

# Mesomorphism in a Binary Mixture of Non-mesogens: A Dielectric Spectroscopy Investigation

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Z. Naturforsch. **59a**, 659 – 664 (2004); received June 14, 2004

We report on thermal microscopy and low frequency dielectric relaxation of a liquid crystal formed by mixing cholesterol with 1-hexadecanol. Though both components are non-mesogenic, the mixture is found to exhibit a smectic A phase. A 1 V<sub>p-p</sub> a. c signal of 100 kHz was used to study the dielectric response, while the frequency was varied from 5 Hz to 10 MHz for relaxation studies. The dielectric loss in the smectic A phase exhibits a single Debye-type off-centered relaxation in the MHz region. The temperature variation of the relaxation frequency is presented by Arrhenius plots, and the corresponding activation energy is estimated. The temperature variation of the dielectric strength ( $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ ) and the distribution parameter  $\alpha$  in the smectic phase are estimated. The mesomorphic behavior of binary systems, where both components are non-mesomorphic, is discussed.

*Key words:* Smectic Liquid Crystals; Dielectric Permittivity; Dielectric Relaxation.

## 1. Introduction

Low frequency dielectric spectroscopy yields valuable information about the molecular arrangement, intermolecular interactions and dynamics of liquids and liquid crystals. The importance of liquid crystalline materials in electro-optical devices has stimulated the study [1–3] of their dielectric behavior and the relevant re-orientational motions. It has become a challenging task for the synthetic chemists to find liquid crystal molecules with an improved electro-optic response for their use in displays under a confined geometry. The study [4–5] of dielectric dispersion provides valuable information regarding the dipolar response to an external stimulus. Recent liquid crystal dielectric research [6] tries to find smectic polymorphs with faster electro-optic response in comparison to nematics with millisecond response time.

Liquid crystalline phases imply an ever-growing range of quite diverse materials. Numerous liquid crystals are characterized by long-range orientational order. Certain phases exhibit long-range positional order. Both orders have strong influence on the molecular motion of these phases.

Liquid crystallinity in binary mixtures whose components are non-mesogens [7] is known. The forma-

tion of mesomorphic phases by mixing molten cholesterol with a variety of systems has been reported; best known is cholesterol mixed with fatty alcohols [8]. In this paper we report the temperature and frequency dependence of the permittivity ( $\epsilon'$ ) and the dielectric loss ( $\epsilon''$ ) and the activation energy of liquid crystal mixtures of molten cholesterol and 1-hexadecanol. Though both components are non-mesogenic, the mixtures exhibit a smectic A phase.

## 2. Experimental

The sample was prepared by mixing cholesterol (Aldrich, U.K) and 1-hexadecanol (Merck Ltd., U.K) in the volume fraction 30%:70%. The mixture was heated to a temperature well above the melting point with continuous stirring. The homogeneous mixture was quickly cooled and solidified by quenching in ice. The procedure was repeated until constant melting and transition temperatures were obtained. An Olympus (BH-2) polarizing microscope and a Linkam (TMS-94) heating stage with a temperature resolution of  $\pm 0.1$  °C were used for the microscopic textural studies. The heating and cooling rate, followed by thermal microscopy, was 0.1 °C per minute. Microscopic textural observations have confirmed that the

