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Enhanced conductivity and dielectric absorption in discotic liquid crystalline columnar phases of a vanadyl complex

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A liquid crystalline vanadyl complex has been studied by DSC, polarizing optical microscopy, the reversal current technique, X-ray diffraction and frequency domain dielectric spectroscopy. The compound exhibits three columnar phases: rectangular ordered ($\text{Col}_{r,o}$), rectangular disordered ($\text{Col}_{r,d}$), and hexagonal disordered ($\text{Col}_{h,d}$), all of which show a dielectric relaxation process at low frequencies. In the $\text{Col}_{r,o}$ low temperature phase this process seems to be connected with a slow relaxation of polarized polymeric chains inside the columns (mHz frequency range). However, in the $\text{Col}_{h,d}$ high temperature disordered phase this relaxation is faster (Hz range). It is interesting that the liquid crystalline phases studied show enhanced conductivity which changes by four orders of magnitude from 10^{-9} S m^{-1} in the orientationally disordered crystal (an ODIC phase) to 10^{-5} S m^{-1} in the $\text{Col}_{h,d}$ high temperature phase. Such a value of the conductivity is typical for semiconducting materials.

1. Introduction

Recently, we published a paper devoted to dielectric and electro-optic properties of two achiral vanadyl liquid crystalline complexes [1]. The molecular structure of these compounds is shown in figure 1. A symbolic

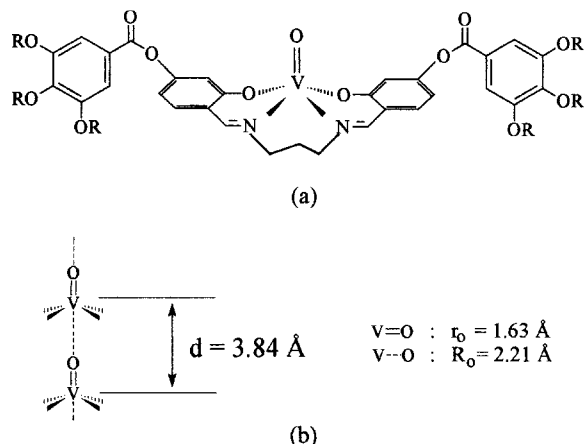


Figure 1. (a) Molecular structure of the substance studied **1(10)** ($R = \text{C}_{10}\text{H}_{21}$). (b) General structure of vanadyl linear chain complexes. The bond lengths indicated are taken from the crystal structure data for a related complex [2].

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name for a particular homologue is **1(n)**. In that previous paper, **1(12)** and **1(14)** were presented. Both compounds display a low temperature ordered rectangular columnar phase ($\text{Col}_{r,o}$) and a high temperature disordered hexagonal ($\text{Col}_{h,d}$) columnar mesophase. Compound **1(12)** shows additionally a disordered rectangular columnar phase ($\text{Col}_{r,d}$). There is a short range coupling between the molecules—two of them form a complementary disc-like entity. Due to a long range coupling in the ordered columns there are polar chains that should contribute to the low frequency dielectric relaxation process. It is a tempting idea that the chains could be ordered in a ferroelectric or antiferroelectric manner. In such a case one would have a proper ferroelectricity or antiferroelectricity in non-chiral materials. In the previous paper we expressed some doubts as to whether the low temperature columnar phase was ferroelectric or not. One important argument for ferroelectricity was that reversal current peaks had been observed and an apparent spontaneous polarization could be found. However, the apparent polarization [2, 3] and its temperature dependence measured by the reversal current method is not typical for ferroelectric or antiferroelectric behaviour.

