Determination of Ionic Mobility in Mesomorphic Materials

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Determination of Ionic Mobility in Mesomorphic Materials

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Ionic mobility has been measured in isotropic and mesomorphic state of the following cholesteric esters: cholesteryl oleate, cholesteryl myristate, cholesteryl pelargonate and cholesteryl erucate, and nematic material PCB. There was attempts to orient the materials in magnetic field, however no orientation has been obtained for cholesteryl esters. The mobility anisotropy in PCB has been found to be 1.54.

1   INTRODUCTION

The electrical conductivity of liquid crystals has inspired scientific research for several decades already, and recent progress in the development of optoelectronic devices and related studies have stimulated this interest even more. In general, the opinion is that the electrical conductivity of these materials is due to the motion of ions[1], but several papers have suggested the possibility of electron injection.[2] Unfortunately, the lack of knowledge regarding the charge carrier mobilities and the dependence of mobility on temperature and electric field makes it difficult to interpret experimental results. In the present contribution some results of ionic mobility determination, primarily in cholesteric liquid crystals, are reported.

2   EXPERIMENTAL

2.1   The materials

The following cholesteryl esters were used in the studies: cholesteryl oleate, cholesteryl myristate, cholesteryl pelargonate and cholesteryl erucate. The cholesteryl myristate, manufactured by Merck AD Darmstadt, was purified

TABLE I

The mesophase range in different materials

Material	Mesophase °C		
	Optical measurements	Microscopic measurements	DSC[a]
cholesteryl oleate (ChO)	42.0–52.0	42.7–52.5	42–50.3
cholesteryl myristate (ChM)	68.5–86.5	68.7–86.8	71.5–83.6
cholesteryl pelargonate (ChP)	72.5–90.5	72.6–91.0	74–90
cholesteryl erucate (ChE)		47.8–49.5	—
PCB	21.1–34.8	21.2–35.1	—

[a] Differential scanning calorimetry.

chromatographically, whereas the oleate, pelargonate and erucate, obtained from the Institute of Basic Chemical Science of the Medical Academy in Lodz, were purified by triple recrystallization and then by columnar chromatography.

In accordance with literature data, these materials feature an intricate diagram of phase transitions. Data on the phase transitions of these substances are given in Table I. Microscopic examinations and literature data indicate that the oleate and myristate can exist in forms with smectic and cholesteric structure, the pelargonate only in the cholesteric structure, whereas the erucate in the smectic A mesophase. These facts have been confirmed by microscopic studies.

The nematic material used pentacyanobiphenyl (PCB), was received from the Institute of Organic Chemistry of Technical University of Warsaw, Poland, and was purified by recrystallization and vacuum destillation.

2.2 The method

To determine the carrier mobility in insulating liquids the time of flight method is frequently adopted. To inject the ions into the liquid one can use either the pulse of strongly absorbed light or the pulse of ionizing radiation or the injection of the ions from the properly chosen electrode. The main problem encountered here is the distortion of electric field present in the sample because of non-ohmic character of an electrode as well as the space charge of injected charges.

The problem has been solved for the case of thermal injection of charge carriers. This has been done for the electronic insulator,[3,4] however the results can be applied for any type of insulator with field independent charge carrier mobility. The correction factor given by this theory is relatively small.

For charge carrier drift in unperturbed uniform field one can have well known formula for the transit time,

$$t_p = \frac{d^2}{\mu V}$$ (1a)

where: d = thickness of a sample (plane geometry), μ = mobility, V = voltage. In the case of thermally injected space charge perturbed current flow

$$t_p = 0.79 \frac{d^2}{\mu V}$$ (1b)

The theory of other type of carrier supplying electrodes (emission limited: Fowler–Nordheim or Schottky) was not worked out. However such electrodes are often used in time of flight experiments. In the present paper the ions were injected (field extracted from electrolyte) from an electrode. The idea has been explored for solids[5] as well as insulating liquids.[6] According to Shuwaew and Sazin the energy necessary to extract the ion is of the order of

$$W = \frac{q^2}{8\pi r \varepsilon_0} \left(\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2} \right)$$ (2)

where: r = the ionic radius

         q = the charge of an ion

         ε_1 = dielectric permeability of the medium

         ε_2 = dielectric permittivity of electrolyte solution (injecting electrode).

