Low Frequency Dielectric Relaxation Process in Liquid Crystals with Nematic and Liquid-Like Smectic Phases

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Results of dielectric studies of the low frequency relaxation process in several substances exhibiting nematic–smectic C polymorphism are presented. They are compared with the data obtained recently for substances with nematic–smectic A and nematic–smectic B phase sequences. It was found that the rate of molecular reorientation around the short axes does not change at the transition between the nematic and a liquid-like smectic phase (Sm A, Sm C), whereas it is considerably retarded at that of the nematic–solid-like smectic (Sm B) phase. However, the activation barrier for this motion is markedly lower in the orthogonal smectics (Sm A, Sm B) than in the nematic and Sm C phases. The analysis of numerous experimental data on the activation enthalpy in the nematic phase shows that the Arrhenius equation conforms better with results than the Diogo-Martins approach, if the nematic range exceeds 10 K.

Introduction

Dielectric relaxation studies of liquid crystals (LCs) showing nematic and smectic polymorphism can give interesting information about the rotation of molecules in different surroundings, especially for the low frequency (l.f.) relaxation process connected with rotations of molecules about the short axes. This motion should change essentially between the nematic phase and a smectic phase having additionally a positional order in form of a layer structure. Taking into account the structural features of smectics, one can distinguish between liquid-like smectic phases, Sm A and Sm C, and solid-like smectic phases, Sm B, Sm G, Sm E, ..., in which some elements of long-range orientational and/or positional order of the molecules can be found [1, 2].

The experimental evidence of the influence of the phase structure on the l.f. dielectric relaxation processes is rather scarce [2–9]. The studies have shown jump-wise changes at the nematic-smectic phase transition of the relaxation times $\tau_\parallel$ and activation enthalpies $\Delta H_\parallel$ characterizing the molecular motions about the short axes. As one could expect, the relaxation times become usually longer in smectic phases, but surprisingly the activation enthalpy is lower in the Sm A and Sm B phases than in nematics [2–9]. This was established for single substances [2–4, 6–8] as well as for homologous series [5, 9].

The present paper deals with six substances showing the nematic and Sm C polymorphism, and a substance with the N–Sm A–Sm C phase sequence. The results are compared with the data of a series of substances with the N–Sm A polymorphism [5] and the N–Sm B polymorphism [8, 9]. The applicability of some activation equations for the description of $\tau_\parallel(T)$ behaviour in the nematic phase having different temperature intervals is discussed.

Experimental

Table 1 contains the chemical structure and transition temperature of the substances studied. They were synthesized by one of us (R. D.), except of HOAB produced by Merck. The measurements of the complex dielectric permittivity, $\varepsilon_\parallel^*(v) = \varepsilon_\parallel'(v) - i\,\varepsilon_\parallel''(v)$, were performed in the frequency range 1–13 MHz using an HP 4192 A impedance analyzer. A parallel-plates capacitor was calibrated with standard liquids. The samples were oriented by a magnetic field (~ 0.7 T). The measurements started in the N phase, and then the samples were cooled down step by step. However, the alignment of the samples usually failed when the transition to a smectic phase was achieved. The temperature of the sample was stabilized within ± 0.1 K.