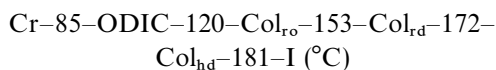
This paper is devoted to **1(10)**, the shorter even homologue which also shows interesting phase behaviour. The aim of this paper is to study the low frequency

dielectric relaxation processes in the low temperature columnar rectangular phase of the vanadyl complex which forms a one-dimensional chain-like structure ordered on a rectangular or hexagonal lattice. As known from IR studies [4], these vanadyl complexes form long range ordered chains in the columnar phases, whereas in the isotropic phase the molecules are not bound in any form of chains or clusters. A second important aim was to check carefully if the reversal current switching is accompanied by any changes in light transmission.

2. Experimental

2.1. DSC and polarizing optical microscopy

The compound denoted as **1**(10) ($R = C_{10}H_{21}$) shows the following phase sequence:



ODIC refers to the orientationally disordered crystal state. The phase diagram was established using a Perkin Elmer DSC (figure 2); a Leitz-Wetzlar Orthoplan polarizing optical microscope was used for the texture observations and electro-optical studies.

2.2. X-ray diffraction

The X-ray diffraction (XRD) experiments were performed on a focusing horizontal two-circle diffractometer (Stoe Stadi 2) equipped with a home-made oven. The CuK_α radiation was focused on a curved Ge(1 1 1) monochromator. For experiments using fast diffractometry, a linear position sensitive detector (Stoe Mini PSD) was employed.

The structure of compound **1**(10) was investigated by XRD at several temperatures to characterize the meso-

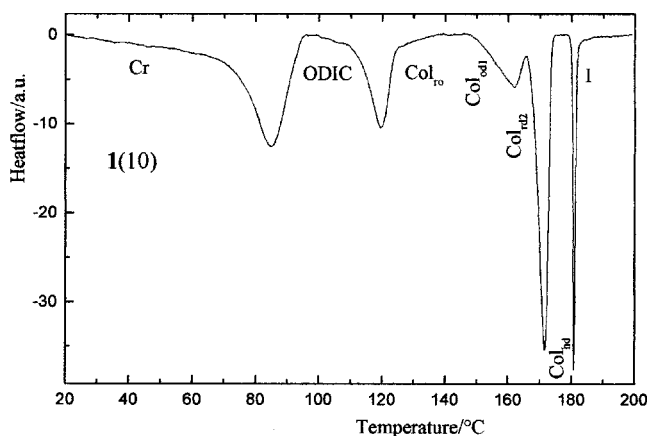


Figure 2. DSC data acquired for the vanadyl complex **1**(10) on heating. The high peak between the Col_{rd} and Col_{hd} phases is connected with the first order transition between the structures with ordered columns and liquid-like columns.

phase types. The compound **1**(10) exhibits three columnar mesophases which display characteristic X-ray patterns (figure 3).

2.3. Dielectric spectroscopy

Frequency domain dielectric spectroscopy (FDDS) has been applied to study the dielectric behaviour of the mesogenic vanadyl complex **1**(10) over the frequency range 10 Hz to 13 MHz by using a computer controlled HP4192A impedance analyser [4]. The dielectric spectra measured contain up to 15 experimental points per decade, and gold electrodes, separated by 23 μm mica spacers, were used to cover the whole frequency range of the analyser. By using dielectric spectroscopy we were able to detect the phase transitions between the columnar phases (Col_{ro} , Col_{rd} and Col_{hd}) and the isotropic phase as well. Due to the dielectric chain relaxation process, the dielectric permittivity shows dispersion in the low frequency range. This process is merged with interfacial polarization [5] and migration of ions and holes [6]. The latter is typical for columnar mesophases [7].

The samples for the dielectric and electro-optical measurements were filled under vacuum after heating the compound slightly above the clearing point. The substance was first homogenized by expelling entrapped gases and residual solvents from the synthesis and purification. The filling process was monitored by the HP 4192A self-balancing impedance analyser set to a frequency of 100 kHz. Upon saturation of the dielectric permittivity, the sample was slowly cooled under vacuum to room temperature. For electro-optical studies, a standard EHC-10 μm cell was used. Reversal current measurements were made under different experimental conditions by varying the frequency and voltage of the driving triangular wave form.

