Broad Band Relaxation Studies of a Substance with the Nematic, Smectic A, and Smectic B Polymorphism

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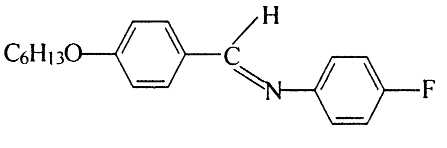
Results of dielectric studies of *p*-hexyloxybenzelidene-*p*′-fluoroaniline (FAB-OC6) are presented. The temperature range covered all phases: isotropic, nematic, smectic A and smectic B. The complex dielectric permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, was measured with the aid of two experimental set-ups: an impedance analyser (1 kHz - 20 MHz) and a time domain spectrometer (20 MHz - 4 GHz). This allowed two main relaxation processes in all phases studied to be separated: the low frequency, l. f., process connected with molecular reorientations around the short axes, and the high frequency, h. f., process connected with the rotations around the long axes. The corresponding relaxation times and activation enthalpies were obtained. The l. f. relaxation time changes step-wise at the phase transition points, whereas the h. f. one passes smoothly through all phases. The results of the studies are confronted with those obtained in recent NMR studies of the substance.

Key words: Liquid Crystals; Nematic; Smetics; Dielectric Relaxation; NMR.

1. Introduction

Dielectric spectroscopy is a powerful tool to study the stochastic reorientational motions of molecules in mesomorphic phases if the constituting molecules possess a permanent dipole moment. The wide frequency range available in this method (from sub-hertz up to several gigahertz) enables one to follow very slow as well as very fast rotations of molecules or their polar parts. On the other hand, a straightforward relation between the measured spectrum, i. e. the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, and the parameters characterizing the rotating molecules (dipole moment μ and the relaxation time τ) facilitates the molecular interpretation of observed relaxation processes. The substance studied, *p*-hexyloxybenzelidene-*p*′-fluoroaniline (FAB-OC6),



has three dipole groups connected with the fluorophenyl ⊘-F group, the bridging aniline CH=N group and the hexyloxy tail, respectively. The dipole moment of the first mentioned group is directed along the main molecular axis, whereas the two others give larger contributions to the transverse dipole moment. In such a case both principal molecular motions, i. e. the rotation around the short axis as well as that connected with rotation around the long axis, should contribute to the dielectric relaxation spectrum. The former process falls in the MHz frequency range and is called the low frequency, l. f., relaxation process. The second one is observed at hundred of MHz or even GHz frequencies and is named the high frequency, h. f., relaxation process. The rates of molecular motions strongly depend on the molecular arrangements in the mesomorphic phases, and the characteristic frequencies can change considerably at the phase transitions [1 - 4]. This especially concerns the l. f. process. FAB-OC6 exhibits the following phase sequence: isotropic (Is) - nematic (N) - smectic A

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(S_A) - smectic B (S_B). Such variety of phases must be reflected in the measured spectra, and thus the values of the quantities characterizing the motions (relaxation times τ and activation enthalpies ΔH) should change considerably at the transitions. Therefore, a broad frequency band is needed to study all possible relaxation processes. For this aim two experimental set-ups were applied: an impedance analyser covering the frequencies from ca. 1 kHz to 20 MHz, and a time domain spectrometer (TDS) for the range 20 MHz - 4 GHz.

The studied substance has recently been investigated by the ^{2}H nuclear magnetic resonance (NMR) method [5, 6]. The spectral densities of FAB-OC6 deuterated in the benzelidene methine, in the aniline ring, and in the hexyloxy chain were analysed giving the orientational order parameters. The quadrupole spin-lattice relaxation times were also determined. They were discussed within rotational diffusion models for the reorientational motions, taking also into account internal rotations and collective fluctuations. Some aspects of these studies will be discussed, taking into consideration the present dielectric relaxation results.

