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Dielectric studies of liquid crystals under high pressure

II. Low frequency relaxation process in 4-*n*-pentyl-4′-cyanobiphenyl in relation to theories of the nematic state

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The results of high pressure dielectric studies of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) are analysed in terms of theories of the nematic state. The retardation factor $g_{\parallel} = \tau_{\parallel}/\tau_0$ and the effective, single-particle potential of mean torque were calculated at the nematic–isotropic transition temperature T_{NI} and along the isothermal, isobaric and isochoric paths within the nematic phase of 5CB. The potential of mean torque is compared with the order parameter known for the same conditions. The values of parameter γ relating the potential to the volume is discussed.

1. Introduction

High pressure studies of thermotropic liquid crystals have been performed for many compounds with the aim of obtaining information about the (p, T) phase diagram (see for example [1–3]) or the order parameters at constant volume in the nematic phase [4–7]. There is a lack of experimental data which could be related to other parameters characterizing the nematic state, for example the potential of mean torque. Such information can be deduced from studies of the dielectric relaxation process connected with the reorientation of molecules around their short axes. Recently we have performed high pressure dielectric studies of 4-*n*-pentyl-4′-cyanobiphenyl (5CB). In Part I [8] the results obtained were analysed in terms of molecular associations (static permittivity) and molecular reorientation around the short axes (relaxation time $\tau_{\parallel}$) in the nematic phase of 5CB. It was concluded that relatively low pressure markedly influences the monomer–dimer equilibrium involving the breaking of the antiparallel dipole–dipole correlations of molecules.

Here we discuss the results obtained in terms of theories of the nematic state [9–18]. Many of them were worked out within the molecular field approximation. We shall use the notions introduced in the Maier–Saupe theory [9] as it has been extended to explain the dielectric properties of the nematic phase [19–24]. We realize, of course, that this theory, as well as any other molecular field theories, should not be used for quantitative comparisons with the experiments. Nevertheless, it seems worthwhile to do that in order to check the real discrepancies between the predictions of the theory

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and the experimental results. According to our best knowledge it has not been done to such an extent yet. In the Maier–Saupe theory the potential energy of one rod-like molecule in the field generated by its interactions with the neighbouring molecules is predicted to be

$$U(\cos\theta) = -qP_2(\cos\theta), \tag{1}$$

where $P_2(\cos\theta)$ is the second Legendre polynomial and θ is the angle between the molecular symmetry axis and the nematic director. The strength parameter q is related to the order parameter $S=\langle P_2(\cos\theta)\rangle$ by $q=\varepsilon S$. The interaction coefficient ε is defined by [10]

$$\varepsilon = \rho\int dr_{12} 4\pi r_{12}^2 v(r_{12}) g(r_{12}), \tag{2}$$

where ρ is the number density, r_{12} is the intermolecular distance, $g(r_{12})$ is the radial distribution function, and $v(r_{12})$ is the radial part of the pair potential which determines the distance dependence of the intermolecular potential. All of the quantities introduced depend on temperature T and volume V: $S(T, V)$, $\varepsilon(T, V)$ and $q(T, V)$. Thus, the pressure measurements can give some information about these dependences.

The volume dependence of the interaction energy is approximated by [9, 10]

$$\varepsilon = \varepsilon_0 V^{-\gamma}, \tag{3}$$

where γ is treated as an adjustable parameter in fitting theory to experiment [10, 15–18, 25]. For London dispersion forces assumed in the Maier–Saupe theory $\gamma=2$ (it corresponds to an r^{-6} dependence of the potential). However, Cotter [13] has shown that γ must equal 1 for molecular field theories, although Emsley *et al.* [16] have argued that this difficulty could be avoided if ε is treated as a purely phenomenological parameter. McColl [5] introduced a thermodynamic coefficient Γ, defined as

$$\Gamma = -(\partial \ln T/\partial \ln V)_s \tag{4}$$

which is identical to γ for the potential in equation (1) [10, 15]. The γ values determined experimentally for different nematogens are usually larger than 2 which indicates that repulsive forces must be taken into account. We shall return to this problem later.

