Study of the Dielectric Properties of 7PCH (4-(trans-4-heptyl-cyclohexyl)-benzonitrile)

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The results of dielectric studies of 7PCH (4-(trans-4-heptyl-cyclohexyl)-benzonitrile) in the nematic and isotropic phases are presented. The complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured in the frequency range 1 kHz–5 GHz, with the use of an impedance analyzer and a time domain spectroscopy (TDS) set-up. The relaxation times: longitudinal $\tau_\parallel$ and transverse $\tau_\perp$ in the nematic phase, and $\tau_i$ in the isotropic phase, were obtained. They served for calculation of the activation barriers for different molecular rotation processes occurring in both phases. Additionally, the retardation factors $g_\parallel$ and $g_\perp$ were calculated. Two theoretical models (Meier-Saupe and Coffey et al.) were applied for the calculation of the nematic potential $q$. A critical analysis of accessible literature data on the order parameter $S$ is given. On that basis the relation $q = qS$ is tested. The obtained values of the strength parameter $q$ are lower for 7PCH than for 5PCH. Possible contributions to the total energy barrier hindering the molecular rotation around the short axis in the nematic phase are considered.

Introduction

Dielectric properties of the 4-(trans-4-alkyl-cyclohexyl)-benzonitrile (nPCH)

![Diagram of the molecule](image)

homologous series have been investigated in a few labs [1–5], but usually the measurements were carried out in a limited range of frequencies so that only part of the properties could be recognized sufficiently. In the present paper, the dielectric spectra obtained for the heptyl-member 7PCH in a broad range of frequencies covering all main relaxation processes taking place in the nematic and isotropic phase are analysed. The spectra were obtained by the use of two experimental techniques: an impedance bridge (1 kHz–13 MHz) and a time domain spectroscopy (TDS, \(\sim 10\) MHz–\(\sim 5\) GHz) method. The measurements were performed for two orientations of the nematic sample (\(E \parallel n\) and \(E \perp n\), \(E = \) measuring electric field, \(n = \) director) which allowed to calculate the relaxation times: longitudinal $\tau_\parallel$ and transverse $\tau_\perp$ in the nematic phase, and $\tau_i$ for the isotropic phase. On that basis the retardation factors $g_\parallel$ and $g_\perp$ were calculated and were used for the estimation of the “nematic potential” according to Meier et al. [6, 7] and Coffey et al. [8–12] formulae. In order to relate the obtained quantities with the predictions of mean-field theories, the order parameter $S = (3\cos^2 \theta - 1)/2$ has to be known. Because of a great scatter of the accessible literature data on $S(T)$ [13–16], a critical analysis of them is given.

Experimental

The 7PCH sample was obtained from R. Dąbrowski, Military Technical University, Warsaw (TDS measurements), and from Merck (impedance measurements). Both samples had the same transition temperatures: melting point $T_m = 30.0^\circ C$ and clearing point $T_{nl} = 59.0^\circ C$, which agree very well with the literature data.

The measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, at \(E \parallel n\) geometry (low frequency (L.F.) relaxation process) were performed in the Bochum University in a cylindrical capacitor normally used for high pressure studies (for details see [17]). The nematic sample was oriented by applying a constant electric field of $E \sim 300\ V/cm$. The TDS set-up in the Uppsala University was used for measurements in the isotropic phase and for $E \perp n$ geometry in the nematic phase. In
this case a magnetic field of about 0.5 T oriented the sample (for details see [5, 18]). In the TDS experiment two time windows were used (10 ns and 100 ns) which give good quality spectra in the range ca. 100 MHz–5 GHz and ca. 10 MHz–400 MHz, respectively. Then both spectra were spliced in the range 100–400 MHz giving one broad spectrum used for further analysis.