2. Experimental

The sample was synthesized as described in [7]. Its phase transition temperatures detected in the cooling rate were: Is - 62.3°C - N - 59.8°C - S_A - 55.7°C - S_B - 30°C - Cr, which are slightly different from those reported in [7]. The measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were performed with the aid of two sets of apparatus. In the frequency range 1 kHz - 20 MHz an Agilent 4194A impedance analyser was used. The plane capacitor ($C_0 \sim 50$ pF) has gold covered plates. In the N phase the sample was oriented by means of a magnetic field ($B = 0.8$ T). To study the high frequency processes taking place in the substance the time domain spectrometer (TDS) at Uppsala University was used to cover the frequency range 20 MHz - 4 GHz. Two time windows, 10 ns and 50 ns, were used and then the spectra were spliced [8]. All measurements were carried out only on cooling the sample. During collection of the spectra the temperature was stabilized within ±0.1 K.

3. Results

The static permittivity, measured in all phases of FAB-OC6, are shown in Figure 1. In the N phase the sample could be aligned by the magnetic field, but at the transition to the S_A phase the orientation of the sample was always lost, even in the case of very slow cooling rates. Thus, in the smectic phases we measured a 'polycrystalline' sample.

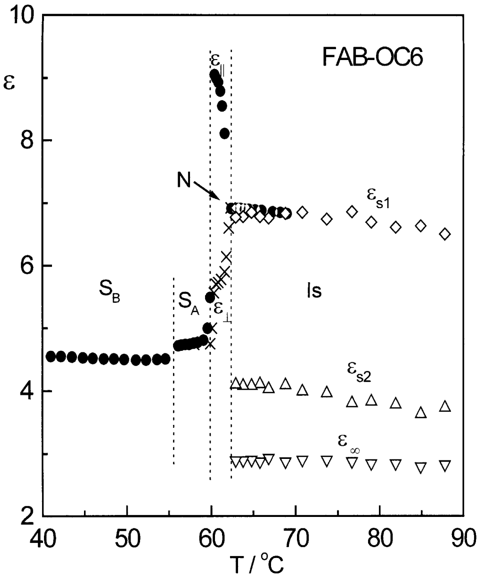

Fig. 1. Static permittivities measured in different phases of FAB-OC6. Open symbols come from the TDS measurements, the others from the impedance analyser. ε_{s1}, ε_{s2} and ε_∞ were determined from the analysis of the TDS spectra as shown in Fig. 2 (compare (2)).

Typical relaxation spectra collected for particular phases of FAB-OC6 are presented in Fig. 2 in the form of Cole-Cole diagrams. The depressed semicircles shown result from the well known equation

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}}, \tag{1}$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and α characterizes a distribution of the relaxation times τ. When necessary, the conductivity term was added to (1). Open symbols indicate the spectra obtained with the aid of the TDS set-up, whereas the full symbols correspond to the data from the impedance analyser.

In the isotropic phase (Fig. 2a) the l. f. and h. f. processes merge, giving one broad relaxation spectrum. The corresponding relaxation times can be calculated by fitting the spectrum to a model function assuming two relaxation processes:

Table 1. The activation enthalpy $\Delta^{\#}H$ (in kJ/mol) for the relaxation processes in the isotropic and LC phases of FAB-OC6 as determined from the dielectric relaxation and NMR [6] studies.

	Phase			
	Isotropic	Nematic	Smectic A	Smectic B
DS:				
l. f. process	36 ± 3	200 ± 20	144 ± 5	102 ± 2
h. f. process	26 ± 4	26 ± 4	26 ± 4	26 ± 4
NMR:				
$D_\perp$	—	39.4 ± 2.1	39.4 ± 2.1	
$D_\parallel$		48.1 ± 2.5	48.1 ± 2.5	36.6 ± 5.4
D_R		39.0 ± 4	39.8 ± 2.2	35.5 ± 2.6