Table 1. Substances studied and their phase transitions.
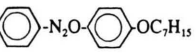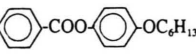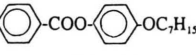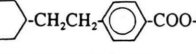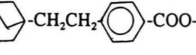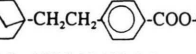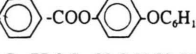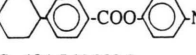
Substance and phase transitions [°C]	Abbreviation
H₁₅C₇O-◯-N₂O-◯-OC₇H₁₅ Cr-74.0-S_C-95.3-N-124.1-Is	HOAB
H₁₇C₈O-◯-COO-◯-OC₆H₁₃ Cr-55.4-S_C-66.7-N-91.0-Is	C8O/OC6
H₁₇C₈O-◯-COO-◯-OC₇H₁₅ Cr-62.0-S_C-70.0-N-89.0-Is	C8O/OC7
H₁₁C₅-◇-CH₂CH₂-◯-COO-◯-OC₈H₁₇ Cr-66.8-S_C-84.2-N-156.0-Is	C5CyC2/OC8
H₁₃C₆-◇-CH₂CH₂-◯-COO-◯-OC₈H₁₇ Cr-77.6-S_C-90.8-N-201.0-Is	C6BCyC2/OC8
H₁₃C₆-◇-CH₂CH₂-◯-COO-◯-OC₉H₁₉ Cr-74.5-S_C-105.3-N-192.2-Is	C6BCyC2/OC9
H₂₁C₁₀O-◯-COO-◯-OC₆H₁₃ Cr-61.0-S_C-77.0-S_A-83.0-N-89.5-Is	C10O/OC6
H₂ₙ₊₁Cₙ-◇◯-COO-◯-NCS [5] Cr-109-S_A-124.5-N-239-Is Cr-117-S_A-129-N-235-Is Cr-104-S_A-146.5-N-225-Is Cr-109.5-S_A-155.5-N-222-Is	nPCHB-NCS 4PCHB-NCS 5PCHB-NCS 6PCHB-NCS 7PCHB-NCS

Table 2. Activation enthalpies $\Delta H_{\parallel}$ and the ratios of the relaxation times $\tau_{\parallel}$ at the transition temperature between the nematic and smectic A or smectic C phases for particular substances.

Substance	$\Delta H_{\parallel}$ [kJ/mol]			τ_{SmA}/τ_N	τ_{SmC}/τ_N
	N	Sm A	Sm C		
HOAB	90±4		93±3		2.82
C8O/OC6	115±3		105±3		1.26
C8O/OC7	125±4		113±4		1.41
C5CyC2/OC8	79±2		100±2		1.22
C6BCyC2/OC8	76±2		102±4		1.27
C6BCyC2/OC9	79±3		115±4		1.16
C10O/OC6	233±10	128±10	107±4	1.18	(1.10)*
4PCHB-NCS [5]	59±3	38±5		0.95	
5BCHB-NCS	61±3	41±5		0.78	
6PCHB-NCS	55±3	40±3		0.82	
7PCHB-NCS	66±5	46±3		0.87	

* Corresponds to τ_{SmC}/τ_{SmA}.

Results

Because the orientation of the samples could not be well established in the smectic phases, the measured permittivity values do not characterize properly the stubstances under study. Therefore, the temperature dependence of the static permittivities will not be analyzed. The observed relaxation processes for all substances were of the Debye-type. The relaxation times were calculated from the frequencies corresponding to the maxima of losses ε''_{max}: $\tau_{\parallel} = 1/(2\pi\nu_{max})$. As an example, Fig. 1 shows the absorption spectra measured in the nematic and Sm C phase of two substances. The relaxation times obtained for the substances with N and Sm C polymorphism are presented in Fig. 2 in the form of log $\tau_{\parallel}$ versus $(1/T - 1/T_{NC})$ plots (T_{NC} corresponds to the N–Sm C transition) in order to avoid shifts in the transition temperature. The same coordinates are used in Fig. 3, showing the results obtained recently for nPCHB-NCS homologous series with the N–Sm A polymorphism [5]. Separately, in Fig. 4 a plot of log $\tau_{\parallel}$ vs. $1/T$ for the substance with two smectic phases is shown. The activation enthalpies $\Delta H_{\parallel}$ were calculated from the Arrhenius equation

$$\tau_{\parallel} = \tau_0 \exp\left(\frac{\Delta H_{\parallel}}{k_B T}\right) \tag{1}$$

and are listed in Table 2.