Results and Discussion

Figure 1 presents the static permittivities $\varepsilon_{s,||}$, $\varepsilon_{s,\perp}$, and $\varepsilon_{s,\text{is}}$ within the nematic and isotropic phase of 7PCH. The present results (open points) are compared with the data of Schad and Osman [1] (full points) and Kędziora and Jadzyn [3] (triangles). (We neglect here the results by Sen et al. [2] as their $\varepsilon_{s,||}$ values are considerably lower than the other ones). A marked discrepancy of the results in the nematic phase is observed, whereas in the isotropic phase all data agree very well. This means that the discrepancy in the nematic phase is caused by the insufficient strength of the orienting magnetic field. The same was observed in the studies of 5PCH and nCB compounds [4, 19–22]. In LC substances most of the diamagnetic susceptibility anisotropy arises from the benzene rings [13]. Thus, 7PCH having one benzene ring needs a considerably stronger magnetic field in order to achieve a perfect orientation of the nematic sample. The orientation by the electric field depends on the value of the dielectric anisotropy $\Delta \varepsilon$, which is large for nPCH and nCB compounds. However, in that case the substance under study must be very pure in order to avoid the hydrodynamic effects which may appear due to ion motions. In spite of differences in the values of the permittivity components, the mean value $\bar{\varepsilon} = (\varepsilon_{s,||} + 2\varepsilon_{s,\perp})/3$ agrees very well for both sets of data [1, 3] and is distinctly lower than the extrapolated $\varepsilon_{s,\text{is}}$ value. Such behaviour is typical for strongly polar compounds [23, 24] and is caused by antiparallel associations of molecules. Taking our $\varepsilon_{s,||}$-data and the mean values of $\bar{\varepsilon}$ from the figure we calculated the $\varepsilon_{s,\perp}$ values (open points). They are found to be slightly lower than the previous experimental ones. On the other hand, the static permittivity $\varepsilon_{s,\perp}$ calculated from the extrapolation of the TDS spectra (crosses, see below) are consistent with that. After freezing the sample, the permittivity dropped to 2.66 at 27°C and 2.35 at 16°C.

Figure 2 shows measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, in the isotropic (a) and nematic (b and c) phase of 7PCH. They are presented in the form of the Cole-Cole diagrams. The particular spectra were analyzed with the well known Debye, Cole-Cole, Davidson-Cole or Jonscher equations [25]. In the case of the $E || n$ geometry we are dealing with a single relaxation process well described by the Debye equation with the relaxation time $\tau ||$ as the fitting parameter (see Figure 3). In the two other cases the dielectric spectra are much more complex and must be analyzed with care.

The molecule of 7PCH has one strongly polar CN group, so the dipole moment should, in principle, be directed along the main molecular axis. However, due to the large flexibility of the cyclohexyl and heptyl groups, the effective dipole moment [3] derives from the long molecular axis by ca. 20°. For molecules having both parallel and perpendicular components of the dipole moment, the Nordio et al. [26] model predicts contributions to the relaxation spectra from both main molecular reorientations, those around the long and around the short axes. Thus, these motions can influence the spectra measured in both experimental geometries in the nematic phase. Also in the isotropic phase both motions can influence the dielectric spectra [27, 28].

The dielectric spectra measured at $E \perp n$ geometry are very broad (see Fig. 2b) and cannot be described
Fig. 2. Cole-Cole plots for the isotropic phase and two orientations of the nematic phase of 7PCH. (a) The solid line corresponds to the Davidson-Cole equation; the dashed semicircles illustrate a possible division of the spectrum into two Debye-type relaxation processes. (b) The line corresponds to the Davidson-Cole equation with \( \varepsilon_{\perp} \) (extrapolated) shown in Fig. 1 (crosses). (c) The line is a semicircle indicating the Debye relaxation process.

Fig. 3. Activation plots for particular processes shown in Figure 2. The points in the isotropic phase: (vvv) and (aaa) correspond to the two semicircles shown in Fig. 2a; (ooo) come from the Jonscher equation.

by the Cole-Cole equation. Two Debye-type equations fit the spectra quite well, but the dielectric increments \( (\varepsilon_{\perp} - \varepsilon_{\parallel})_{1,2} \) and the relaxation times \( (\tau_{\perp})_{1,2} \) do not depend regularly on the temperature. Therefore we applied the Davidson-Cole equation for finding \( \tau_{\perp} = 1/2 \pi f_{\max} = 1/\omega_{\max} \) according to a procedure described in [25] \( (f_{\max}) \) corresponds to the maximum of losses). The obtained relaxation times are shown in Figure 3. According to the Nordio et al. [26] model the observed process can be attributed to the molecular rotation around the long axis and a small angle fluctuation of the dipole moment in respect to the director.

Recently Jadźyn et al. [27, 28] have found two absorption bands in the dielectric spectra of the isotropic phase of substances having strong longitudinal dipole moments. They assumed that the l.f. band corresponds to the molecular rotation around the short axis, whereas the h.f. band is due to rotation around the long axis or to a small angle fluctuation of the direction of the dipole moment. Both bands are described by the Debye-type equations. In the case of 3CHBT (that can be related to 3PCH with CN\( \rightarrow \)NCS) the ratios of the dielectric increments and the relaxation times characterizing the low and high frequency bands are ca. 4 and ca. 6, respectively. Both processes exhibit also a marked difference in the temperature dependence of the relaxation times.