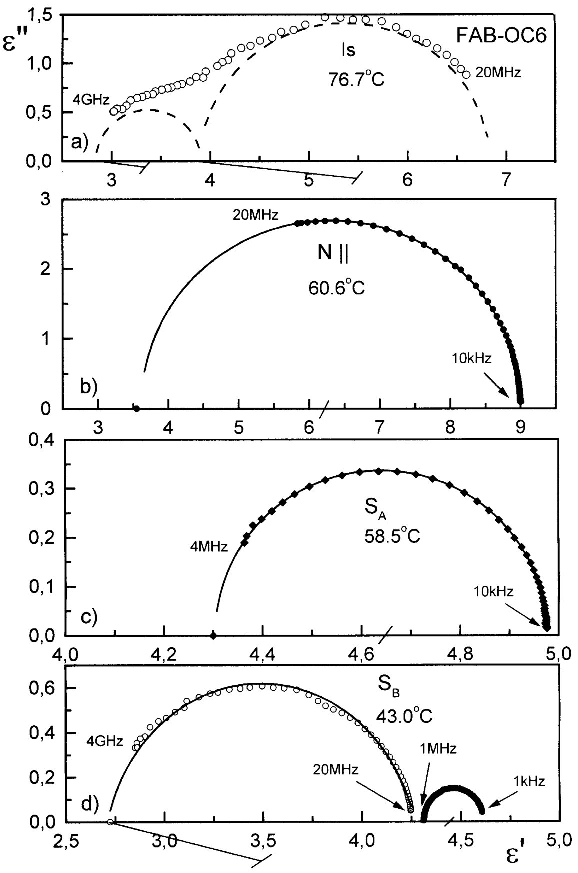

Fig. 2. Cole-Cole plots for the a) isotropic, b) nematic, c) smectic A, and d) smectic B phases of FAB-OC6. The spectra marked by open points were obtained by the TDS method, the others were measured by the impedance analyser.

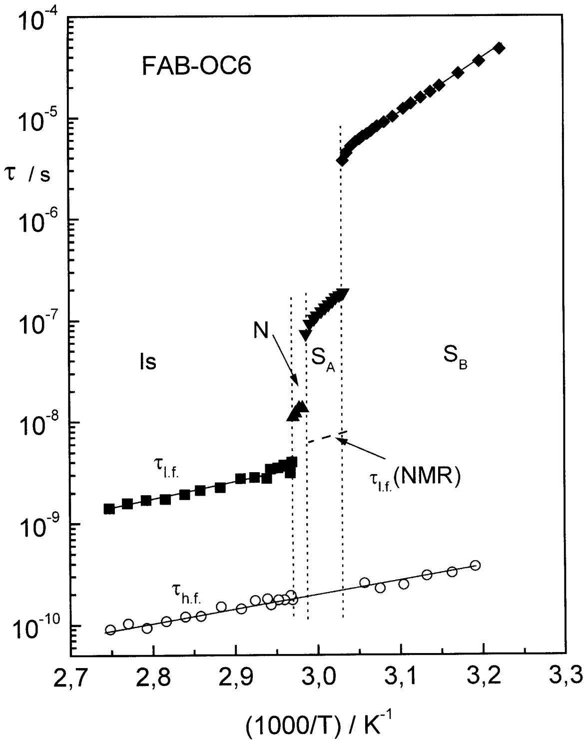

Fig. 3. The relaxation times determined from the analysis of the dielectric relaxation spectra in different phases of FAB-OC6. The l. f. relaxation time calculated from the rotational diffusion constant $D_\perp$ is also marked (see text).

$$\varepsilon_s - \varepsilon_\infty = \frac{\delta_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\delta_2}{1 + (i\omega\tau_2)^{1-\alpha_2}}, \quad (2)$$

where $\delta_1 = \varepsilon_s - \varepsilon_{s2}$ and $\delta_2 = \varepsilon_{s2} - \varepsilon_\infty$ are the strengths (increments) of the two relaxation processes and depend on the dipole moments responsible for a given relaxation process ($\delta \sim \mu^2$). τ-values corresponding to both processes observed differ by a factor of ca. 17 (Fig. 3). Unfortunately, for lack of sample orientation the TDS spectra collected for the N and S_A phases could not be univocally separated into two relaxation processes, although no doubt the h. f. process is characterized by τ-values close to those determined for the Is and S_B phases. In the S_B phase both processes were analysed independently using (1). The calculated relaxation times are shown in Fig. 3 as the Arrhenius plots. The slopes of the lines give the activation enthalpy $\Delta^{\#}H = R(\partial \ln \tau / \partial T^{-1})$ (R = gas constant). Due to the above reason a common line was plotted through the points corresponding to the h. f. relaxation process. The values of $\Delta^{\#}H$ are gathered in Table 1.