In the case of such a process one can expect the Schottky—type barrier at the electrode.

The apparatus used in present measurements and the cell are shown on Figures 1 and 2. The particular current transient obtained are displayed on Figure 3.
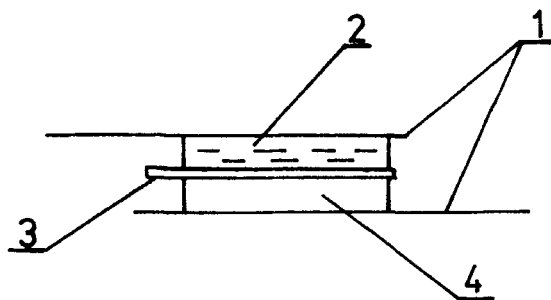

FIGURE 1   Schematic presentation of the measuring cell 1 = electrodes, 2 = liquid crystals, 3 = membrane, 4 = electrolytic solution.
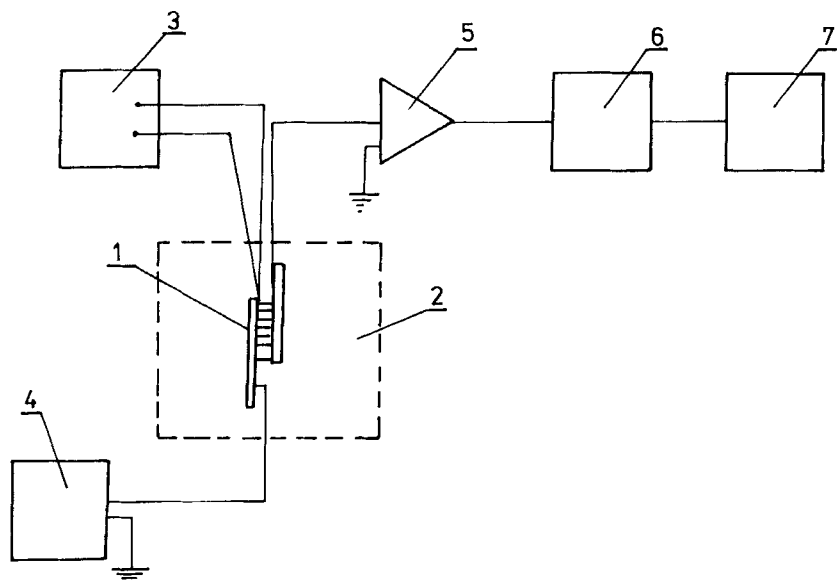
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FIGURE 2   Block diagram of measuring setup 1 = cell, 2 = thermostat vessel, 3 = temperature indicator, 4 = power supply, 5 = amplifier, 6 = recorder, 7 = CRO.

To avoid the direct contact in between liquid crystal and the electrolyte the neutral or cation exchanging membranes have been used, as in other papers.[7,8] The following check of the validity of the method was performed by i) the measurements of the transit time vs. voltage or the sample thickness. The dependence measured is plotted versus voltage Figure 4 or the square of the sample thickness Figure 5. As one can see the relation (1a) is obeyed ii) the measurement of the dependence of the transient current (Im) maximum on the voltage (plotted as ln Im vs. $E_2^{\frac{1}{2}}$) Figure 6. The relation obtained is valid for the emission limited current. From the slope, the comparison with formula (2) and the Schottky coefficient $(q^3/4\pi\varepsilon_1\varepsilon_0)^{1/2}$ was made. The results obtained for ChO are shown in the Table II.