The strength parameter q for 5CB can be calculated using the formula derived by Meier and Saupe [20, 21]

$$g_{\parallel} = \tau_{\parallel}/\tau_0 = \frac{RT}{q}\left(\exp\frac{q}{RT} - 1\right), \tag{5}$$

where $g_{\parallel}$ is called the retardation factor. $\tau_{\parallel}$ is the relaxation time characterizing the molecular rotations around the short axes in the nematic phase, whereas τ_0 is the (hypothetical) relaxation time for the same motion but in the absence of the ordering potential. For the nematic phase τ_0 can be estimated by an extrapolation from the isotropic phase [23, 24].

2. Results

In Part I [8] we have presented the results of high pressure studies of 5CB in the nematic and isotropic phases. Figure 2 presents the plots of $\ln\tau_{\parallel}$ and $\ln\tau_{is}$ versus p at different temperatures. As we can see the relaxation times $\tau_{\parallel}$ exhibit a markedly stronger dependence on pressure than τ_{is}. For the calculation of the retardation factors

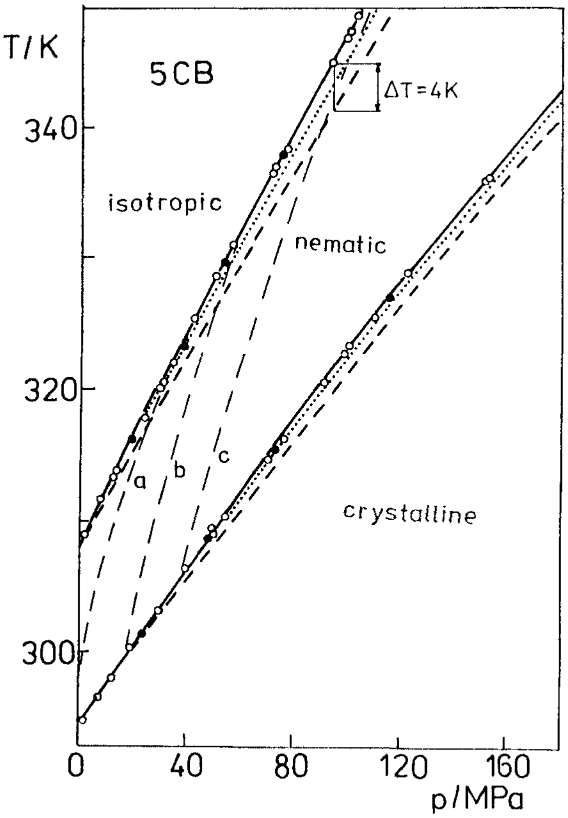


Figure 1. Phase diagram for 5CB. The heavy solid curves with points were obtained in the present study [8], dashed curves were obtained by Horn [2] and dotted curves by Shashidhar and Venkatesh [3]. The dashed curves marked by a, b and c are isochores for molar volumes 246, 244 and 242 cm^3/mol, respectively.

$g_{\|}(p, T)$ we have taken the values of $\tau_{\|}(p, T)$ from the lines averaging the experimental points whereas the values of $\tau_0(p, T)$ were obtained from a linear extrapolation of $\tau_{is}(p)_T$ to the nematic phase (see figure 2).

The data on the order parameter $S(T, p)$ and the specific volume $V_m(T, p)$ in the nematic phase of 5CB were obtained from the refractive index measurements reported by Horn [2]. However, due to incorrect measurement of pressure in Horn's experiment [8, 26], see figure 1, they had to be recalculated. We used our $T_{NI}(p, T)$ values. A scaling factor relating the molar volume with the refractive index data was also changed to obtain consistency with the densities of 5CB measured by Dummer and Miller [27]. We have assumed that the scaling factor is constant in the limited range of temperature and pressure explored in our experiment. If it was treated as temperature and pressure dependent (according to Emsley *et al.* [15]) the calculated $V(p, T)$ values showed marked inconsistency with other data.