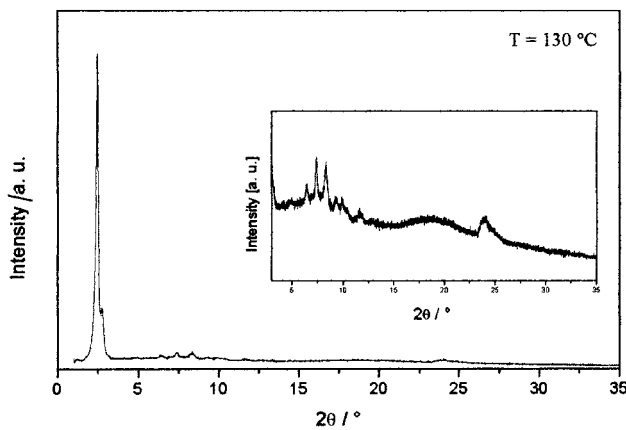
2.4. Electro-optical and reversal current measurements

To observe electro-optical switching we used the Leitz-Wetzlar Orthoplan polarizing optical microscope equipped with a Mettler FP28 hot stage driven by an FP80 Central Processor. The HP 33120A waveform generator and the FLC Electronic F20A voltage amplifier were used to apply high voltage signals to a 10 μm EHC cell. To record polarization currents of the cell, an HP 54603B digital oscilloscope was attached to the computer. The oscilloscope recorded the voltage drop on a 100 k Ω resistor put in series with the EHC measurement cell.

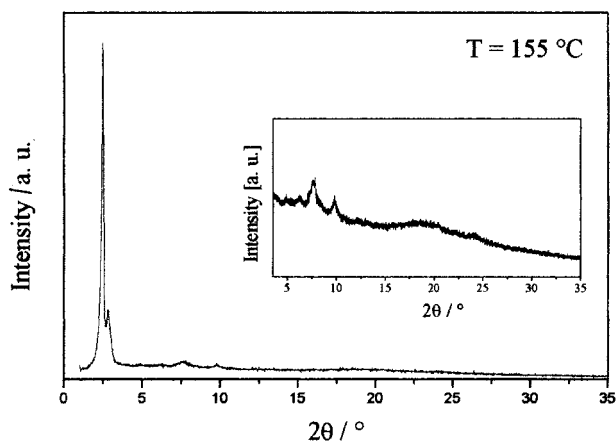
3. Results and discussion

3.1. Phase transitions

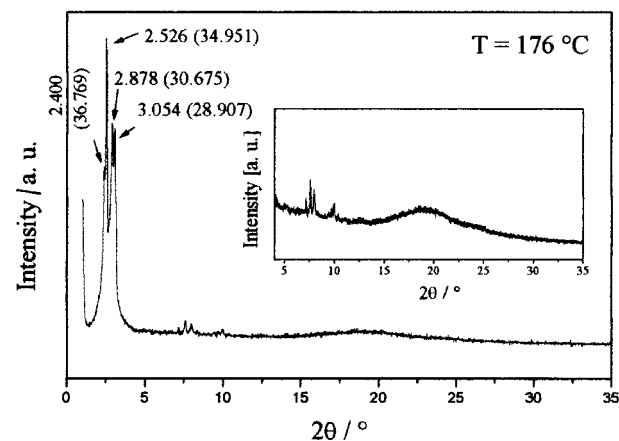
As shown by Serette and Swager [4], the V=O stretching mode in columnar LC phases is shifted to



(a)



(b)



(c)

Figure 3. X-ray diffraction patterns of **1(10)** obtained at selected temperatures (a) 130°C, (b) 155°C and (c) 176°C.

