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Low Field Conduction of Nematic Liquid Crystals Studied by Means of Electrodialysis†

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Abstract—An elementary theory of electrodialytic purification in insulating liquid crystals is developed by considering both the degree of ionic dissociation and the kinetic rates of dissolved impurities. It is shown that, on application of a uniform electric field with open electrodes, the only species which exhibit strong dissociation, or fast kinetic rates, can be eliminated from the solution; the molecular concentrations of other species remain unaffected by every ionic depletion process. Distinction is made between an irreversible molecular purification, which takes place when electrolytic impurities are definitively removed, and a reversible displacement of the ionic equilibrium by electrodialysis. The ionic concentrations of species having slow kinetic rates are lowered by the electric field, but they grow back to their initial values when the voltage is switched off.

These conclusions lead to propose a model for the interpretation of transient and stationary electrical characteristics of several nematic compounds, when no injection phenomena occur.

The temperature dependance of the residual conductivity is studied for several nematic liquid crystals. An exponential-like behaviour is observed in both isotropic and nematic phase and a singularity appears near the transition. The conductivity variations are discussed in terms of number and drift mobility of ionic charge carriers and liquid crystal viscosity.

Introduction

The dc characteristics obtained with metallic electrodes in liquid crystals generally do not lead to a good understanding of bulk conductivity mechanisms. In most cases, the current arises from the superposition of various phenomena, difficult to control and separate, such as secondary electrochemical reactions at the electrodes

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which lead to macroscopic space charges and electrohydrodynamic convection currents. The importance of these phenomena can be reduced by the use of ion-exchange membranes electrodes$^{(1-2)}$ where ions are instantaneously removed from the solution. This electrodialysis method, which first leads to the elimination of various ionic impurities, can then be used to study the residual bulk electrical conductivity mechanisms in liquid crystals with quite ideal open and non injecting electrodes.

We shall first present theoretical considerations on the electrolytic purification in liquid crystals. The electrical behaviour of residual impurities will then be described and compared in the second part with experimental results.

1. Electrolytic Purification of a Liquid

1.1. EQUATIONS

Let us consider a single electrolytic impurity AB dissolved in an insulating liquid, and giving rise to the following dissociation equilibrium:

$$\underset{\nu}{AB} \underset{k_R}{\overset{k_D}{\rightleftarrows}} \underset{n}{A^+ + B^-}$$

ν and n are the molecular and ionic concentrations respectively and k_D and k_R are the kinetic rate constants of dissociation and recombination respectively.

The electrolyte AB is characterized by the chemical relaxation time $\tau_R = 1/(2\sqrt{k_R\, k_D\, \nu})$, calculated by Langevin.$^{(3)}$ When the equilibrium is weakly displaced, the kinetic rate towards the restored equilibrium is characterized by a time constant equal to the chemical relaxation time τ_R.

If an electric field is applied to this system, ions are removed from the liquid by electrolysis, and the ionic depletion speed is characterized by the mean ionic transit time $\tau_T = [2L/E(\mu^+ + \mu^-)]$ (L electrode spacing, E electric field, μ^+ and μ^- mobilities of positive and negative ions).

Assuming that diffusion and convection are strong enough to keep all concentrations homogeneous, the variations of the ionic and molecular concentrations are governed by the differential equation system:

$$\begin{cases} \dfrac{dn(t)}{dt} = k_D \nu(t) - k_R n(t)^2 - \dfrac{i(t)}{eL} \\ \dfrac{d\nu(t)}{dt} = k_R n(t)^2 - k_D \nu(t) \end{cases}$$

$i(t)$ is the electric current density, and thus, the term $i(t)/eL$ expresses the ionic depletion speed by electrolysis.

The general solution of the system is complex. However, simple forms are obtained for particular conditions which are defined by the comparison of τ_R and τ_T, that is to say by considering the degree of perturbation caused by electrolysis on the ionization equilibrium.

1.2. IRREVERSIBLE IONIC PURIFICATION

The simplest form is obtained when the impurity AB is a strong electrolyte. The initial ionic concentration n_0 is equal to the concentration of dissolved electrolyte ν_0. The ionic depletion rate is then given by :

$$\frac{dn(t)}{dt} = -\frac{i(t)}{eL} = -\frac{E(\mu^+ + \mu^-)}{L} n(t)$$

This leads to the transient current density

$$i(t) = i_0 \exp\left(-\frac{2t}{\tau_T}\right)$$

The ionic concentration decreases from its initial value n_0 to 0, with a time constant equal to half the mean ionic transit time, and the impurity AB is entirely and irreversibly removed from the liquid.

In the case of a weak electrolyte with fast kinetics (this corresponds to a value of τ_R much lower than τ_T), the ionization equilibrium is not appreciably perturbed by the electric field. The molecular concentration is then governed by the following equation:

$$\frac{d\nu(t)}{dt} = -\frac{i(t)}{eL} = -\frac{E(\mu^+ + \mu^-)}{L} \sqrt{\frac{k_D \nu}{k_R}}$$

This leads to the current density:

$$i(t) = i_0\left(1 - 2k_D \frac{\tau_{R0}}{\tau_T} t\right)$$

Here, i_0 is the initial current density and τ_{R0} the initial chemical relaxation time. This linear relation between current and time is always observed in aqueous media and expresses the solvent purification by irreversible elimination of the impurity. The current remains always ohmic and, if the dissociation constant k_D is not too small, the purification may be very efficient. However, in organic media such as liquid crystals, the ionization constants are so weak that the current remains very small even when high voltages are applied. Consequently, the current variations are very slow and the electrical purification which is limited by the value of the ionization constant may become negligible. The residual species give a quasi-constant contribution to the current which then increases linearly with the electric field.