3. Discussion

Information about the values of the potential of mean torque in nematogens is rather scarce. Partly it is due to the fact that only compounds having dipole moments directed along the symmetry axis can be used. Only in such cases do the relaxation

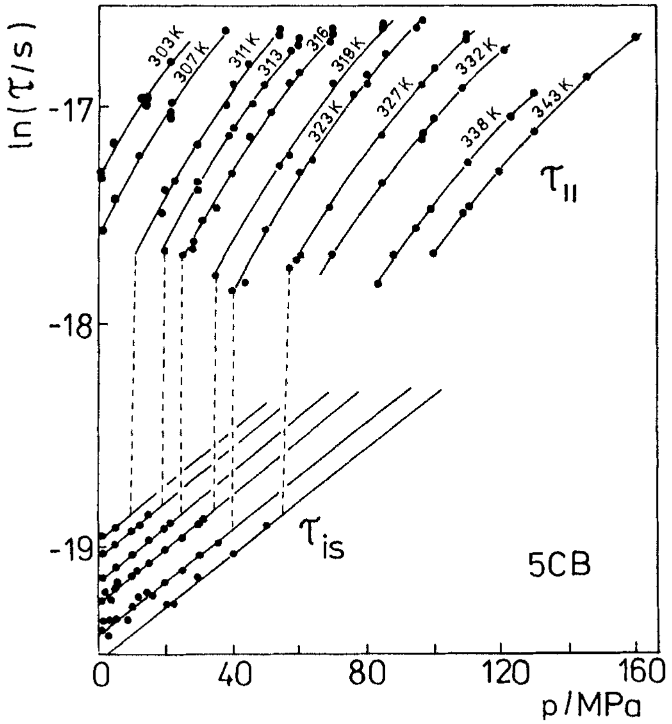
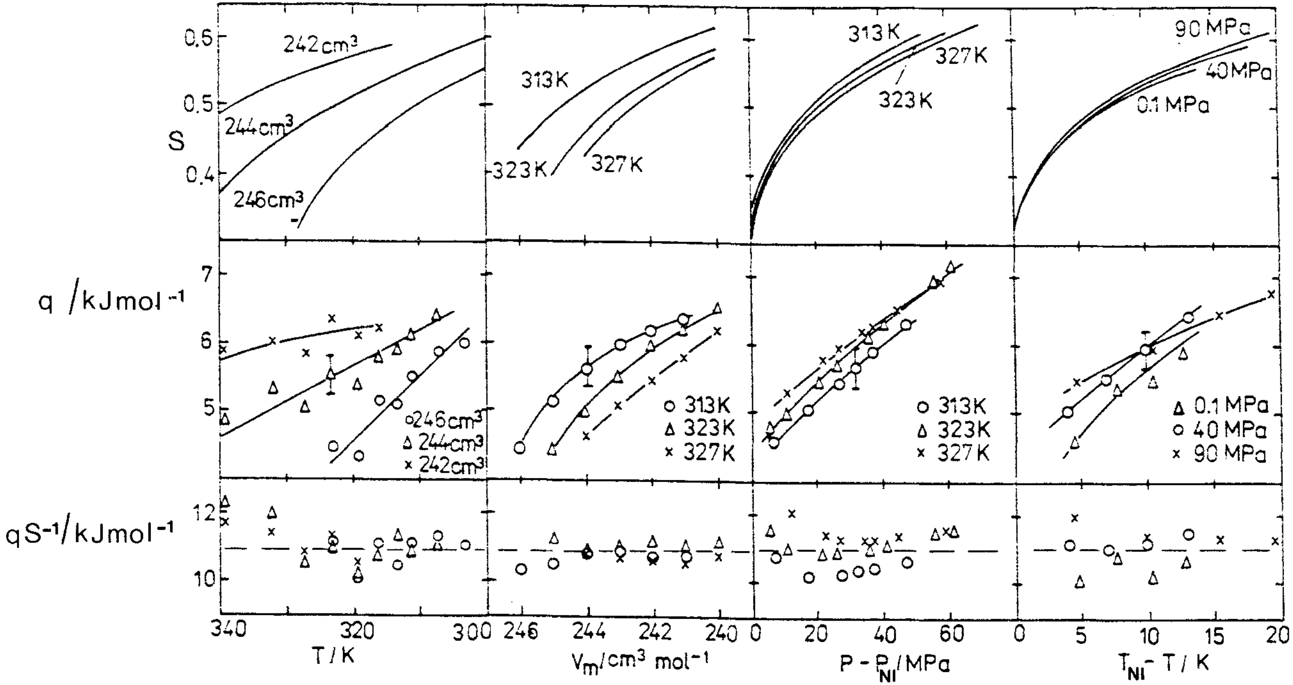