lower frequencies by *ca.* 150 cm⁻¹ due to intermolecular coupling. Our XRD study (figure 3) also substantiates the presence of some long range order inside the columns. The diffraction patterns of **1(10)** at 130 and 155°C showed many sharp reflections in the low angle region, attributed to a two-dimensional rectangular lattice, and a diffuse halo at 4.6 Å. The mesophase at 130°C also exhibited a strong but broader reflection at 3.7 Å corresponding to the vanadyl–vanadyl repeating distance within the chain. Therefore, the mesophase at 130°C is identified as a discotic rectangular ordered columnar phase Col_{ro} (lattice constants: $a = 63.5$ Å and $b = 43.2$ Å). In the mesophase at 155°C the diffraction from the polymer repeating unit is lost. This mesophase is characterized as a discotic rectangular disordered phase Col_{rd} (lattice constants: $a = 62.6$ Å and $b = 42.9$ Å).

It seems that at higher temperatures, one additional mesophase for **1(10)** was found within a narrow temperature range. However, it was impossible to obtain a diffraction pattern of the single mesophase in this temperature range. The diffraction pattern of **1(10)** at 176°C exhibited four sharp reflections in the low angle region that give evidence for the coexistence of different mesophases. The sharp reflections in the low angle region also show different temperature dependences. Due to these increasing and decreasing intensities, the reflections can be assigned to the different mesophases. The sharp peak at 30.7 Å can be assigned to a two-dimensional hexagonal lattice with lattice constant $a = 35.4$ Å. Therefore the high temperature mesophase is identified as a hexagonal disordered columnar phase Col_{hd}.

As known from IR studies of discotic liquid crystals [8], on heating one usually obtains a planar heterogeneous alignment of columns that may transform into a homeotropic alignment at higher temperatures when the transition to the low viscosity Col_{hd} phase occurs. Such a transition is observed for **1(10)** at about 168°C when the conductivity starts to increase remarkably (figure 4), showing the typical behaviour observed before for the other discotic liquid crystals [6, 8]. This phase transition was also observed by polarizing optical microscopy as a transition to a homeotropic texture.

3.2. Dielectric behaviour

At room temperature these vanadyl complexes are very good insulators. Figure 4 shows the temperature dependence of the conductivity measured at 10 Hz for **1(10)**. As can be seen, the conductivity starts to increase with temperature in the orientationally disordered crystal (ODIC); there is a small enhancement of the conductivity at the ODIC–Col_{ro} transition. In the Col_{rd} phase, the conductivity displays a non-Arrhenius behaviour that may be due to a disorder in the polar chains observed

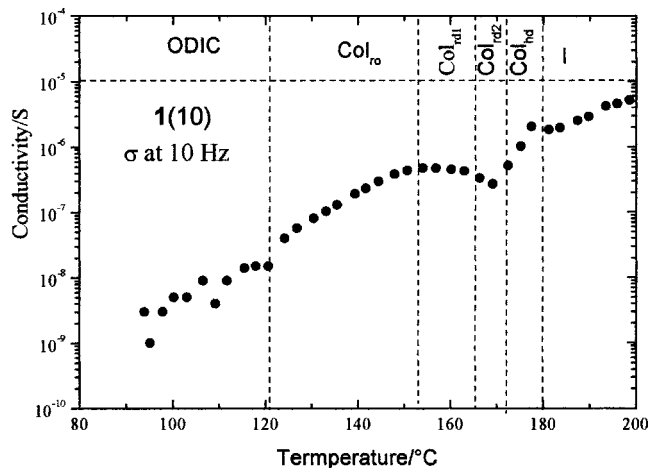


Figure 4. Temperature dependence of the conductivity in the ODIC, Col_{ro}, Col_{rd}, Col_{hd} and isotropic phases.

by XRD. The conductivity resumes growing with temperature in the Col_{hd} phase and continues to grow in the isotropic phase. As the conductivity increases, the low frequency part of the dielectric spectrum is also enhanced (figure 5), leading to a very strong absorption at around 10 Hz. This low frequency dielectric absorption has been observed by us for a few systems and it originates from the diffusion of ions [1, 3, 5]. The dielectric parameters of this process strongly depend on the geometry of the cell. It is particularly interesting to study this process when one of the metal electrodes is isolated from the dielectric studied by a layer of highly insulating materials such as polymer alignment layer.

