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Dielectric study of the S\textsubscript{Ad} - S\textsubscript{A2} phase transition of new thermotropic liquid crystals

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Abstract. — In this paper, we will report on the study, in a large frequency range, of some new thermotropic liquid crystals whose phase sequence is made up of S\textsubscript{Ad} - S\textsubscript{A2}-type transitions. At this transition, we observe a dielectric behaviour appreciably different from one sample to another : there is variation in the dielectric static anisotropy and variation in the activation energy of the « flip-flop » rotation in the parallel measurement direction. Our results confirm those obtained elsewhere by means of other investigation techniques like microscopic observations, DSC experiments and X-ray data.

1. Introduction.

The existence of polymorphism in smectic A phases is now well established [1, 2]. The definitions and descriptions are given elsewhere [3, 4]. Smectic phases have been the topic of numerous dielectric investigations [5, 9]. To our knowledge, only one is concerned with the S\textsubscript{Ad} - S\textsubscript{A2} transition [9]. Here we present the dielectric behaviour of mesomorphous substances showing the S\textsubscript{Ad} - S\textsubscript{A2} transition. Some previous physical studies have already been performed on the original samples : microscopic observations, DSC experiments and X-ray studies [10-13]. They reveal the connection between the variations of enthalpy, reduced layer thickness and the optical character of the S\textsubscript{Ad} - S\textsubscript{A2} transition. Dielectric data complete these previous results.

2. Experimental.

We have characterized four original substances whose structural formulae and phase sequences are given in table I. All patterns present the following phase sequence with decreasing temperature : I - N - S\textsubscript{Ad} - S\textsubscript{A2} - K. The complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ is measured within each phase in a large frequency range (5 Hz-1 GHz) by two impedance analysers, an HP 4191 A and an HP 4192 A (respectively 1 MHz-1 GHz and 5 Hz-13 MHz), controlled by an HP 87 computer. They perform automatic measurements and give, in real time, the complex permittivity of the sample, which can then be easily plotted. The measuring cell consists of two plane capacitors located at the end of a coaxial line [14]. Only a small sample volume is necessary (10 mm\textsuperscript{3}). In anisotropic phases, the permittivities $\varepsilon_{\parallel}(\mathbf{E} / \mathbf{n})$ and $\varepsilon_{\perp}(\mathbf{E} \perp \mathbf{n})$ are obtained when the applied electric field is parallel or perpendicular to the director $\mathbf{n}$ respectively. A magnetic field of 1.2 T is used to orient the sample optical axis in the nematic phase. The temperature ranges from the ambient to about 230 °C, and we used an inert atmosphere (nitrogen) to prevent sample degradation, especially in the high temperature range. The accuracy of the temperature determination is below 1 % of the set point.

The overall accuracy of the measured complex permittivities is better than 2 % for $\varepsilon'$ and 5 % for $\varepsilon''$. The described apparatus makes it possible to give
Table I. — Structural formulae and phase sequence of the compounds.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Structural formulae and transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$\text{C}_7\text{H}_4\text{O} - \text{O} - \text{C} - \text{O} - \text{C} - \text{O} - \text{CN}$</td>
</tr>
<tr>
<td></td>
<td>K 130.5 S$<em>{A2}$ 174 S$</em>{Ad}$ 181 N 246 I</td>
</tr>
<tr>
<td>B</td>
<td>$\text{C}<em>{10}\text{H}</em>{21}\text{O} - \text{Cl}$</td>
</tr>
<tr>
<td></td>
<td>K 104 S$<em>{A2}$ 110 S$</em>{Ad}$ 152 N 163 I</td>
</tr>
<tr>
<td>C</td>
<td>$\text{C}<em>{11}\text{H}</em>{23}\text{O} - \text{O} - \text{C} - \text{O} - \text{CH}_2\text{CN}$</td>
</tr>
<tr>
<td></td>
<td>K 106 S$<em>{A2}$ 127 S$</em>{Ad}$ 155 N 160 I</td>
</tr>
<tr>
<td>D</td>
<td>$\text{C}<em>{10}\text{H}</em>{21}\text{O} - \text{O} - \text{C} - \text{O} - \text{C} - \text{O} - \text{CN}$</td>
</tr>
<tr>
<td></td>
<td>K 129 (S$<em>c$ 118) S$</em>{A2}$ 178 S$_{Ad}$ 210 N 230 I</td>
</tr>
</tbody>
</table>

20 measurement points per decade, i.e. more than 150 points in the given frequency range at each measurement temperature.

