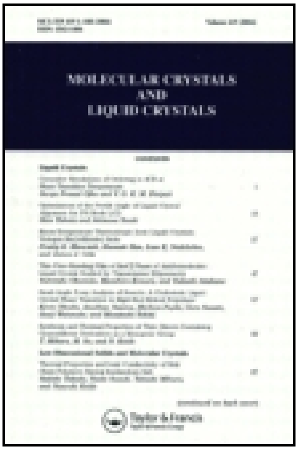

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Roland Germer [a], Frank Giesselmann [a], Peter Zugenmaier [a] & Carsten Tschierske [b]

[a] Institute of Physical Chemistry, Clausthal University of Technology, D-38678, Clausthal-Zellerfeld, Germany

[b] Institute of Organic Chemistry, Martin-Luther-University Halle, D-06120, Halle, Germany

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Anomalous Electric Conductivity in Amphiphilic Smectic Liquid Crystals with Terminal Diol-Groups

ROLAND GERMER[a], FRANK GIESSELMANN[a],
PETER ZUGENMAIER[a] and CARSTEN TSCHIERSKE[b]

[a]*Institute of Physical Chemistry, Clausthal University of Technology, D-38678 Clausthal-Zellerfeld, Germany and* [b]*Institute of Organic Chemistry, Martin-Luther-University Halle, D-06120 Halle, Germany*

Conductivity measurements on a smectic liquid crystal with terminal diol-groups are reported. The average conductivity in the liquid crystalline state *exceeds* the conductivity of the isotropic melt by a factor of 2. This strongly unusual behaviour supports the assumption of fast protonic conductivity in smectic diols, which is favoured in the ordered liquid crystalline state and less efficient in the disordered isotropic state.

Keywords: amphipilic liquid crystals; electric conductivity

INTRODUCTION

Most thermotropic liquid crystals are insulating dielectric materials with typical electric conductivity of about 10^{-7} – 10^{-12} S cm^{-1} due to electrolytic impurities [1]. In carefullly purified samples electric conductivities can be achieved as small as some 10^{-14} S cm^{-1}. Depending on the symmetry of the phase, the electric conductivity may be anisotropic in liquid crystals. In smectic phases the diffusion of ionic impurities is easier along the smectic layers than across the layers and leads to an anisotropy $\sigma_n - \sigma_p < 0$, where σ_n and σ_p denote the electric conductivities perpendicular and parallel to the smectic layer plane, respectively. Typically, σ_p/σ_n is about 2…10, depending on the smectic mesophase and the nature of the electrolytic impurities. The average conductivity

$$\sigma_{av} = \frac{1}{3}(2\sigma_p + \sigma_n) \tag{1}$$

of a liquid crystal is considerably larger than the average conductivity of its crystalline state(s) and smaller than the conductivity of the isotropic melt.

In 1950 Ubbelohde and Rogers [2] observed in solid polycrystalline samples of organic compounds containing *"co-operative assemblages of hydrogen bonds"* an ac-electrical conductivity which is typically a hundred times higher than the conductivity of aprotic solids. In order to explain these findings Pollock and Ubbelohde [3] suggested in 1956 a high proton mobility in the crystalline structure due to the Grotthuss or chain mechanism [4], where a protonic charge is rapidly transferred along a chain of hydrogen bonds (proton translocation):

The Grotthuss mechanism originally applies to high ionic conductivity of H^+ and OH^- in aqueous solution. Following the work of Pollock and Ubbelohde proton conductivity in solids attracted considerable interest in the field of solid state physics and chemistry [5]. Applications of solid-state protonic conductors have been proposed for solid-state batteries, supercapacitors, electrochromic devices (ECD) and solid-state gas sensors.

EXPERIMENTAL CONSIDERATIONS

Today, fast protonic conductivity in the liquid and in the crystalline state is well established. To our knowledge, it has not been discussed so far for the liquid crystalline state. Considering the structural requirements for fast protonic conductivity (hydrogen bond chains), smectic phases of amphiphilic molecules with terminal OH-groups should be ideal candidates to observe fast proton conductivity in liquid crystals: If amphiphilic

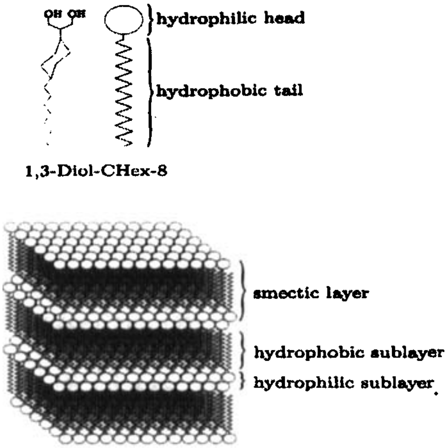

FIGURE 1 Arrangement of amphiphilic molecules (like 1,3-Diol-CHex-8) in liquid crystalline smectic layers: The hydrophilic head groups and the hydrophobic tails are separated in a hydrophilic and a hydrophobic sublayer, respectively.

molecules are arranged in a smectic layer, the hydrophilic OH-head groups and the hydrophobic tails are separated in hydrophilic and hydrophobic sublayers, respectively (Fig. 1). In the hydrophilic sublayers, the OH-head groups are pre-oriented to form extended hydrogen-bond chains or networks which enables fast charge transport by protonic impurities in a chain mechanism. The relaxation time of the OH-reorientation in amphiphilic diols is about 250 ps, reflecting an almost water-like dynamics of the hydrophilic sublayer [6].