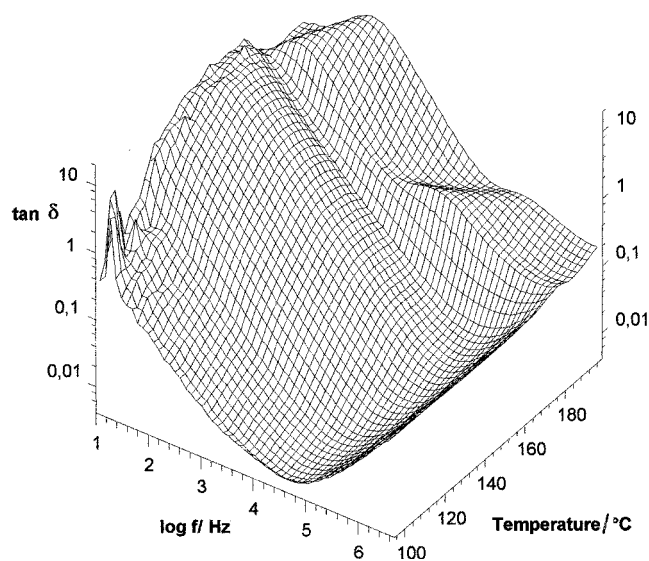
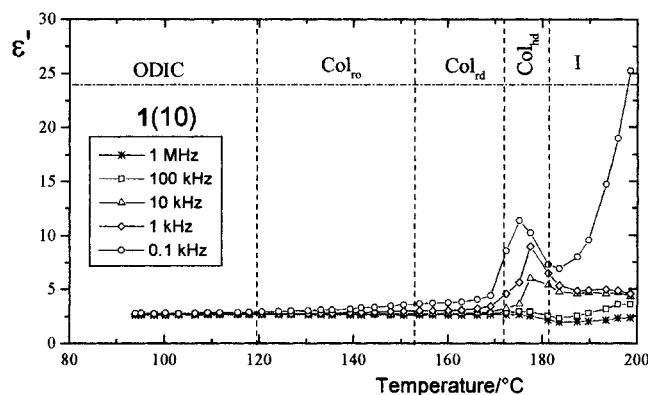


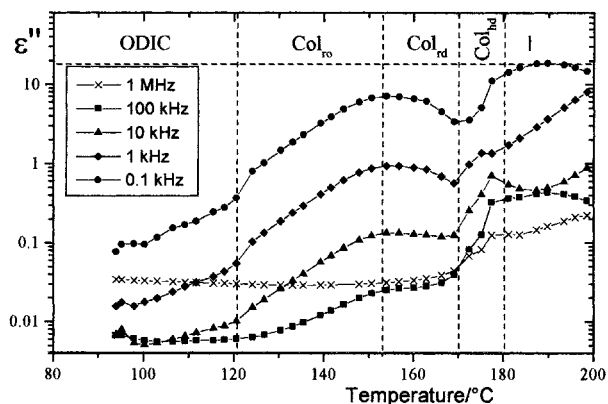
Figure 5. 3D plot of the dielectric loss factor ($\tan \delta = \epsilon''/\epsilon'$) measured for the different phases of **1(10)**.

In the Col_{hd} high temperature phase, the dipole moments inside the columns are disordered and the dielectric spectrum displays a broad peak (figure 5) below 1 Hz. In the Col_{hd} phase and at the Col_{hd}-I phase transition, two dielectric relaxation peaks are present—one falling in the hertz frequency range and the other appearing at around 10 kHz. The low frequency process has a large intensity and may be connected with interfacial polarizations similar to those that we have observed for other LC systems [4]. The high frequency process is due to reorientation of polar molecules in the columns. Below the Col_{hd} phase there is a Col_{rd} phase displaying a broad absorption centred around 50 Hz which might be due to fluctuations of the chain dipoles. This absorption becomes smaller in the Col_{ro} phase due to better antiparallel ordering of the chains.