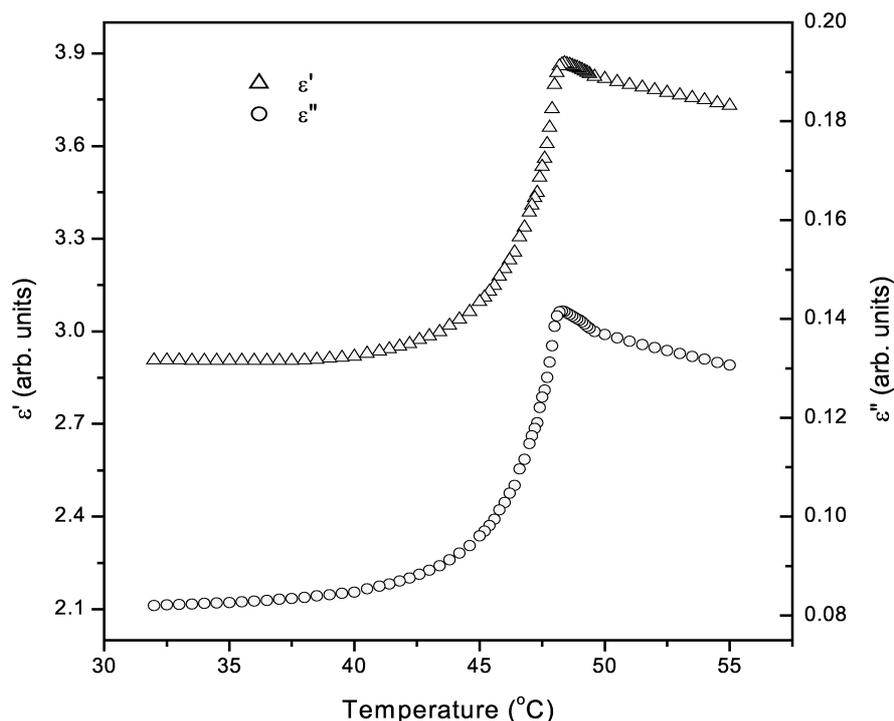


Fig. 1. Temperature variation of the dielectric permittivity ( $\epsilon'$ ) and the dielectric loss ( $\epsilon''$ ) observed at 100 kHz.

mixture under investigation exhibits smectic A phase below 48.2 °C.

Cells [Device Tech Inc., USA] of two transparent conductive (ITO) coated glass plates with 10  $\mu\text{m}$  served for the experimental study. Homogeneous alignment of the sample was achieved by using cells with additional polymer buffing on the conductive-coated glass plates. The temperature of the cell was controlled by a Linkam [TMS 94] temperature controller. The cell was simultaneously observed through a polarizing microscope to ensure homogeneity of the alignment. All experiments were carried out by heating the sample to 3 °C above its isotropic transition temperature and then cooling it to the temperature of the liquid crystal phase of interest at a rate of 0.5 °C per hour. The dielectric permittivity  $\epsilon'(\omega)$  and loss factor  $\tan\Delta(\omega)$  measurements were carried out at 5 Hz to 10 MHz, using a Hewlett Packard Impedance Analyzer (HP-LF4192A) in conjunction with an HP-16047C Test Kit. An a.c sinusoidal wave of 1  $V_{p-p}$  (with variable frequency) was used for the dielectric studies. The empty dielectric cell was calibrated, and the leads permittivity  $\epsilon'_{\text{leads}}$  was determined using standard organic liquids (AR-Benzene) at room temperature. The  $\epsilon'_{\text{leads}}$  was found to be independent of temperature up

to 100 °C from ambient temperatures. The permittivity of the empty cell almost varied by  $\sim 0.001\%$  at 25 °C to 100 °C.

### 3. Results and Discussion

The dielectric permittivity ( $\epsilon'$ ) and the dielectric loss  $\epsilon''$  were studied with decreasing temperature in the range 55–30 °C using 1  $V_{p-p}$  oscillating level at 100 kHz frequency. The permittivity increased (Fig. 1) with decreasing temperature in the isotropic phase and reached a maximum at the isotropic to smectic A transition temperature. The increasing permittivity reflects the increasing dipole correlation as one approaches the isotropic-smectic A transition. At the transition temperature the permittivity drops abruptly.  $\epsilon''(\omega)$ , estimated by multiplying  $\tan\Delta(\omega)$  with  $\epsilon'(\omega)$  also shows a similar trend of variation. The found transition temperature, 48.2 °C, agrees with that of thermal microscopy.

The permittivity and loss factor were studied at 5 Hz to 10 MHz and different temperatures in the smectic phase (see Fig. 2). The peak value of the dielectric loss in the smectic phase shifts to higher frequencies with decreasing temperature. The peak in the loss corresponds to the relaxation frequency  $f_R$ . The observed