Taking into consideration the above findings we have analyzed the dielectric spectra of the isotropic phase of 7PCH in two steps. Firstly, we assumed that the spectra consist of two bands described by the Debye-type equations (see Figure 2a). The fits are very good giving ratios of the increments and relaxation times of ca. 5 and ca. 7, respectively. Both these quantities show also reasonable temperature dependencies. However, as one can see in Fig. 3, both processes have close activation barriers which would hinder very different molecular motions if the interpretation given by Jadźyn et al. should be valid here. Additionally, the h.f. process in the isotropic phase ought to correspond to the \( E_{\perp} n \)-process in the nematic phase, whereas a large step at the nematic-
isotropic phase transition between \( \tau_\perp \) and \( \tau_{b.r.} \) (full triangles) is observed. Therefore we think that the division of the spectra under consideration into two different bands is not well established.

In that situation it seems more appropriate to treat the spectra of the isotropic phase of 7PCH as governed by one relaxation process with a distribution of the relaxation times. Figure 4 presents the log-log plot showing marked asymmetry of the low and high frequency parts of the loss spectrum. We prefer to use the Jonscher equation \([25, 29, 30]\) to localize the frequency of maximum of losses \( \varepsilon''(f) \). The obtained relaxation times \( \tau_\text{rel} \) are presented in Fig. 3 (circles); in fact, they are almost the same as those previously obtained for the l.f. process discussed above (open triangles). Also the fits with the use of Davidson-Cole equation give very close \( \tau_\text{rel} \)-values. The fitting parameters are listed in Table 1 (appropriate formulae are also shown). According to the Dissado and Hill theory \([31]\), the dielectric relaxation is coupled to the dynamics of intermolecular processes. At short times the correlation of intercluster vibrations is described by the parameter \( n \). At intermediate times the clusters relax at the rate \( \omega_\rho \). At long times the correlated regions are able to exchange molecules between neighbored clusters. This low-frequency process is governed by the parameter \( m \) \([25, 30–32]\). When \( m = 1 - n \), the loss curve is symmetric and \( \omega_\rho \) is related to the maximum of \( \varepsilon'' \). As can be seen in Fig. 4 and Table 1, the spectra of the isotropic phase of 7PCH reveal asymmetry. Both Jonscher parameters increase with raising temperature. That means that the relaxation far above the clearing point comes closer to Debye. Additionally, the increase of \( n \) with decreasing temperature indicates a higher degree of structural order close to \( T_N \).

Table 2 contains the activation enthalpies \( \Delta^aH \) calculated with the use of the Arrhenius equation, \( \tau = \tau_a \exp (\Delta^aH/RT) \), for the particular relaxation processes observed in the nematic and isotropic phase of 7PCH. They are compared with those obtained recently for 5PCH \([5]\). It is interesting that in the nematic phase of both compounds the activation enthalpies are practically the same, whereas in the isotropic phase the rotation of the longer molecule is hindered by a higher activation barrier originating from the viscosity of the system.

As one can see in Fig. 3, a large step in the relaxation time characterizing the molecular reorientation

\[
\tau = 1/(\omega_\text{max}) = 1/2 \pi f_\text{max}. 
\]

D.-C.: \( \varepsilon''(\omega) = (\varepsilon_\infty - \varepsilon_\infty) \cos^2 \varphi \sin \varphi \beta; \ \omega \tau_0 = \tan \varphi; \ f_\text{max} = f_0 \tan \left( \frac{\pi/2}{\beta + 1} \right). \]

Jonscher: \( \varepsilon''(\omega) = \frac{A}{(\omega/\omega_\rho)^m + (\omega/\omega_\rho)^{1-n}}; \ f_\text{max} = f_p \left( \frac{m}{1-n} \right)^{-n} \).
around the short axis is observed on passing the isotropic–nematic phase transition. This is a consequence of the “nematic potential q” which must be additionally overcome due to nematic order of the molecules. To characterize the slowing down of this motion, Meier et al. [6, 7] have introduced the so-called “redaration factor” $g_{||} = \tau_{||}/\tau_0$, where $\tau_0$ corresponds to $q=0$ and is obtained by an extrapolation of $\tau_{is}$ to the nematic phase [5–7, 17, 19–22, 24] (see Figure 3). The knowledge of the retardation factor can serve for calculating the values of the nematic potential $q$. There are two formulae relating the retardation factor $g_{||}$ with the nematic potential barrier $\sigma = q/RT$:

$$g_{||} = \frac{\tau_{||}}{\tau_0} = \frac{e^{\sigma} - 1}{\sigma}, \quad (1)$$

$$g_{||} = \frac{1}{e^{-\sigma}} \left( \frac{2}{1 + \sqrt{1 + 2e^{-\sigma}}} \right)^{-1}. \quad (2)$$

The first formula was derived by Meier and Saupe [6] on the base of the Maier-Saupe potential [33], and the second was obtained by Coffey et al. [8–11] in a more general way. Recently both equations have been used to calculate the nematic potential for 5PCH [5] which showed that the $q$-values obtained from (2) are ca. 25% larger than those calculated from (1). Then the main assumption of the Maier-Saupe theory was tested, i.e. the proportionality between the nematic potential and the order parameter: $q = \xi S$, where the strength coefficient $\xi$ is supposed to be independent of temperature but dependent on molar volume.