TABLE II

Formula	Theor. values	Exp. values
$\left(\dfrac{q^3}{4\pi\varepsilon_1\varepsilon_0}\right)^{1/2}$	$3.0\ 10^{-24}\ (\text{JmC})^{1/2}$	$4.1\ 10^{-24}\ (\text{JmC})^{1/2}$
$\dfrac{q^2}{8\pi r\varepsilon_0}\left(\dfrac{1}{\varepsilon_1}-\dfrac{1}{\varepsilon_2}\right)$	0.34eV	$(0.28 \pm 0.1)\,\text{eV}$

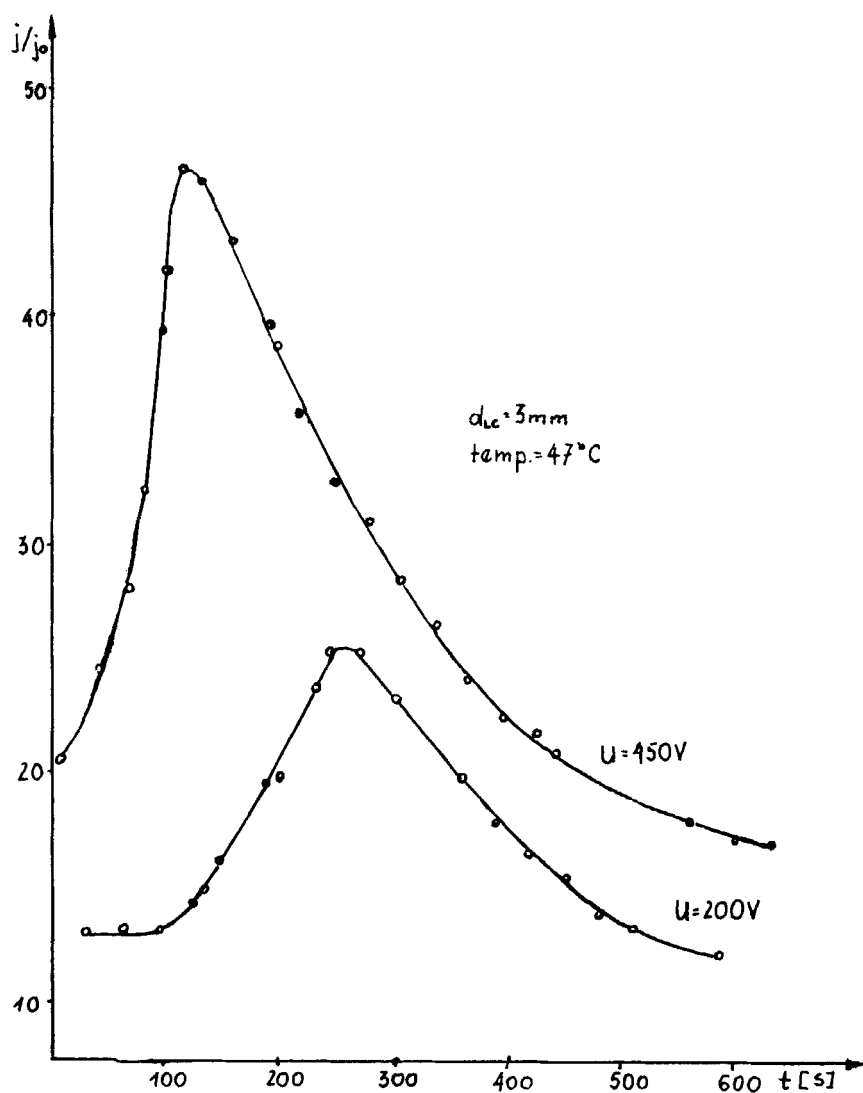Where: $\varepsilon_1 = 4$, $\varepsilon_2 = 80$, $r = 5 \cdot 10^{-10}\text{m}$.

