. Measurements and calculations of the frequency and the time of relaxation for



Acoustic			Dielectric*		
T [°C]	f_R [MHz]	$\tau_R\cdot 10^{-8}$ [s]	T [°C]	f_R [MHz]	$\tau_R\cdot 10^{-8}$ [s]
31.5	1.74 24.60	9.345 0.645	30.0	1.04	15.000
34.5	2.00 25.20	7.958 0.624	27.2	0.78	20.400
38.3	2.58 36.00	6.169 0.442	31.5	1.20	13.000
45.0	3.49 39.00	4.556 0.408	34.5	1.69	9.418
			38.3	2.40	6.634

* the measurements were carried out by the author in The M. Luther University in Halle.

It is possible to interpret the results of the ultrasonic absorption, if we assume that two relaxation regions exist in the frequency range under examination. It has been found [4] that for the nematic mesophase of liquid crystals at temperatures $T \leqslant T_{nc} - 15$ °C (T_{nc} — the temperature of the transition from the nematic phase to an isotropic liquid) relaxational processes occur with more than one relaxation time.

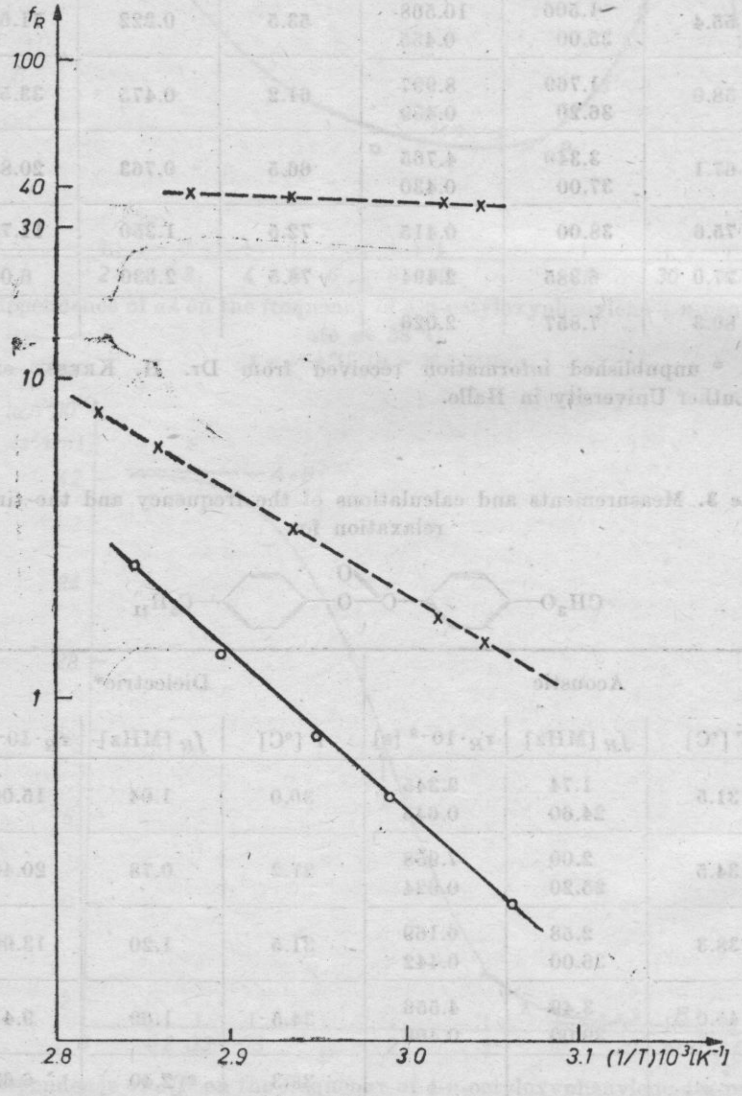


Fig. 4. The dependence of the natural logarithm f_R on $1/T$ of 4-*n*-octyloxyphenylene-4-*n*-pentyloxybenzoate

x — acoustic measurements, o — dielectric measurements

When we are dealing with only a single relaxation process then the expression for the absorption coefficient depends on the frequency and we can state it according to Lamb's formula as follows:

$$\frac{a}{f^2} = \frac{A}{1+\left(\frac{f}{f_R}\right)^2} + B, \tag{1}$$

where the constant A contains information on the contribution of the relaxation process to the absorption, whereas the constant B corresponds to the classical part of the absorption, and f_R denotes the frequency of relaxation. To determine the relaxation time for the lower frequencies, mathematical methods were employed together with the theoretical curve of relaxation given in Lamb's formula. Fig. 3 shows the results obtained for the sample in question over a frequency range of 0.1 to 20 MHz.