The dielectric permittivities and dielectric absorption, figures 6(a) and 6(b) acquired at low frequencies for



(a)



(b)

Figure 6. (a) Dielectric permittivities (ϵ') vs. temperature measured at different frequencies for **1(10)**. (b) Dielectric absorption (ϵ'') vs. temperature measured at different frequencies for **1(10)**.

columnar phases of **1**(10) also reveal interesting information. There is a low frequency dielectric relaxation process in the ODIC phase caused mainly by melting of the alkoxy chains. The intensity of this process increases in the Col_{ro} phase wherein the mobility of chains is also enhanced (figure 5). Upon further heating to the Col_{hd} phase, there is an increase in the dielectric permittivity due to the transition to a homeotropic alignment which exhibits a higher linear dielectric polarization (figure 5) due to breaking of the polar ($-V=O-V=O$) chains and the enhancement of ionic currents leading to interfacial polarization. The latter is an analogue of the sub-hertz frequency relaxation mechanism found in chiral materials [5].

3.3. Temperature hysteresis of the dielectric permittivity

The dielectric permittivities and losses measured for **1**(10) show contributions from different relaxation processes (see figure 5). In the ODIC phase there is a relaxation process coming from stochastic motions of the alkoxy chains. The intensity of this process increases in the Col_{ro} phase and a new process is present due to the polarization of chains. In the Col_{hd} phase an additional process arises, figures 5, 6(a) and 6(b), which overwhelms the chain relaxation contribution. In the isotropic phase, in addition to the molecular contribution (overall reorientation of individual molecules), a strong low frequency collective process appears from interfacial polarization of ions as discussed above.

Measurements of quasi-static dielectric permittivities vs. temperature (figure 7) display an interesting temperature hysteresis connected with the anisotropy of the columnar phases. As seen, upon the transition from ODIC to Col_{ro} phase, there is an abrupt decrease by more than 0.2 due to the transition to a planar

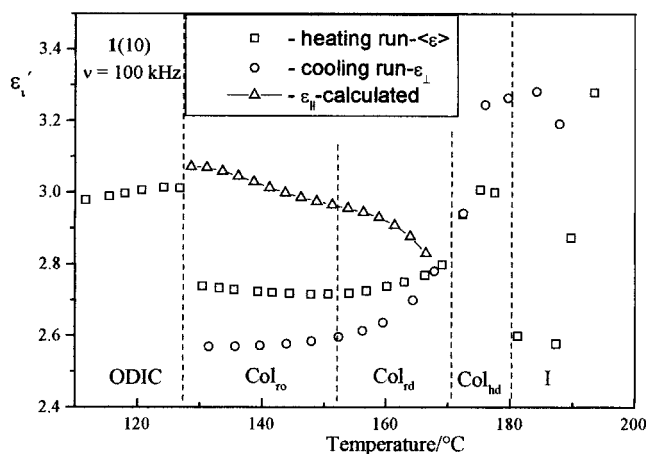


Figure 7. Temperature hysteresis of the dielectric permittivity measured at 100 kHz for **1**(10). The parallel component ($\epsilon_{||}$) of the dielectric permittivity was computed from the measured values of $\bar{\epsilon}$ and ϵ_{\perp} by using formula (1) (see text).