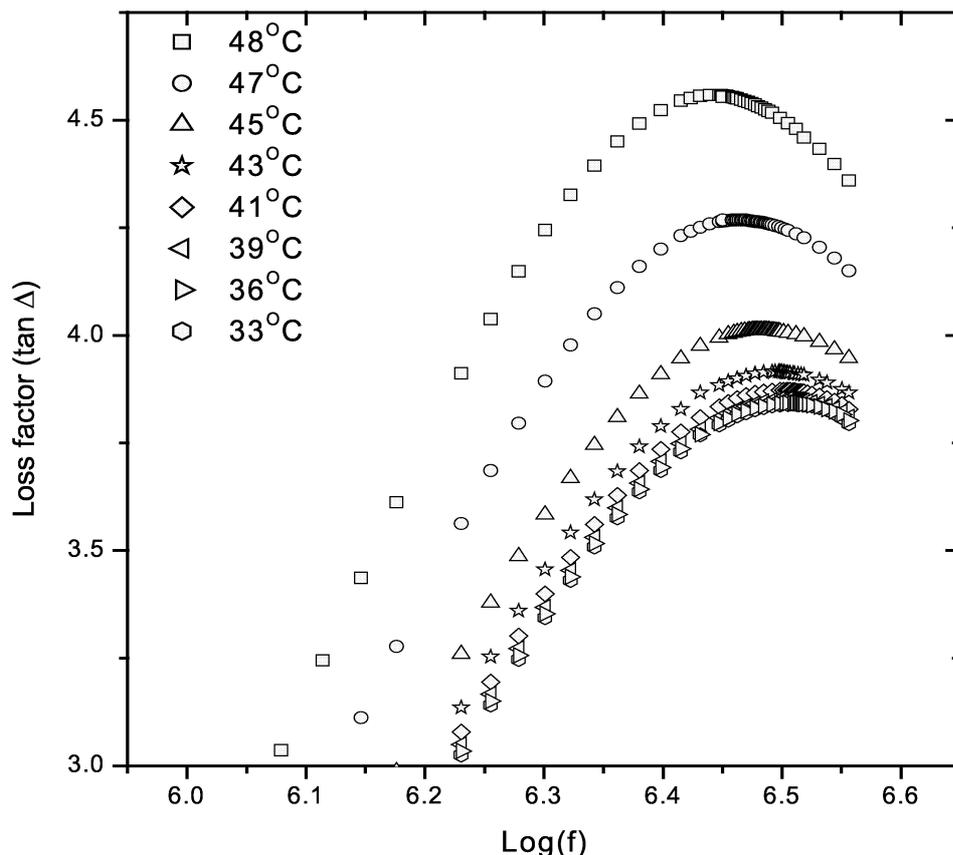


Fig. 2. Frequency variation of the loss factor (in arbitrary units) in the smectic A phase at different temperatures.

relaxation frequencies at different temperatures in the smectic phase is within the range of the reported values of other liquid crystals [9–10].

The observed dielectric loss variation (at different temperatures in the smectic phase) suggests a Debye type off-centered dispersion [11, 12], given by the relation

$$\varepsilon^*(\omega) = \varepsilon_\infty - \left[ \frac{\Delta\varepsilon}{1 + j(\omega\tau)^{1-\alpha}} \right], \quad (1)$$

where  $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$  is the complex dielectric permittivity and  $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$  is the dielectric strength calculated from the data of static permittivity ( $\varepsilon_0$ ) and high frequency permittivity ( $\varepsilon_\infty$ ) values corresponding to the Cole-Cole plots drawn for the observed dispersion at different temperatures in the smectic phase. Further,  $\omega = 2\pi f$ ,  $\tau = 1/f_R$  and  $\alpha$  is the distribution parameter reflecting the degree of freedom of the dipole.

In order to further study the a.c field frequency response in the observed smectic phase (especially in the

Table 1. Temperature variation of the relaxation frequency ( $f_R$ ), relaxation time ( $\tau_R$ ), dielectric loss ( $\tan\Delta$ ) at  $f_R$  and distribution parameter ( $\alpha$ ).

| Temperature in °C | Relaxation frequency $f_R$ in MHz | Relaxation time $\tau_R$ in $\mu$ m | Dielectric loss ( $\tan\Delta$ ) at $f_R$ | Distribution parameter $\alpha$ |
|-------------------|-----------------------------------|-------------------------------------|---|---------------------------------|
| 48                | 2.89                              | 0.346                               | 4.558                                     | 0.144                           |
| 47                | 2.95                              | 0.338                               | 4.268                                     | 0.144                           |
| 45                | 2.99                              | 0.334                               | 4.013                                     | 0.151                           |
| 43                | 3.05                              | 0.327                               | 3.916                                     | 0.153                           |
| 41                | 3.13                              | 0.319                               | 3.872                                     | 0.157                           |
| 39                | 3.20                              | 0.312                               | 3.851                                     | 0.159                           |
| 36                | 3.27                              | 0.305                               | 3.842                                     | 0.162                           |
| 33                | 3.35                              | 0.298                               | 3.840                                     | 0.167                           |