FIGURE 3 Dependence of the injected current intensity on time in cholesteryl oleate.
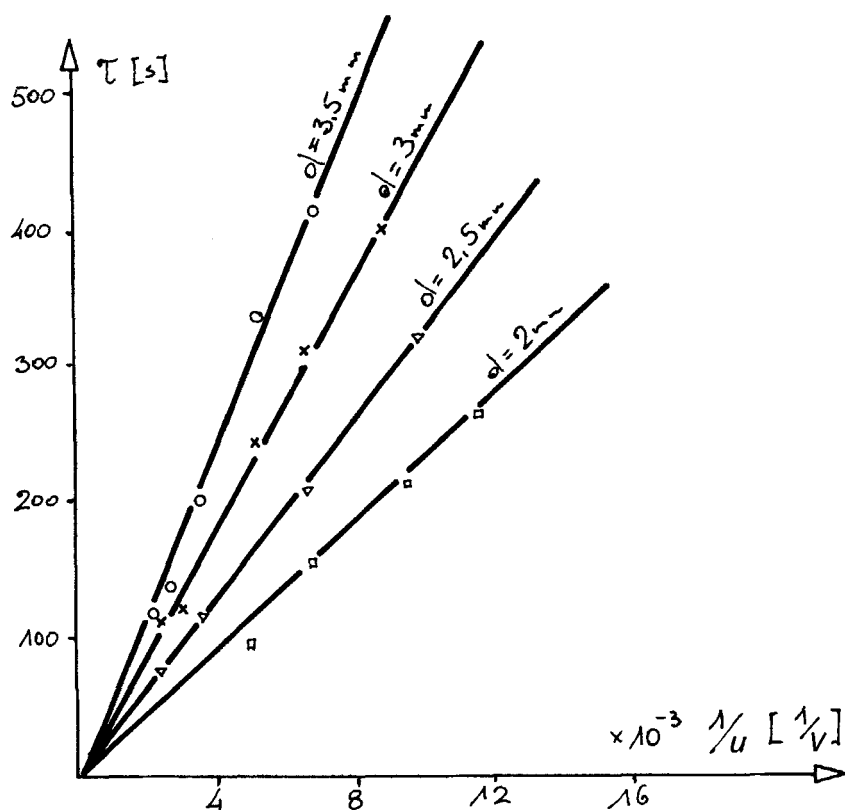
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FIGURE 4   Ionic time of flight vs voltage for different sample thickness for cholesteryl oleate at constant temperature.

The results obtained are in agreement with the literature picture of the process of ionic injection. Also, one can argue, that the electric field distortion, above the emission current flow threshold can be neglected because of large sample thickness. The influence of the electrochemical processes is more difficult to discuss. In our opinion this influence was important after times longer that the carrier transit time.

By the application of the long enough waiting time (ca 30 min. in between the measurements) this difficulty was omitted.

3   INTERPRETATION

The phenomenon of injection of ions from an electrolyte to a liquid crystal is nor fully explained. The studies made now speak for the Schottky type mechanism of injection, i.e. electric field stimulated emission through the
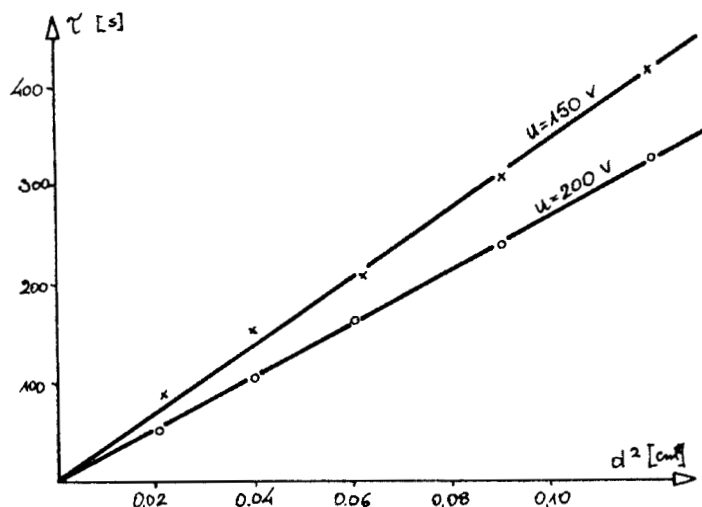
FIGURE 5   Ionic time of flight vs. square of sample thickness for cholesteryl oleate at different voltages at constant temperature.
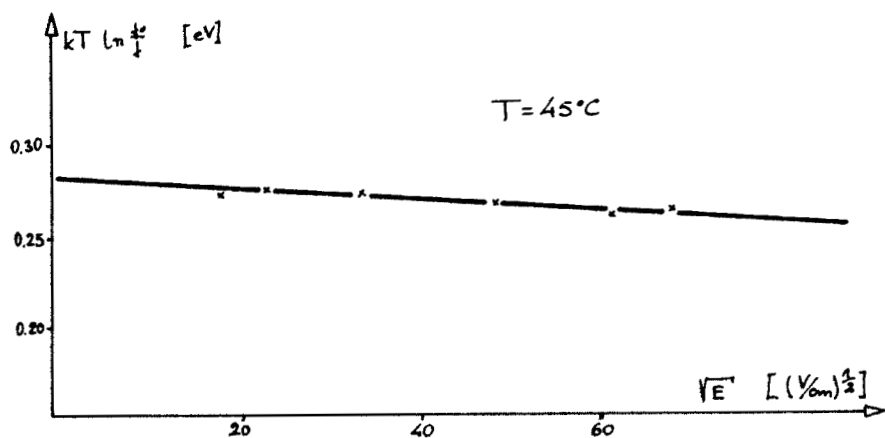
FIGURE 6   Density of transient current vs. square root of electric field strength for cholesteryl oleate at 45°C.