4. Discussion

The dipole moment of the FAB-OC6 molecule can be estimated using the group dipole moments method [9, 10], which leads to $\mu \approx 2.8$ D along the *para*-axis of the benzene ring and $\mu \approx 2.1$ D along the axis perpendicular to it. However, the long molecular axis treated as the axis corresponding to the minimum of the moment of inertia of the molecule must differ from the *para*-axis due to nonlinearity of the bridging aniline group and the conformation motions of the alkoxy tail. In order to estimate the angle β which the effective dipole moment forms with the long molecular axis, let us consider the dielectric increments characterizing both principal relaxation processes in the isotropic phase. The dielectric increment reflects the strength of the dipole moment taking part in the corresponding molecular motion: $\delta \sim \mu^2$ [11]. Taking the experimental increments from Fig. 2a one gets $\tan^2\beta = \mu_t^2/\mu_l^2 \approx \delta_2/\delta_1$ which gives $\beta \approx 30°$.

It is worth to note that the l. f. process is of the Debye-type in all liquid crystalline phases (i. e. it is described by (1) with $\alpha = 0$). The same has been observed in other studies [1 - 4]. On the other hand, the h. f. process shows a distribution of relaxation times ($\alpha \approx 0.04$ in the Is phase and $\alpha \approx 0.18$ in the S_B phase – compare Fig. 2); this may be connected with slightly different reorientation rates for particular polar fragments of the molecule. The internal rotation motions in the FAB-OC6 molecule were also postulated on the basis of the NMR studies [5, 6].

Figure 3 presents the relaxation times determined for particular phases of FAB-OC6 in a logarithmic scale versus inverted temperature. As is seen, the l. f. relaxation time $\tau_{\text{l.f.}}$ exhibits considerable changes at the transition points, whereas the h. f. one, $\tau_{\text{h.f.}}$, passes smoothly through all transitions. On the other hand, in the NMR studies [6] three rotational diffusion constants were established: $D_\perp$ and $D_\parallel$ characterizing the molecular reorientations around the short and the long axes, respectively, and D_R which characterizes the rotations of the fluoro-phenyl ring alone. According to Zakharov and Dong [12], in the nematic phase the l. f. relaxation time is related to $D_\perp$ via a factor dependent on the order parameter $S = \langle 3\cos^2\theta - 1\rangle/2$,

$$\tau_{\text{l.f.}} = \tau_\parallel = \left[D_\perp \frac{2-2S}{1+2S}\right]^{-1}. \qquad (3)$$

By using this equation it is therefore possible to relate $\tau_{\text{l.f.}}$ to $D_\perp$ (the relation between $\tau_{\text{h.f.}}$ and $D_\parallel$ was not mentioned in [12]). It has been shown recently, however, that a critical analysis of the NMR relaxation data leads to non-univocal values of $D_\perp$ [13]. In the nematic phase, for instance, a global fitting of the data within the Nordio diffusional model gives a well determined value of $D_\parallel$: (7 - 9,8·10^9 s^{-1}) but two quite different minima for $D_\perp$: (1,7·10^8 s^{-1} and 8,9·10^6 s^{-1}). On the basis of the DR value for $\tau_{\text{l.f}}$ it is therefore possible to make a choice between these values, and a value of $D_\perp$ (1,7·10^8 s^{-1}) is consistent with the data from the two methods.

This is not so in the case of the smectic A phase. Taking the order parameter determined for the S_A phase [6], S = 0,8, one can calculate the $\tau_{\text{l.f.}}$ (NMR) values shown in Fig. 3 as dashed lines. A considerable difference between the corresponding values of the relaxation times can be noted. This disagreement is even greater within the SmB_{cryst} phase.