The electric conductivity has been investigated for the amphiphilic diol trans-2-(4-octyl-cyclohexyl)-propane-1,3-diol. (1,3-Diol-CHex-8) (see Fig. 1) with the mesophase sequence [7]:

cryst. 93 °C SmB 98 °C SmA 114 °C isotr.

The formation of hydrogen-bonded sublayers is well established for this compound from previous investigations [8]. The electric conductivity of the material was measured in a simple home-made measurement cell (Fig. 2a): Two metallic wires (silver or constantan, 75 μm diameter) are fixed on a glass substrate by an epoxy resin in a parallel arrangement 1 mm apart. The glass substrate with the electrode wires is placed in a hot stage. About 10 mg of the material are placed between the wires and heated into the isotropic melt. The material and the wires are covered by a thin cover slide. The remaining melt outside the covered area is carefully removed. Two principal measuring geometries are available by this setup, depending on the subsequent alignment procedure:

- *Homeotropic geometry:* The isotropic sample is slowly cooled to the liquid crystalline state and the smectic layers align parallel to the glass substrate (Fig. 2b). In this geometry the optical axis (normal to the layers) is normal to the glass substrate and the sample appears completely dark (homeotropic) between crossed polarizers (Fig. 2b). Except for some minor misalignment close to the lower electrode wire in Fig. 2b, an almost perfect alignment of the liquid crystal is obtained by this procedure. In this geometry, the electric field between the electrodes measures the conductivity σ_p parallel to the smectic layers.

- *Polycrystalline geometry:* The isotropic sample is rapidly cooled to the crystalline state, resulting in a polycrystalline morphology with small crystallites. An increase of the temperature into the liquid crystalline SmB state results in an isomorphous texture, consisting of many small smectic domains, randomly distributed in their orientation. This geometry of the smectic mesophase (Fig. 2c) is called the polycrystalline alignment. In the polycrystalline geometry, the electric field between the electrodes measures the average conductivity σ_{av} of the material and some extra conductivity due to defects and grain boundaries which will be neglected in a first approximation.

The conductivity was measured on application of a sine-wave voltage of 40 V amplitude and 10 kHz frequency. At frequencies higher than 1 kHz, the current response was found to be basically independent of the measuring frequency. Below 100 Hz, a considerable phase shift between the applied voltage and the electric current through the cell is observed, indicating an increasing capacitance due to the electric double layer formation.

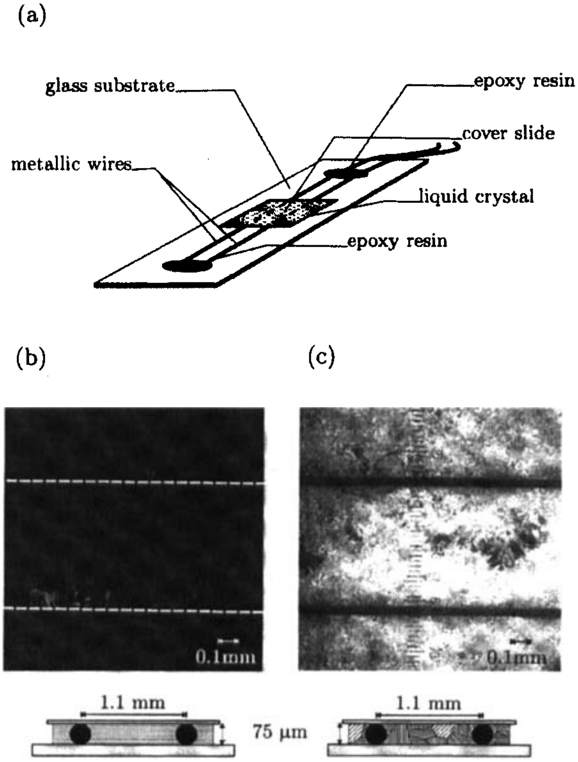

FIGURE 2 Measurement cell and geometry for investigations on the conductivity in amphiphilic smectic liquid crystals. Explanation see text.

RESULTS AND DISCUSSION

The results of these measurements are depicted in Fig. 3: The average conductivity σ_{av} of the polycrystalline sample is well below 0.1 μS cm^{-1} in the crystalline state. At the crystalline - SmB transition a stepwise increase of the conductivity by more than an order of magnitude is observed. The mean conductivity σ_{av} of the SmB phase at 93 °C is about 1.2 μS cm^{-1} and the conductivity σ_p parallel to the smectic layers is about 30% higher (1.6 μS cm^{-1}). At the SmB - SmA transition only minor changes are observed. The conductivity mechanism is marginally affected by the change of the intra-layer order which is hexatic in SmB and fluid in SmA. Just below the clearing temperature at 112 °C. the conductivities σ_p and σ_{av} have reached values of 2.5 and 1.8 μS cm^{-1}, respectively. On passing the clearing temperature, both conductivities, σ_p and σ_{av}, drop to ≈ 1 μS cm^{-1} in the isotropic phase, indicating the breakdown of the conductivity mechanism, responsible for the anomalously increased conductivity of the liquid crystalline states. The conductivity σ_n normal to the smectic layers can be estimated from σ_p and σ_{av} by Eq. (1) and is also plotted in Fig. 3. In the liquid crystalline states, the conductivity σ_n shows quite a normal behaviour, mediating the conductivities of the crystalline and the isotropic state.