3. Results.

3.1 Static permittivity ($\varepsilon'$). — The study of the static permittivities was performed at a frequency low enough to prevent dispersion mechanisms and high enough to avoid the influence of conductivity. When the latter is too large (an effect of temperature), the static permittivity is given by the prolongation of the dispersion domain (conductivity is deduced [15]). Figures 1, 2, 3 and 4 show the variations of $\varepsilon'_\parallel$, $\varepsilon'_\perp$, and $\bar{\varepsilon} = (2 \varepsilon'_\parallel + \varepsilon'_\perp)/3$ versus temperature for the four samples. For samples B and C, a strong decrease of $\varepsilon'_\parallel$ with decreasing temperature can be noticed in

Fig. 1. — Static permittivities versus temperature for sample A.

Fig. 2. — Static permittivities versus temperature for sample B.

Fig. 3. — Static permittivities versus temperature for sample C.
the $S_{\text{Ad}}$ and $S_{\text{A2}}$ phases, while $\varepsilon_1'$ behaves exactly opposite, since it increases with decreasing temperature. The curves $\varepsilon_0'(t \, {^0}\text{C})$ and $\varepsilon_1'(t \, {^0}\text{C})$ cross in the vicinity of the $S_{\text{Ad}} - S_{\text{A2}}$ transition, and the sign of the anisotropy reverses. This behaviour is also observed for samples A and D. In case A, $\varepsilon_1'$ continues to decrease while $\varepsilon_1''$ increases, and the change in the sign of $\Delta \varepsilon'$ appears in the metastable $S_{\text{A2}}$ phase. In case D, $\varepsilon_1'$ decreases slightly with decreasing temperature when a strong decrease of $\varepsilon_1''$ is observed, and this leads to a reversal in the sign of $\Delta \varepsilon'$ near the $S_{\text{A2}}$ - Metastable $S_{\text{c}}$ phase transition.

3.2 DYNAMIC PERMITTIVITY ($\varepsilon^* = \varepsilon' - j \varepsilon''$).

3.2.1 Direction $E//n$. — Figures 5, 6, 7 and 8 give the Cole-Cole plots in each phase for the four samples. When the electric field is parallel to the director, the absorption diagram obtained for nematic (N), partial bilayer ($S_{\text{Ad}}$) and bilayer ($S_{\text{A2}}$) phases is a half circle centred on the abscissa. This is known to be a Debye-type mechanism characterized by only one relaxation time [16]. The width of this domain decreases with decreasing temperature in the $S_{\text{Ad}}$ and $S_{\text{A2}}$ phases. When we plot the variations of the critical frequency of the domain versus the inverse temperature, we obtain a diagram made up of straight lines. In figures 9, 10, 11 and 12 we show the type of curves obtained for all the compounds studied. The Arrhenius law (1) has been used to find the activation energy ($W$) of the mechanism involved [15]

$$F_\varepsilon = F_0 \exp(-W/kT)$$

where $T$ is the absolute measurement temperature and $k$ is Boltzman's constant. Because of the narrowness of the $S_{\text{Ad}}$ phase (4.5 °C) in case A, the activation energy obtained must be considered under an angle...
more qualitative than quantitative; so it is for the nematic phase (5 °C) of sample C and the $S_{A2}$ phase of sample B (6 °C).

3.2.2 Direction $E \perp \text{n}$. — When the electric field is perpendicular to the director, we observe a distributed relaxation domain located in a higher frequency band ($\varepsilon''$ is found far over 1 GHz). Figure 13 shows the Cole-Cole plots of the samples quoted in the $S_{A2}$ phase. Quite similar absorptions are observed in the other mesomorphic phases. This type of spectrum can be attributed to the simultaneous intervention of several mechanisms that can be studied by supposing a superposition of a few simple Debye-type mechanisms [16]. The decomposition of the spectra has not been performed because they are incomplete, and it is possible that new relaxation mechanisms appear at frequencies over 1 GHz.

3.2.3 Isotropic phase. — The spectra in this phase were obtainable for all the samples investigated except A and D because of the limitation in working temperature. The Cole-Cole plots obtained are shown in figure 14. The critical frequencies found in this phase are in all cases higher than in the other phases in the parallel direction measurement. The domains observed are of the Debye type at low frequencies (rotation around a transverse axis) and become slightly distributed at higher frequencies where we expect other relaxation mechanisms [16].
4. Discussion.