Figure 2. ln $\tau_{\parallel}$ and ln τ_{is} versus p plots for the nematic and isotropic phases of 5CB at different temperatures [8].

spectra measured in the isotropic phase give correct values of the relaxation times τ_0 characterizing the molecular reorientations about the short axes in the absence of the ordering potential. Meier and Saupe [20] have calculated the $g_{\parallel}$ factor and the strength parameter q for 4,4′-dimethoxyazoxybenzene (PAA) obtaining $g_{\parallel}=100$ and $q=21$ kJ/mol. These values seem to be distinctly over-estimated as the dielectric spectrum of the isotropic phase of PAA is strongly contaminated by molecular reorientations around the long axes which are faster than those around the short axes [28].

For the cyanobiphenyls (*n*CB), which are models in that respect, the q values (atmospheric pressure) have been estimated for 7CB [29, 30] (*c.* 7·7 kJ/mol), and for 8CB [31] (*c.* 7 kJ/mol). Similar value (*c.* 7·7 kJ/mol) can be obtained from the results of dielectric studies of 6-CHBT [4-(trans-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene] which also has a strong dipole moment directed along the main molecular axis [32]. For 5CB at atmospheric pressure we have obtained $q \approx 6{\cdot}5$ kJ/mol in reasonable agreement with these results. Therefore, it seems possible to use the obtained values of the strength parameter to check some relations arising from the Maier–Saupe theory.

Figure 3 presents the comparisons of the order parameter and the strength parameter obtained under different conditions: (*a*) as a function of temperature and at constant volume, (*b*) as a function of molar volume and at constant temperature, (*c*) as a function of pressure and at constant temperature and (*d*) as a function of temperature and at constant pressure. A common feature of these plots is that the strength parameter q and the order parameter S show roughly similar behaviour in every



(*a*) (*b*) (*c*) (*d*)

Figure 3. The dependence of the order parameter S, the strength parameter q and the ratio $q/S = \varepsilon$ on different thermo-dynamic parameters within the nematic phase of 5CB. p_{NI} and T_{NI} correspond to the nematic–isotropic transition.

conditions although they were obtained in different experiments. It seems to indicate, therefore, that the approximations made in the calculations of the q values were reasonable. Moreover, the ratio $\varepsilon = q/S$ is nearly constant and equal to 11 ± 1 kJ/mol in the isochoric, isothermal and isobaric conditions. Very similar values of ε coefficients were obtained by Emsley *et al.* [15] from the analysis of the temperature and pressure dependence of the quadrupole splittings along the alkyl chain of deuteriated 5CB. Thus, one of the essential assumptions of the Maier–Saupe and other molecular field theories, i.e. the proportionality between q and S, seems to be well fulfilled in the nematic phase of 5CB. Additionally, as figures 3 (*c*) and (*d*) show, the values of $\varepsilon = q/S$ remains roughly constant up to the nematic–isotropic transition which gives for the transition temperature, according to the Maier–Saupe theory, $T_{NI} = 0{\cdot}22\,\varepsilon/k_B \approx 290$ K, in good agreement with the real value. At the same time, $\varepsilon/k_B T_{NI} \approx 4{\cdot}5$, which is distinctly higher than the values predicted by many theoretical models (less than 1 [12]). However, the values of the retardation factors $g_{\parallel}(T_{NI})$, equal to *c*. 2·6, and the ratios $q(T_{NI})/RT_{NI}$, equal to *c*. 1·6, are markedly lower than the Maier–Saupe theory predicts (4 and 2·92, respectively [23]).