heterogeneous alignment of columns observed usually on heating from the solid phase [8]. There is a change of slope of $\epsilon'(T)$ in the vicinity of the transition between the Col_{ro} and Col_{rd} phases. The distinct change in the quasi-static dielectric permittivity takes place at the Col_{rd}–Col_{hd} phase transition and this effect is most probably due to the planar heterogeneous to homeotropic texture change that was observed by the polarizing optical microscopy. On cooling, the quasi-static dielectric permittivities are distinctly smaller (figure 7, cooling) than those arising during heating. This might be due to the planar homogeneous alignment of columnar structures formed upon slowly cooling. There is one interesting comment to figure 7: if one assumes that, on heating, an average dielectric permittivity ($\bar{\epsilon}$) is measured, whereas on cooling the perpendicular component of the dielectric permittivity tensor (ϵ_{\perp}) is being measured, the parallel component ($\epsilon_{||}$) can be easily computed from the well known formula:

$$\bar{\epsilon} = \frac{2\epsilon_{\perp} + \epsilon_{||}}{3} \quad (1)$$

The computed temperature dependence of the parallel component is shown in figure 7. These data may mean that in the ODIC and the Col_{rd} phases we must give special consideration to the homeotropic alignment of the polar chains. The dielectric data presented in figure 5 also show that the Col_{rd}–Col_{hd} phase transition is first order, also in accord with the comparatively large peak in the DSC trace (figure 2).

3.4. Molecular relaxation in Col_{hd} and I phases

The dielectric spectra obtained for the liquid crystalline phases of **1**(10) are complex—figures 5, 6(a) and 6(b)—and it is difficult to separate uniquely a particular relaxation process from the whole spectrum. There is one process appearing in the kHz range in the Col_{hd} phase, as well as in the isotropic phase, which we were able to analyse. By fitting a Cole–Cole formula we obtain the τ_0 dielectric relaxation time shown in figure 8. The activation enthalpy, computed by assuming Arrhenius-type behaviour of the process under discussion, is very high and equal to:

$$\Delta H = (194 \pm 5) \text{ kJ mol}^{-1}.$$

Such a high value of the activation energy is typical for the soft mode dielectric relaxation process observed in the paraelectric SmA* phase of chiral compounds. This process is most probably connected with the breaking of bonds between two molecules of the disc-like entities. In the high temperature Col_{hd} phase, the columns are liquid-like, showing great reorientational mobility of the molecules inside the columns. In addition to the polar

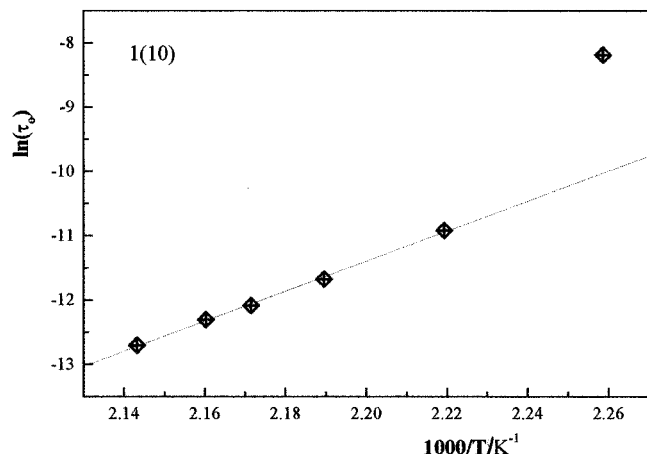


Figure 8. Arrhenius plot for the molecular relaxation process observed in the high temperature phase of **1(10)**.

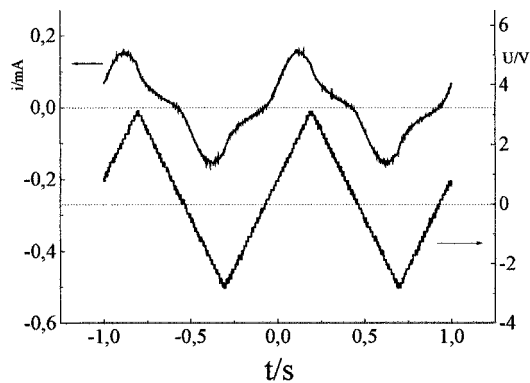
chains, the local discs break up giving a distinct contribution to the dielectric absorption due to the reorientation of molecules around their long axes. Eventually the individual molecules transform to a monomeric state which are not disc-like entities and there is a transition to the isotropic phase.