Coffey and Kalmykov [12] have found the relations between the retardation factors $g_{||}$ and $g_{\perp} (= \tau_{\perp}/\tau_0)$ and the order parameter $S$:

$$g_{||} = \frac{2S + 1}{1 - S}, \quad g_{\perp} = \frac{2 - 2S}{2 + S}. \quad (3)$$

Thus, both retardation factors are inter-related, $(g_{||} + 1)g_{\perp} = 2$.

All these relationships can be used for discussing the results of present dielectric studies on 7PCH. In order to do that, the proper values of the order parameter as function of temperature have to be known. However, the literature data show considerable differences concerning the values of $S$ as well as its temperature dependence. This is seen in Fig. 5, where the data obtained from various experimental techniques are collected: diamagnetic anisotropic [13] (full line), Raman scattering [14] (crosses), optical dichroism [15] (full triangles) and deuterium NMR spectroscopy [16] (full points). The low values of the NMR-result arise from the fact that the order parameter was obtained from the quadrupole splitting for the deuterons in a sample of anthracene-d10 dissolved in 7PCH. Also optical measurements give information about the order parameter via dissolved dye molecules. However,
it seems that both these methods provide a correct temperature dependence of $S$. On the other hand, we believe that the magnetic susceptibility measurements give a proper value for $S$ far from the clearing point (that additionally coincides with the Raman data). So, we decided to combine both these features, and all the data were normalized to $S=0.7$ at $T_{NI}-T=30$ K. After doing that, the NMR and dichroic data (open circles and triangles, respectively) coincide nicely in the whole range of the nematic phase. The normalization factors are: 1.4 for NMR data and 1.2 for optical data. The $S$-values read from the line averaging those points will be used for further analysis.

Figure 6 presents the retardation factors obtained from the data of Fig. 3, which are compared with those calculated using (3). One can observe a disagreement between the experimental and theoretical retardation factors, but contrary to the 5PCH case, the parallel retardation factors converge when the clearing point is reached. The ratio of the perpendicular retardation factors is almost constant within the nematic phase and equals to $0.85 \pm 0.1$. The relation $(g_{||}+1)g_{\perp}=2$ is quite well fulfilled close to $T_{NI}$, whereas at $T_{NI}-25$° it is 2.5. The possible reasons for the observed discrepancies have been discussed in [5].

The nematic potentials $q$ calculated according to (1) and (2) are shown in Fig. 7 together with the order parameter $S$. One can see rough proportionality between both quantities, that is better seen on the $q$ vs. $S$ plots in Figure 8. For comparison the data for 5PCH are also plotted in this figure. The slopes of the lines drawn through the experimental points and the origin give the following values of the strength coefficient $\delta$: 19.6 and 16.1 kJ/mol for 5PCH, and 17.0 and 13.4 kJ/mol for 7PCH, with errors of ca. $\pm 5\%$ (first figures correspond to the Coffey et al. formula,
whereas the second ones to the Meier-Saupe formula). At the same time the value of $S$ obtained for 5CB is markedly lower (11 kJ/mol according to (1) [19]. Thus it can be concluded that the molecular interactions in the nematic phase are stronger for the shorter homologue of $n$PCH series. This corresponds with the observation that in the nematic phase the molecules of 5PCH are closer packed than in the case of 7PCH [34].

It is worthwhile to analyze which factors decide about the value of the activation barrier hindering the molecular reorientation around the short axis in the nematic phase. The activation enthalpy $\Delta^a H = 70$ kJ/mol is considerably larger than the sum of the nematic potential $\Omega$ (ca. 6–12 kJ/mol) and the activation enthalpy for the rotational viscosity coefficient $\gamma_1$ (40.5 kJ/mol for 5PCH and 38.8 kJ/mol for 7PCH [35], which can be compared with the activation enthalpy obtained for the isotropic phase, see Table 2).

In order to complete this energy balance it is necessary to take into account the energy of molecular associations which considerably influence the dielectric properties of $n$PCH molecules [1, 3, 4, 36]. This energy is estimated to be of the order of a few $RT$ for LCs with the CN group in the para-position [1, 36].

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