Taking into account the data on T_{NI}, V, S and q we have calculated the relation between the reduced temperature $T_R = TV^2/T_{NI}V_{NI}^2$ and these parameters at different pressures. According to [22], $T_R = KS/(q/RT)$. The values obtained for parameter K are: $4{\cdot}5 \pm 0{\cdot}3$ (0·1 MPa), $4{\cdot}1 \pm 0{\cdot}2$ (20 MPa), $4{\cdot}0 \pm 0{\cdot}2$ (30 MPa) and $3{\cdot}8 \pm 0{\cdot}2$ (40 MPa). Thus, they are markedly lower than $K = 6{\cdot}82$ predicted by the Maier–Saupe theory and decrease systematically with increasing pressure. Therefore, the validity of the above equation seems to be doubtful for the nematic phase of 5CB.

The Maier–Saupe theory predicts that the order parameter is a universal function of the reduced temperature [9]. Taking the available data on $S(p, T)$ and $V(p, T)$ we have calculated $S(T_R)$ curves at different conditions for the nematic phase of 5CB. As we can see in figure 4 the curves differ markedly depending on whether we follow the

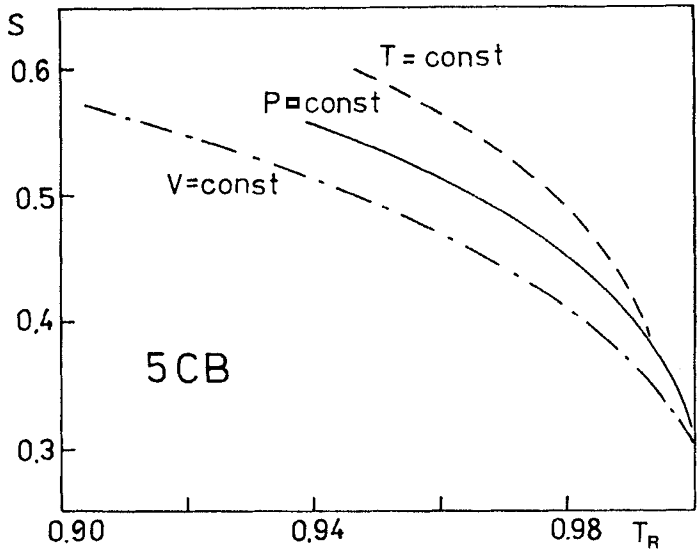


Figure 4. Dependence of the order parameter S on the reduced temperature T_R at isothermal, isobaric and isochoric conditions.

isothermal, isobaric or isochoric paths. For a given condition, however, the $S(T_R)$ curves show only minor differences (for example, at $T_R = 0{\cdot}92$ the S values differ by *c.* 5 per cent between 246 and 242 $cm^3 mol^{-1}$).

The main problem in theories of the nematic state is the form adopted for the intermolecular potential. The potential of mean torque in equation (1) cannot satisfactorily explain the properties of real nematogens. In addition to the molecular field approximation, this is due to the fact that the single $P_2(\cos\theta)$ term is taken to make the sole contribution to the potential. There are more sophisticated theories (see, for example, [10–18, 25]) which show that the anisotropy of the short range intermolecular repulsions may play a very important role. To discuss the true contribution of particular components to the intermolecular interactions it is necessary to find the volume dependence of the molecular field potential characterized by the exponent γ (see equation (3)). For this aim the pressure-temperature studies of liquid crystals are indispensable.