Discussion

Let us first consider whether (1) can be used for the calculation of the activation enthalpy in a nematic phase existing in very different temperature ranges. It has been well established [2, 3, 10, 11] that substances having a narrow range of the N phase exhibit a strong temperature dependence of the relaxation time $\tau_{\parallel}$. This is also observed in present studies, especially in the case of C10/OC6 (see Fig. 4 and Table 2). In Fig. 5 we have gathered the activation enthalpies obtained for 35 substances with a large spread of temperature ranges of the N phase. Only in case of a very narrow $T_{NI} - T$ range (below, say, 10 K), the $\Delta H_{\parallel}$ values are unrealistically large. For broader nematic ranges a large scatter of points seems to suggest that other factors, like molecular lengths and polarity, may influence the magnitude of the activation enthalpies.

Benguigui [3] has generally questioned the applicability of the Arrhenius equation to the N phase. He
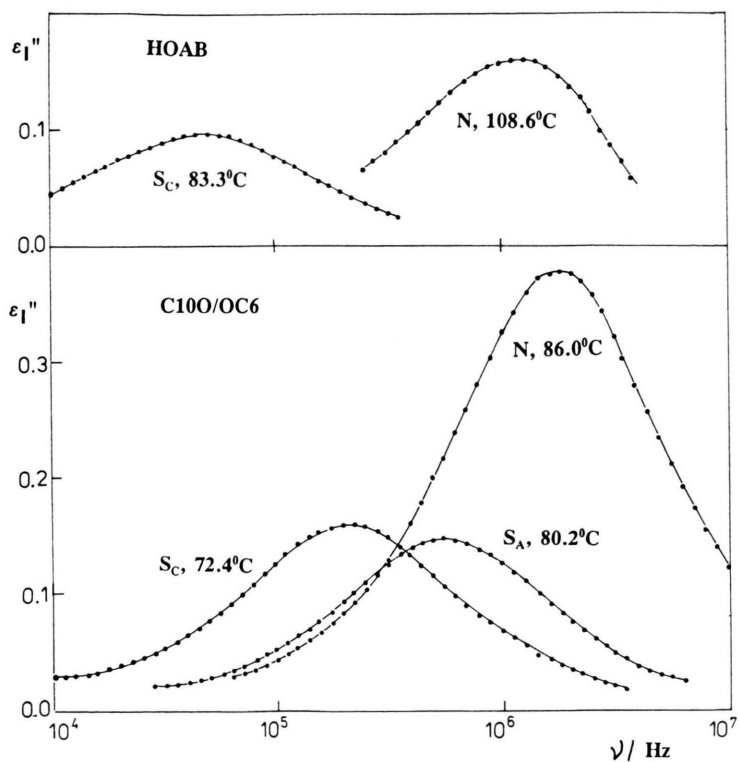
Fig. 1. Examples of the dielectric loss spectra, $\varepsilon''_{\parallel}(v)$, measured for HOAB and C10O/OC6 in different phases.
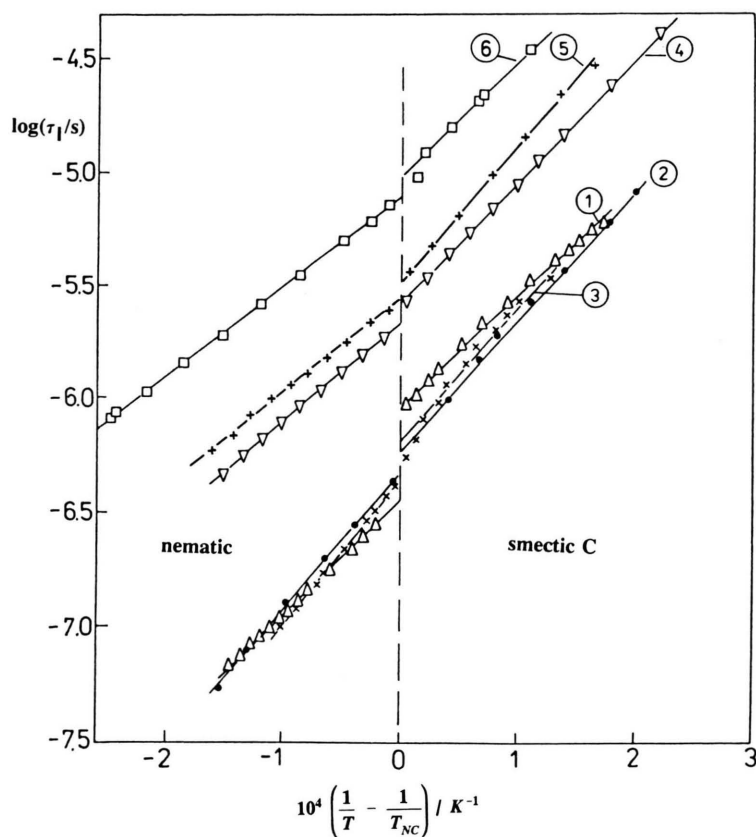