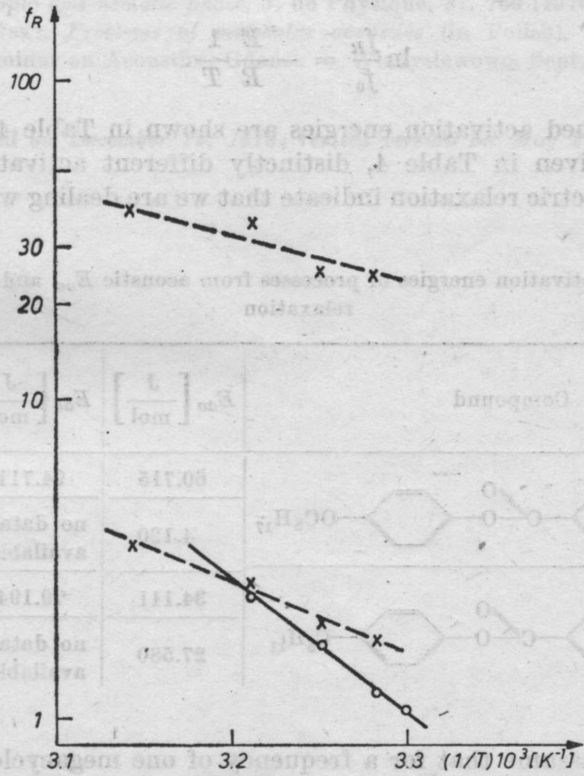


Fig. 5. The dependence of the natural logarithm f_R on $1/T$ of 4-*n*-methoxybenzoate-4-*n*-pentylphenylene
x – acoustic measurements, o – dielectric measurements

The results of measurements and calculations of the frequency of relaxation, and of the acoustic and dielectric relaxation times of the liquid crystals under consideration are given in Tables 2 and 3. The frequencies of relaxation determined in the investigations can be divided into two regions: the first one covers a frequency range up to about 20 MHz the second from 20 - 40 MHz. Figs. 4 and 5 show the dependence of the natural logarithm f_R on $1/T$ for the substances tested. The same figures show the dielectric relaxation data based on independently performed measurements. In both regions the relaxation frequencies increase as the temperature increases.

Making use of the fact that the relaxation frequency of the process is subject to the law of Arrhenius

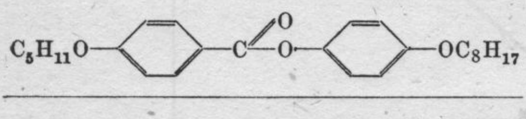
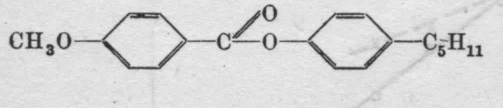
$$f_R = f_0 \exp\left(-\frac{E}{RT}\right), \tag{2}$$

where E denotes the activation energy of the process, R is the gas constant, T is the absolute temperature, and f_0 is a constant, we can determine the activation energy from the dependence

$$\ln\frac{f_R}{f_0} = -\frac{E}{R}\frac{1}{T}. \tag{3}$$

The determined activation energies are shown in Table 4. As we can see from the data given in Table 4, distinctly different activation energies for acoustic and dielectric relaxation indicate that we are dealing with two different processes. If we assume that for a frequency of one megacycle per second the relaxation is based on a mechanism of rotation of the end groups of the molecule, then the results obtained for both substances would testify that different fragments of the molecule are excited in dielectric and in acoustic relaxation.

Table 4. The activation energies of processes from acoustic E_{aa} and dielectric E_{ad} relaxation

Compound	$E_{aa}\left[\frac{\mathrm{J}}{\mathrm{mol}}\right]$	$E_{ad}\left[\frac{\mathrm{J}}{\mathrm{mol}}\right]$	Relaxation band [MHz]
	60.715	94.711	2.5-20
	4.120	no data available	20.0-60
	34.111	79.194	2.5-20
	27.580	no data available	20.0-60

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Received on December 14, 1978; revised version on May 26, 1980