McColl and Shih [6] have determined γ for PAA from the slope of the curves $\log T$ versus $\log V$ at constant S (see equation (4)). Similar studies have been made for other members of the PAA homologous series by Tranfield and Collings [33]. They found that γ decreases gradually from 4 for 4,4′-dimethoxyazoxybenzene (PAA) to 1·9 for 4,4′-di-*n*-hexyloxyazoxybenzene. Taking the improved Horn and Faber data [4] on $S(p, T)$ we are able to repeat this procedure for 5CB. Figure 5 shows that these results also give straight lines with the slope $\gamma = 5{\cdot}3 \pm 0{\cdot}15$. (N.b. Chandrasekhar and Shashidhar report [7] that Horn's original curves for $\log T$ versus $\log V$ at constant S depart from linearity.) The Maier–Saupe theory predicts that

$$T_{NI}/\varepsilon \sim T_{NI} V_{NI}^{\gamma} = \text{const}, \tag{6}$$

so that γ may be obtained from the $\ln T_{NI}$ versus $\ln V_{NI}$ plots. This has been done by Horn and Faber [4] for 5CB ($\gamma = 6{\cdot}0$) and MBBA ($\gamma = 2{\cdot}6$) and by Emsley *et al.* [16] for

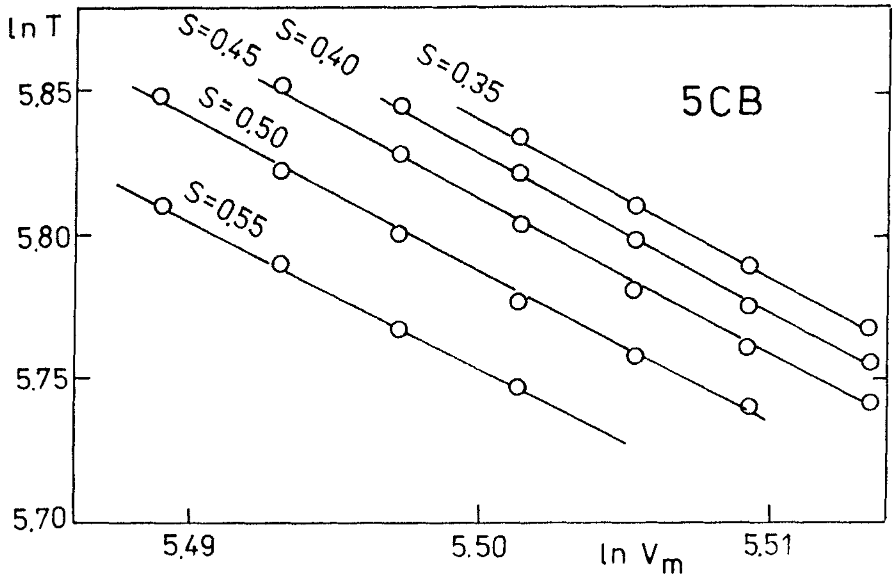


Figure 5. ln T versus ln V_m plots at several constant values of S for 5CB. The $S(V, T)$ data are taken from [2, 4] and corrected as explained in the text.

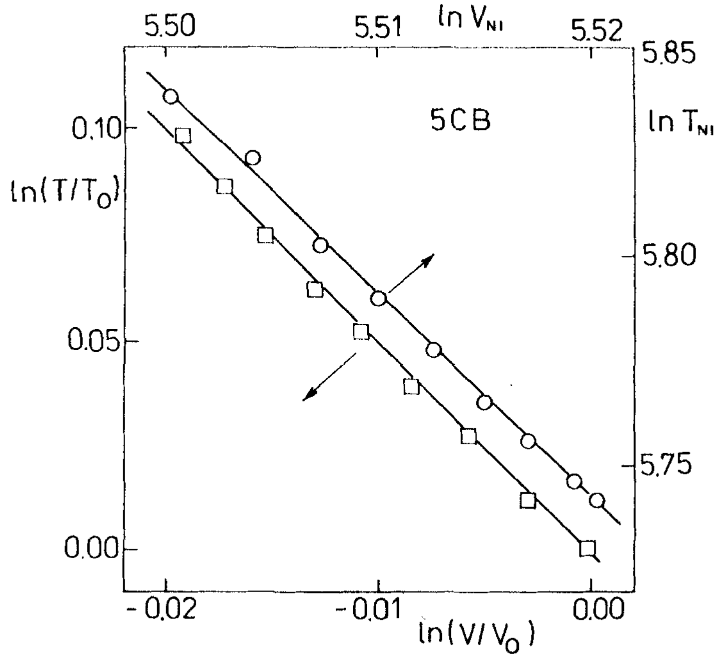


Figure 6. Log–log plots for 5CB according to formulae (6) and (7). The data on T_{NI} are taken from [8] and on V_m from [2, 4] (after correction, see text).