3.5. Reversal current experiments

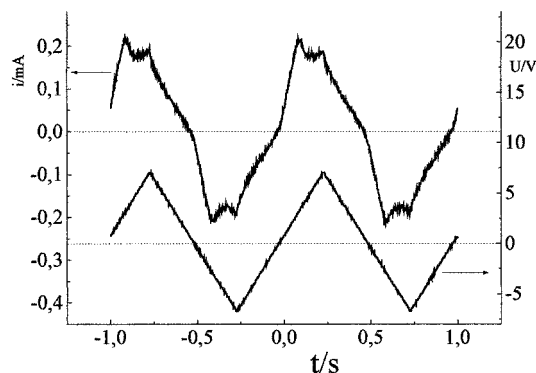
In our previous paper [1], devoted to **1(12)** and **1(14)**, as well as in a conference contribution [10] we have shown that a reversal current response is observed in the low temperature columnar phase. The same kind of behaviour has been observed for **1(10)**. Figures 9(a) and 9(b) show current peaks obtained on heating (a) and cooling (b) of **1(10)**. As seen, on heating the response current is a broad peak apparent only at low frequencies (below 1 Hz) of the driving voltage. On cooling, the response current peaks are sharper, figure 9(b). It is difficult to determine whether the peaks are from a real spontaneous polarization in the system or not. This difficulty is probably due to ions/charges accumulated between the liquid crystal and the polymer aligning layer.

We have established the following arguments against proper ferroelectricity in these VO-complexes:

- (1) For all the substances, we have checked that the reversal current peaks appear only at low frequencies (below 1 Hz), and that they may arise from enhanced ionic conductivity (figure 5) in the columnar phases. The fact that the current peaks are in phase with the driving triangular wave substantiates that this effect has conductivity origins.
- (2) It has recently [11] been found that such reversal current peaks are present not only in the columnar phases, but also in the isotropic phase. Such experiments were not done before because of a short-circuiting in the cells.



(a)



(b)

Figure 9. Polarization reversal current peaks (top curve) and the driving voltage (bottom curve) for **1(10)**. (a) Measurements made while heating; the temperature $T = 120^\circ\text{C}$, the driving voltage frequency $f = 1\text{ Hz}$, the amplitude was $\pm 50\text{ V}$, and the LC layer thickness was $10\ \mu\text{m}$. (b) Measurements made while cooling $T = 130^\circ\text{C}$, $f = 1\text{ Hz}$, amplitude $\pm 60\text{ V}$, LC layer thickness $10\ \mu\text{m}$.

- (3) Electro-optical investigations do not display any electro-optical switching in the temperature range of interest.
- (4) The temperature dependencies determined for the apparent spontaneous polarization [1, 2] are not typical for FLCs.

It is an open problem that for all VO-complexes studied we have observed in the dielectric spectra a broad peak around 1 Hz which may come from a slow reorientation of dipolar chains. It is possible that the dipolar chains do not build up a large spontaneous polarization vector due to weak interactions between the columns.

4. Conclusions

The liquid crystalline vanadyl complex **1(10)** possesses three columnar mesophases— Col_{ro} , Col_{rd} and Col_{hd} —

that display enhanced conductivity and low frequency dielectric absorption. The low temperature phase (Col_{ro}) seems to possess an antiparallel ordering of dipolar chains.

Liquid-like order inside the columns in the high temperature columnar phase (Col_{rh}) has been demonstrated by the presence of a dielectric relaxation process connected with molecular tumbling around the long axis that causes local breakdown of the chain structure.

The apparent polarization measured by the reversal current technique is most probably connected with the interfacial polarization that enhances the low frequency dielectric absorption. As both effects are present in the isotropic phase one should exclude their ferroelectric origin.

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