To check the reversibility of the electrode reaction the measurements were repeated with constantan wires as electrode material and, within experimental errors. the same results obtained. The basic restriction is that the electrode material is not a passive electrode for protons. In the case of copper as electrode material almost no conductivity was found and, indeed, copper is a passive electrode for protons [5]. This observation supports the assumption that protons play an essential role in the conduction mechanism.

Our conductivity experiments proof an anomalous electric conductivity along smectic layers of protic, amphiphilic molecules. Similar results have been obtained for other smectic phases of amphiphilic diols. The experimental observations can be explained by the assumption of a fast cooperative proton conductivity along hydrogen-bond chains in the hydrophilic sublayers. In order to obtain the proton mobility directly. we are now working on amphiphilic smectics where the proton concentration

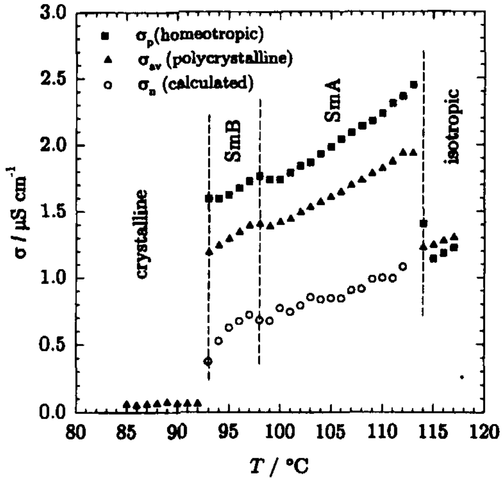

FIGURE 3 Electric conductivity of 1,3-Diol-CHex-8 in homeotropic and polycrystalline geometry: σ_p: electric conductivity parallel to the smectic layers measured in a homeotropic geometry; σ_{av}: average electric conductivity measured in a polycrystalline geometry; σ_n: electric conductivity normal to the smectic layers, calculated from Eq. (1) as $\sigma_n = 3\sigma_{av} - 2\sigma_p$. Measurement conditions: silver wire electrodes, 40 V_{pp}- 1 kHz sine-wave voltage.

can be adjusted by acid dopants. In conclusion, smectic phases of amphiphilic molecules with terminal OH-groups can be considered as a new class of two-dimensional proton conducting materials.

EXPERIMENTAL

Conductivity measurements were performed in a home made cell as described above. The temperature of the sample was controlled by an Instec HS-2 hot stage. After placing a cover slide on the substance and carefully pressing to adjust the gap to the wire diameter, the sample was aligned to homeotropic or polycrystalline geometry as discussed above. The exact cell geometry (diameter $2r$, length l and distance d of the electrode wires) are measured by microscopic observation in order to estimate the cell constant as $C = 2rl/d$. The electrode wires are connected to a 40 V_{pp}-10 kHz sine-wave voltage obtained from a Hewlett-Packard function generator (HP 8116A) and a broad-band amplifier (Krohn Hitc 7500, DC – 1 MHz). The electric current through the sample was measured by the voltage drop over a termination resistor (10 kΩ) and monitored by a Tektronics Oscilloscope (TDS 420). The phase angle between the applied voltage and the current response was checked to be zero. Synthesis and purification of the liquid crystal material 1,3-CHex-Diol-8 are described in the literature [7].

Acknowledgements

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References

[1] L.M. Blinov and V.G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials,* (Springer, New York 1994), Ch. 2.2.

[2] A. R. Ubbelohde and S. E. Rogers, *Trans. Faraday Soc.,* **46,** 1051 (1950).

[3] J.McC. Pollock and A.R. Ubbelohde, *Trans. Faraday Soc.,* **56,** 1112, (1956).

[4] C.T.J. Grotthuss, *Ann. Chem.,* **LVIII,** 54 (1806).

[5] *Proton conductors: Solids, membranes and gels – materials and devices,* edited by Ph. Colomban, (Cambridge University Press, Cambridge 1992).

[6] H. Kresse, A. Dahms, C. Tschierske, and S. Urban, *J. prakt. Chem.,* **333,** 797 (1991).

[7] C. Tschierske, H. Altmann, H. Zaschke, G. Brezesinski. and F. Kuschel. *Mol. Cryst. Liq. Cryst.,* **191,** 295 (1990).

[8] S. Diele, A. Mädicke, E. Geissler, K. Meinel, D. Demus, and H. Sackmann, *Mol. Cryst. Liq Cryst.,* **166,** 131 (1989).