Fig. 2. Activation plots for substances with the nematic–Sm C polymorphism: 1 – HOAB, 2 – C8O/OC6, 3 – C8O/OC7, 4 – C5CyC2/OC8, 5 – C6BCyC2/OC8, 6 – C6BCyC2/OC9. (T_{NC} corresponds to the nematic–Sm C transition.)
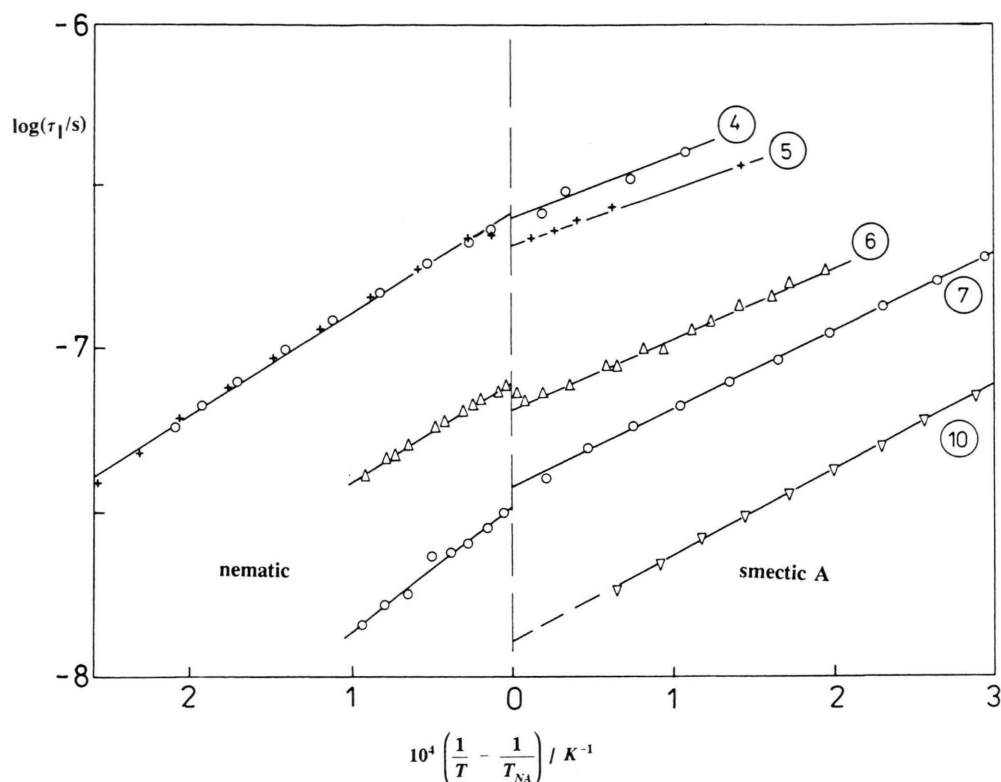
Fig. 3. Activation plots for *n*PCHB-NCS compounds with *n* shown in the Figure (T_{NA} corresponds to the nematic–Sm A transition).