The step-wise changes of $\tau_{\text{l.f.}}$ can be characterized by the retardation factors g defined as the ratios of two relaxation times taken at the transition points: $g_{\text{N-Is}}$ = 3,2, $g_{\text{A-N}}$ = 6,3, and $g_{\text{B-A}}$ = 24,8. As usual, the largest step is observed at the transition between the liquid-like S_A and the crystal-like S_B phase [3]. However, the relatively large $g_{\text{A-N}}$ value differs from that observed for other substances where rather small changes of $\tau_{\text{l.f.}}$ at the N - S_A or N - S_C transitions were established [14].

The most striking differences between both sets of the data collected in Fig. 3 and Table 1 concern the activation enthalpies determined for particular relaxation processes. The activation enthalpies obtained for the l. f. processes in FAB-OC6 from the DS results can be compared with those known for other two-ring compounds having similar chemical structures. Only in the isotropic phase the $\Delta^\# H_{\text{l.f.}}$ values are comparable [2, 3]. In the LC phases the values for FAB-OC6 are distinctly larger in comparison with others. For example, for 6DBT $\Delta^\# H_{\text{l.f.}}$ equals 29 and 53 kJ/mol in the Is and S_A phases, respectively [15]. For 6BT, having the S_E phase, $\Delta^\# H_{\text{l.f.}}$ amounts to 69 kJ/mol in comparison with 26 kJ/mol in the Is phase. The very large $\Delta^\# H_{\text{l.f.}}$ value in the N phase of FAB-OC6 (~200 kJ/mol) is undoubtedly caused by the pretransitional effects; it is well established that in the case of substances having a narrow nematic range (less than ~8 K) the activation enthalpy reaches enormously large values [14].

Contrary to the above, the h. f. process in FAB-OC6 exhibits features common for this type of substances: the relaxation times are of the order of 10^{-10} s, the activation enthalpy is ca. 30 kJ/mol or less, and no remarkable changes of $\tau_{\mathrm{h.f.}}$ at the transitions between the Is, N and different smectic phases are observed [15 - 18]. These results parallel what has been obtained with NMR relaxation methods, which give a value of the order of 10^{10} s^{-1} for $D_{\|}$ (The internal diffusional rotation $D_{\mathrm{R}} = 10^{10}$ can also be determined by NMR methods. D_{R} is probably highly correlated to with $D_{\|}$). The activation energies reported in Table 1 are also comparable within the great uncertainty affecting these values.

5. Concluding Remarks

The broad band dielectric relaxation studies of FAB-OC6 allowed us to establish the relaxation times and activation enthalpies for two main relaxation processes: one connected with the molecular reorientations around the short axis (l. f. process), and the second corresponding to the rotations around the long axis (h. f. process). The h. f. process shows similar features to those established for many other similar substances in different LC phases. However, the l. f. process in the LC phases of FAB-OC6 exhibits two important exceptions from the general behaviour: large activation enthalpies and a jump of the relaxation time at the N - $\mathrm{S_A}$ transition point.

The substantial agreement between the results obtained from DS and NMR within the nematic phase (considering also previous studies) inclines us to say that both methods detect the same molecular motions at least in the nematic phase. The disagreement between the two methods in the highly ordered smectic phases leads us to raise two questions: (i) do both methods detect the same molecular motions in these phases?, and (ii) is it correct to extend to smectic phases the theory used to relate the results of the two methods in the nematic phase?

In the case of the dielectric relaxation studies the way from the experimental spectra to the parameters characterizing the molecular motions in mesomorphic phases is relatively simple and straightforward. A possible weak point may concern the validity of separation of two contributions from the spectra of the isotropic phase. However, a good consistency of the parameters determined in a broad range of temperatures (compare Figs. 1 and 3) corroborates the correctness of the fitting procedure applied.

Further studies of the same LC substance with the aid of the DS and NMR methods would be demanded for elucidating the discrepancies observed in the present case.

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