vicinity of the isotropic - smectic A transition), Cole-Cole plots were drawn at different temperatures. A representative Cole-Cole plot is given in Fig. 3 for two temperatures in the smectic A phase. The values of the relaxation frequency  $f_R$ , relaxation time  $\tau_R$  and the distribution parameter  $\alpha$  corresponding to the dispersion at different temperatures in the smectic phase are presented in Table 1. The dielectric strength, estimated

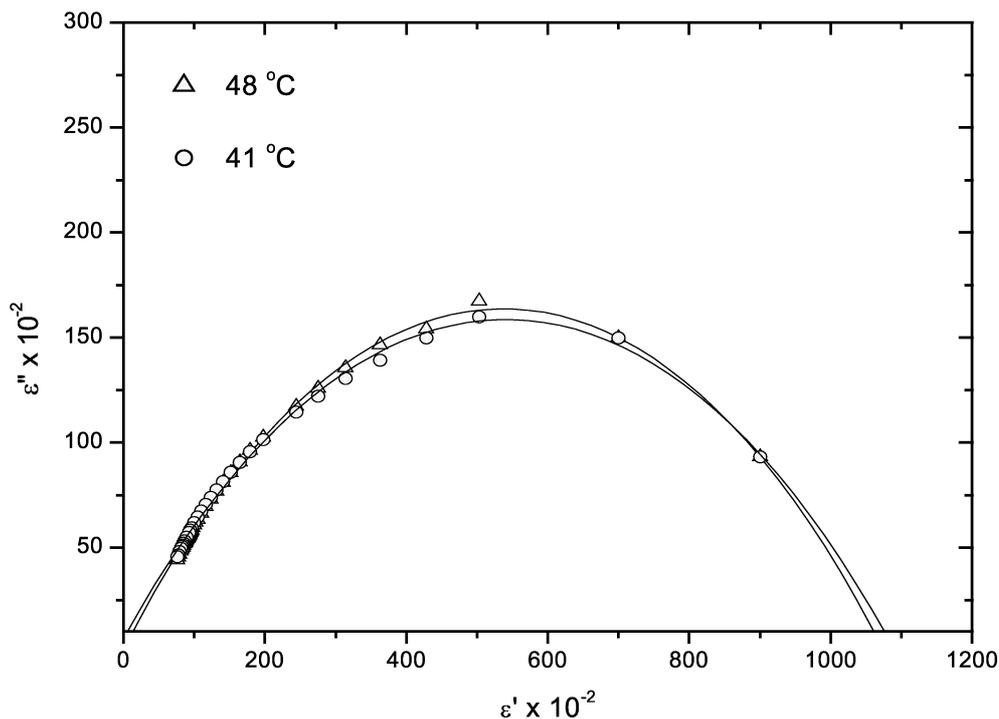


Fig. 3. Representative Cole-Cole plots, drawn at two specified temperatures in the smectic A phase.

from the Cole-Cole plots drawn at different temperatures, is found to vary little with temperature (with a value of  $\Delta\epsilon$  around 10.6), while the distribution parameter  $\alpha$  increases with decreasing temperature (Table 1), reflecting the increasing degree of freedom with decreasing temperature, as experienced by the smectic A structure. Also presented in the table are the loss factors at the relaxation frequency  $f_R$ . The loss factor decreases with decreasing temperature.

The temperature variation of the relaxation frequency is presented through reduced temperature (Arrhenius) plots in Figure 4.  $f_R$  is found to increase with decreasing temperature. This trend of  $f_R$  agrees [1, 5] with that observed in smectic C\* phases where collective dynamics is predominant. The corresponding Arrhenius shift is found to possess an activation energy of 0.91 eV, reflecting the potential barrier experienced by the smectic dipoles during their reorientations in the external field. Similar negative activation energies are reported [10, 13] in smectic C\* phases. The negative activation energy suggests that work is done in annulling traces of cholesteric pitch like regions (or possible dimeric formation due to hydrogen bonding in the presence of alcohol as a component in the binary).