4.1 STATIC. — In the mesomorphic phases, as a consequence of antiferroelectric order, the polar groups \( \mu \) come closer one to another and their contribution to \( \varepsilon'_1 \) is reduced, simultaneously, the dipole-dipole interaction increases the dipole contribution to \( \varepsilon'_1 \). This leads to a decrease of \( \varepsilon'_1 \) (and an increase of \( \varepsilon'_3 \)) with decreasing temperature. This effect is more emphasized in sample B because of the existence of the polar – Cl side group (Fig. 2). Consequently, a reversal in the sign of the anisotropy can take place. Some previously published data which deal with transitions of the N - SA2 or N - SAd type lead to the same conclusion [6, 9, 17]. One can notice that samples A and D, which differ from one another only in alkoxy chain length, have the same dipole moments, calculated by supposing an extended-form molecular chain and using a vector additive law. At the reduced temperature (0.9 \( T_{NI} \)), the anisotropy of sample D is about 50% greater than that of sample A (Figs. 1, 4). For both samples the evolution of \( \varepsilon'_1 \) versus temperature is different. Therefore, we can say that « antiferroelectric type » and « dipole-dipole » interactions are not similar in the two samples.

4.2 DYNAMIC. — For all the samples in the parallel direction, a single relaxation domain of the Debye type is visible in various phases. These domains are characteristic of a single molecular mechanism that can be attributed to the reorientation motion of the molecules around a transverse axis [16]. In cases A, B and C a neat rupture in the energy slopes is noticeable (\( W_{SA2} \leq W_{SAd} \)) (see Figs. 9, 10, 11). Sample D does not follow this rule since the energy remains constant at the SAd - S A2 transition (Fig. 12).

This singular behaviour would mean that, in the case of sample D, the molecular interactions in SAd and S A2 phases are rather similar. The energies found in previous dielectric studies of SAd and S A2 phases are ordered as follows : \( W_{SA2} \gg W_{SAd} \) [16]. As far as we are aware, sample D of the studied series is the first pure compound to show quasi-equal activation energies in the SAd and S A2 phases (\( W_{SAd} \sim W_{SA2} \)).

Table II. — Superposition of the different investigation techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{Ad} - S_{A2} ) transition température</th>
<th>D.S.C.</th>
<th>X-ray</th>
<th>Microscope</th>
<th>Dielectric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Variation at the transition ( S_{Ad} - S_{A2} ) of</td>
<td>( t ) (°C)</td>
<td>( \Delta H/10^{-3} ) (cal. g (^{-1}))</td>
<td>( d/l )</td>
<td>transient textural change</td>
</tr>
<tr>
<td>B [12]</td>
<td></td>
<td>110</td>
<td>0.33</td>
<td>1.5-1.7</td>
<td>yes</td>
</tr>
<tr>
<td>D [11]</td>
<td></td>
<td>178</td>
<td>~ 0</td>
<td>1.52-1.55</td>
<td>no</td>
</tr>
</tbody>
</table>

(*) But less obvious than for cases B and C
(**) With a reversal in the sign of \( \Delta \varepsilon' \) at the transition \( S_{Ad} - S_{A2} \)
5. Conclusions.

In table II we have summarized what can be pointed out from this dielectric study. As a matter of fact, the present work completes the characterization of the $S_{Ad} - S_{A2}$ phase transition of compounds previously analysed by means of other investigation techniques [10-13], and the results are concordant.

It appears that samples which show a variation of the reduced layer thickness ($d/l$), a variation of the enthalpy ($\Delta H$), and a neat transient textural change at the $S_{Ad} - S_{A2}$ transition present a break in the slopes of the activation energy curves ($W_{S_{A2}} \gg W_{S_{Ad}}$) and a strong variation of the static anisotropies.

In particular, for samples B and C, a reversal in the sign of $\Delta'\epsilon$ takes place in the vicinity of the $S_{Ad} - S_{A2}$ transition. It may be also connected with the fact that this transition is neatly visible under the microscope. Sample D exhibits no appreciable variations of $\Delta H$, $d/l$ and texture at the $S_{Ad} - S_{A2}$ transition. Here, no variation of $\Delta'\epsilon$ and $\Delta W$ appears. As mentioned, samples A and D differ from one another only in alkoxy chain length. Although their dipole moments are the same, their anisotropies are ordered as follows : $\Delta'\epsilon_D \gg \Delta'\epsilon_A$. This allows us to suppose that we are dealing with different types of molecular interactions here.

References