argued that the relation derived by Diogo and Martins [13] would be more appropriate:

$$\tau_{\parallel} = \frac{h}{k_B T}\left[\exp\left(\frac{\varepsilon S}{k_B T}\right)\right]\left[\exp\left(\frac{\theta S^2}{T - T_0}\right)\right], \quad (2)$$

where h is Planck's constant, and S the order parameter. ε, θ and T_0 are nonuniversal parameters depending on the materials. The first exponential term is the probability that a molecule has enough energy to jump over the nematic potential $q = \varepsilon S$, whereas the second one is the probability that there is enough room for that motion. As it has been discussed by Massalska-Arodź [14] the second term may be important at low temperatures close to the glass transition (if it exists). In the vicinity of the clearing point, where S changes distinctly, the energy term seems to be important. Really, in case of a narrow temperature range of the N phase, (1) gives unrealistic parameters. For example, in the case of C 10 O/OC 6 the preexponential factor τ_0 is of the order of 10^{-40} s and $\Delta H_{\parallel}$ is over

200 kJ/mol, thus much larger than for other similar compounds.

On the other hand, the plots of $\ln \tau_{\parallel}$ versus $1/T$ are usually straight lines (see Figs. 2–4) which favors (1) rather than (2). Namely, both equations could be equivalent if the order parameter $S \sim (T - T_0)^{0.5}$, whereas it is well described by the Haller equation $S = S_0(T^* - T)^{\lambda}$ with $\lambda \approx 0.2$ [15, 16] (additionally it is necessary to note that T^* is close to T_{NI}, whereas T_0 is supposed to be distinctly lower [3, 13]). Therefore, Benguigui's objections seem to be not substantial, especially when the N phase is very broad and the measurements are performed in temperature intervals which are far below of T_{NI}. That is the case for *n*PCHB-NCS substances, as well as for C 5 Cy C2/ OC 8, C 6 BCy C2/OC 8 and C 6 BCy C2/OC 9 compounds, for which the dielectric spectra were measured at $T < (T_{NI} - 50)$ K [5], where $S(T)$ changes very slowly. In those cases the preexponential factors τ_0 are of the order of 10^{-17} s, like in the smectic phases.
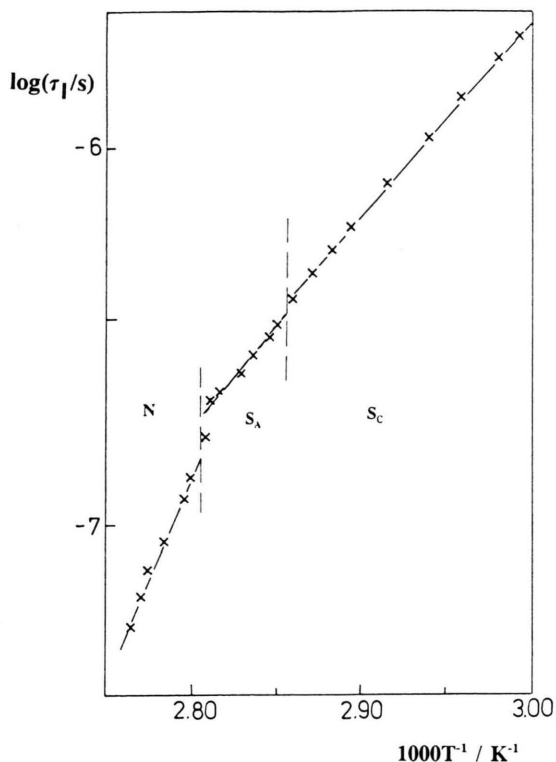
Fig. 4. The Arrhenius plots for C10O/OC6 in different phases.