The values of this activation energy are found to agree with earlier reports of other single component systems [14] or mixtures whose components are all liquid crystals [15].

It has been observed that the present mixture (30% cholesterol + 70% 1-hexadecanol) forms a homogeneous liquid crystalline phase. At higher concentration of cholesterol it was observed that cholesterol crystallizes from the mixture when cooled from the isotropic phase. At lower concentration of cholesterol, the mesomorphic range is very small, with the liquid crystal phase extending only by a few degrees before crystallizing into the solid phase. Dielectric studies have revealed that the present mixture behaves like other single component liquid crystals.

It is interesting to note that, although the two components of the mixture are non-mesogenic, the mixture exhibits smectic mesomorphism. Cholesterol, though non-mesomorphic, must be considered as potentially mesomorphic, since even cholesteryl chloride gives a monotropic cholesteric phase, and it is possible that the hydrogen bonding in pure cholesterol increases the intermolecular cohesion and is responsible for its high melting point. Hydrogen bonding is one of the key in-

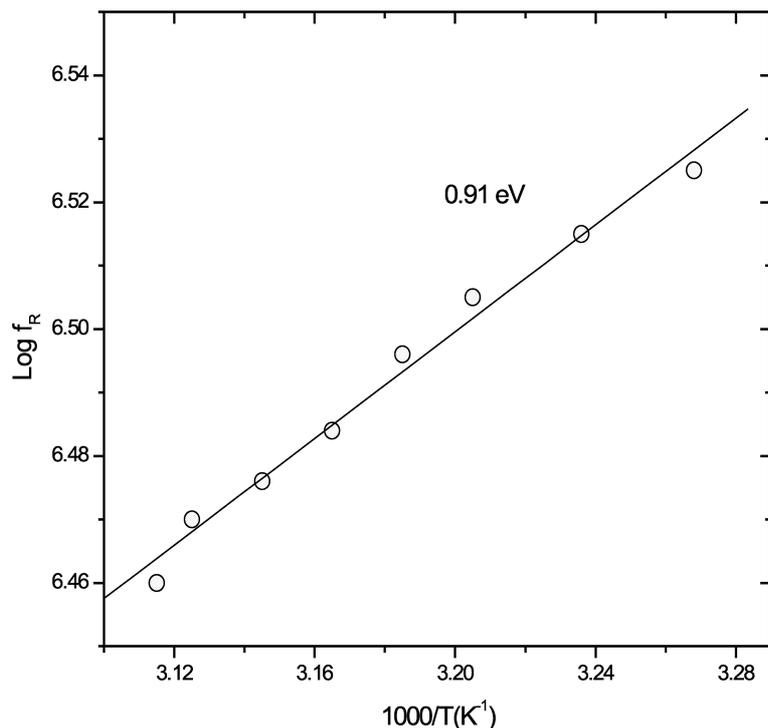


Fig. 4. Temperature variation of the relaxation frequency (Arrhenius plot) in the smectic A phase.

teractions in the case of liquid crystal mixture that results in the creation and stabilization of super structures in liquid crystal materials [16, 17]. In the case of a mixture of two different substances, as in the present case, liquid crystal formation will depend on two factors: first the ability of the molecule to pack into a single liquid crystal “lattice” and secondly, the mean orientational cohesive energy [7, 18]. Introduction of 1-hexadecanol molecules may create alternate sites to which the cholesterol hydroxyl group can hydrogen bond without resulting in the high melting crystal lattice, yet giving sufficiently strong intermolecular attractions to make possible the existence of an anisotropic melt.

As mentioned earlier, the increase in  $f_R$  with decrease in temperature is comparable with the earlier reported [1, 5] high frequency relaxation at the outset of a smectic C\* phase with decreasing temperature (in the vicinity of a smectic A-C\* transition). This anomalous behavior is due to the lifting of the degeneracy of the smectic A high frequency soft-mode into the low frequency ( $\sim 100$  Hz) Goldstone mode and higher frequency mode (anomalous temperature dependence). The anomalous dependence may be due to the coupling of tilt of supermolecular helix in smectic C\* phase. As such, the present observed anomalous trend may originate from supra-molecular (hydrogen bonded) liquid crystal formation.

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