n-heptylcyanophenylcyclohexane, PCH7 ($\gamma = 3{\cdot}6$). We repeat here the Horn and Faber calculation taking the correct values of T_{NI} and $V(T_{NI})$ (see figure 6). The slope of the line gives $\gamma = 5{\cdot}2 \pm 0{\cdot}1$, in excellent agreement with the value obtained from figure 5. This value can be compared with those reported by Emsley *et al.* [15]. These authors have found that Γ decreases steadily along the alkyl chain from $5{\cdot}3 \pm 0{\cdot}1$ for the order parameter of the deuterons nearest to the aromatic core, to $4{\cdot}2 \pm 0{\cdot}1$ for those from the methyl group. On the basis of high pressure volumetric measurements Collings *et al.* [34, 35] calculated γ from

$$\gamma = \partial \ln (T/T_0)/\partial \ln (V/V_0), \qquad (7)$$

where T_0 and V_0 represent a point on the nematic–isotropic coexistence curve. They obtained the following values of γ: 2·07 for 4,4′-di-*n*-heptyloxyazoxybenzene [34], 3·20 for 4-*n*-octyloxy-4′-cyanobiphenyl [34], and about 3 for three 4,4′-di-*n*-alkylazoxybenzenes [35]. Using formula (7) we obtained for 5CB $\gamma = 5{\cdot}3 \pm 0{\cdot}1$ (see figure 6).

The comparison of γ obtained from high pressure studies of different liquid crystals allows us to point out the following regularities: (i) γ is usually larger than 2 which indicates that besides dispersion also repulsion forces determine the intermolecular potential in the nematic phase; (ii) different substances are characterized by different γ values; (iii) in a homologous series γ decreases with increasing chain length; (iv) γ decreases steadily along the alkyl chain. Thus, a balance between the long range attractive and short range repulsive interactions depends upon the structure and flexibility of the molecule.

In principle, the volume dependence of ε should give more straightforward relations to the theories. However, as far as the strength parameter q and then the coefficient ε are calculated on the basis of the Maier–Saupe molecular field theory we cannot expect that ε will correctly depend on the volume. It is demonstrated in figure 3 (*b*) where a comparison of $S(V)$, $q(V)$ and the ratio $\varepsilon = q(V)/S(V)$ at different temperatures is presented. No serious volume dependence of ε is observed. Unfortunately, a lack of extension of the modern theories of the nematic state to the dielectric properties of liquid crystals does not allow us to analyse all of the collected data in that respect.

4. Conclusions

The results of dielectric relaxation studies of 5CB have been interpreted in terms of the Maier–Saupe theory, i.e. within the framework of the molecular field approximation. A disagreement between the parameters obtained from the experiment and those deduced from the theory is observed. The volume dependence of the strength parameter, expressed by the γ coefficient, is the most interesting property which can be deduced from the temperature–pressure studies of liquid crystals. The value of $\gamma \approx 5{\cdot}2$ obtained for 5CB in different ways indicates that both the attractive and the repulsive interactions must be taken into account if a nematic potential is constructed. This has been demonstrated recently by computer simulations of mesogenic molecules with the use of a realistic atom–atom potential [25] as well as the Gay–Berne potential [17]. Analysis of the experimental results indicates, however, that the repulsive and attractive contributions to the interaction energy in the mesogenic systems depend upon molecular structure. Therefore, it can hardly be expected that a general potential parameters can be found.

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