Let us compare the present results with the ones available in literature for other LC substances exhibiting the nematic–smectic polymorphism. At the transitions between N and Sm A, and N and Sm C phases the relaxation times $\tau_{\parallel}$ change rather little (see Figs. 1, 2 and Table 2). On the other hand, at the transition between N and Sm B phases the ratio τ_N/τ_{SmB} is distinctly larger, reaching values ~ 2000 [8, 9]. Thus, the rate of molecular reorientations around the short axes does practically not change when the nematic–liquid-like smectic phase transition point is approached, whereas it becomes distinctly retarded in the solid-like smectic B phase [2, 3, 8, 9].

Surprisingly, the energy barrier hindering the motion under consideration does not behave in the same way. As it can be seen in Table 2, the activation enthalpy is always larger in the N phase than in the Sm A phase. This holds for very different LC substances and different Sm A phases [2–5]. Also, in the Sm B phase activation enthalpy is smaller than in the N phase [8, 9]. In the case of N–Sm C polymorphism the activation enthalpies obtained in both phases are roughly equal for two-rings compounds, and are larger for Sm C phase in case of three-rings compounds. A small increase of a hinderance of the motion is observed for longer members of a homologous
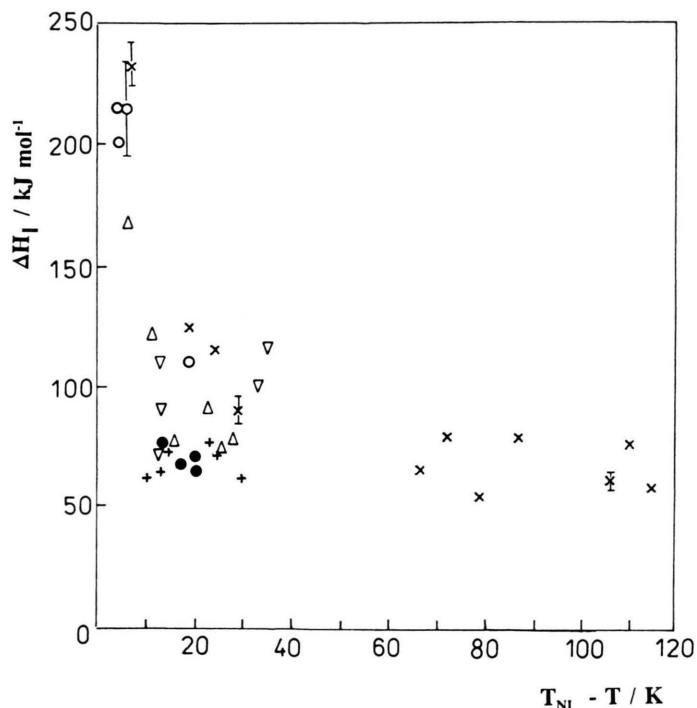

Fig. 5. Values of the activation enthalpy obtained for different compounds in the nematic phase versus the range of the phase. The results come from: × – present paper, ○ – [10], △ – [11], ▽ – [5], + – [12], ● – [7].

series, whereas the replacement of cyclohexyl by a bicyclic ring does not influence the activation barrier markedly.

Conclusions

The results on the low frequency relaxation process in several LC substances exhibiting the nematic and smectic polymorphism allow to conclude that:

– the rate of molecular motions around the short axes becomes practically unchanged in the case of 'nematic–liquid-like smectic' (Sm A, Sm C) phase transitions, whereas the transition 'nematic–solid-like smectic' (Sm B) results in a considerable decrease of the relaxation times;
– the activation barrier hindering the motion under consideration is markedly lowered if the 'nematic–orthogonal smectic' (Sm A, Sm B) transition is passed; however, the question why the relaxation time considerably increases at the N–Sm B transition while the energy barrier decreases is still open;
– at the phase transition 'nematic–Sm C' the values of $\Delta H_{\parallel}$ are almost unchanged in case of two-ring compounds, whereas a marked increase is observed for three-ring compounds;
– the Arrhenius equation seems to be appropriate to the analysis of $\tau_{\parallel}(T)$ dependencies if the nematic range exceeds ca. 10 K.

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