barrier at the electrode. This assumption explains the experimental results, in particular, the existence of definite voltage threshold for the occurrence of injected currents and likewise the non-ohmic nature of the relationship between current and voltage.

The possibility of achieving in liquid crystals ionic injection currents allows the transport of ions to be traced in a controlled manner. In

TABLE III

Values of electrical conductivity and charge carrier mobility

| Material | Temperature °C | Electrical conductivity A/Vcm electrodes | | Mobility $\times 10^{-7}$ cm^2/Vs | Electric field V/cm | Phase[a] | Refs |
		SnO$_2$	Injection				
cholesteryl oleate	47	$5.8 \ 10^{-13}$	6.1×10^{-10}	22.2	3×10^2	ch	
cholesteryl myristate	75			2.8		s	
	81	2.0×10^{-12}	5.0×10^{-11}	11.3	8×10^2	ch	
cholesteryl pelargonate	80	1.4×10^{-12}	1.27×10^{-10}	14.5	5×10^2	ch	
cholesteryl erucate	48.5	1.2×10^{-12}	5.0×10^{-10}	3.5	6×10^2	s	
PCB	25	1.0×10^{-9}	5.0×10^{-8}	50.3	2.5×10^2	n	
cholesteryl palmitate				9.5–20		ch	9
MBBA				10–50		n	7
BBOA				1–30		n	10
CBOA				5–95		s	11
PAA				250–4000		n	12
MBBA				100		n	12

[a] ch = cholesteric, s = smectic, n = nematic.

particular, the type of ions and their density can be kept under control. Hence, this technique creates possibilities of differentiating between the various regimes of ionic current flow, viz., laminar flow and electrohydrodynamic flow. Using the technique in mention let the ionic mobilities of Na$^+$ and Cu^{++} ions to be measured Table III.

The mobility values, for cholesteric materials, are in agreement with the literature data for viscous liquid.[13]

The values of the activation energy of mobility determined for ChM and PCB are the same as the activation energy for the conductivity. This should suggest that the activation energy for the generation process is negligible. However in the case of cholesteryl oleate the activation energy for carrier transport in the mesomorphic phase is much larger, in agreement with conductivity data. This may be due to the change in the mode of the ionic flow. The conditions of Atten and Moreau[14,15] for the occurrence of hydro-dynamical mode of charge carrier transport have been tested.

In the case of cholesteryl oleate, the formula related to weak injection

$$\mu_{\mathbf{EHD}} = \frac{\rho_0 d^2}{8\eta} \tag{3}$$

where: ρ_0 = density of charge carriers formed, η = coefficient viscosity seems to be valid. Thus the activation energy for mobility $W\mu$ is now the sum of activation energy of viscosity $W\eta$ and the activation energy for carrier injection $W\eta$ which is of the order of 0.3eV.

This would explain the anomalous value of activation energy.

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