1.3. Reversible Process

In the case of a weak electrolyte with slow kinetics (when the chemical relaxation time τ_R is greater than the ionic transit time τ_T), ions are removed from the liquid as soon as they are created by dissociation, and ionic recombination can be neglected. Then, the equations governing the concentration variations are reduced to:

$$\begin{cases} \dfrac{\mathrm{d}n(t)}{\mathrm{d}t} = k_D \nu(t) - \dfrac{i(t)}{eL} \\ \dfrac{\mathrm{d}\nu(t)}{\mathrm{d}t} = -k_D \nu(t) \end{cases}$$

This gives after integration, the transient current density:

$$i(t) = (i_0 - i_{s0}) \exp\left(-\frac{2t}{\nu_T}\right) + i_{s0} \exp(-k_D t)$$

when i_0 and $i_{s0} = k_D \nu_0 e L$ are the initial and the saturation current density respectively. This transient shows two parts:

—At first, the ionic concentration decreases from its equilibrium value n_e to a value n_s depending on the applied voltage. During this first step, the concentration of non-dissociated molecules remains unaffected, and in spite of the current decrease, no irreversible purification occurs. Indeed, if the voltage is switched off, the ionic concentration grows back to its initial value.

—The second part following this first ionic relaxation corresponds to a slow irreversible purification which takes place with a time constant equal to the inverse of k_D.

In the case of weakly dissociating media such as liquid crystals, k_D may be so low that no irreversible purification practically occurs. Then a pseudo stationary state follows the initial ionic relaxation.

In conclusion, strong electrolytes and weak electrolytes with fast kinetics, provided that k_D is not too small, are the only species which can be irreversibly removed by electrodialysis; the molecular concentrations of other species remain unaffected by every ionic process.

When a voltage is applied to a compound for the first time, the three previously described behaviours may be observed simultaneously because the sample generally contains many electrolytes with varied kinetics. This is illustrated by Fig. 1 when curve 4 shows

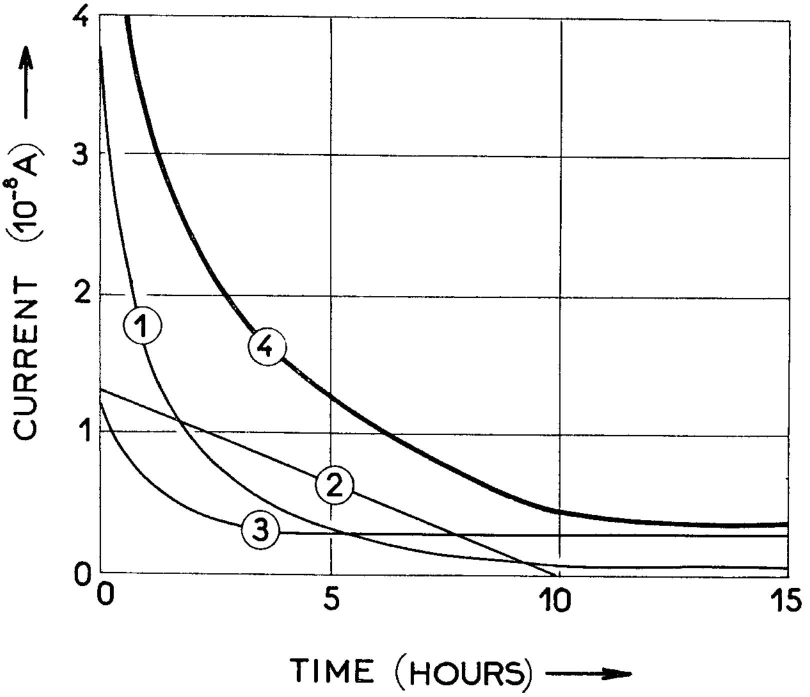


Figure 1. Current variations showing the purification of a liquid. 1. strong electrolyte; 2. weak electrolyte with fast kinetics; 3. weak electrolyte with slow kinetics; 4. addition of curves 1, 2 and 3.

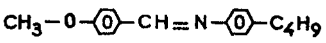
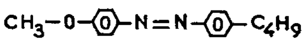
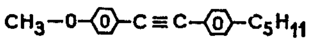
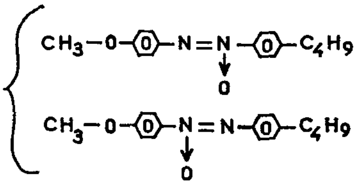
the resulting current obtained by the addition of the three transient currents of each kind of impurity. The relative importance and the speed of every one of these behaviours may be very different from one compound to an other, so that the variations of the overall transient current may appear quite different.

2. Electrodialysis and D.C. Characteristics of Nematic Liquid Crystals

2.1. Experimental

Four different nematic liquid crystals have been studied and are described on Table 1. MBBA was synthetized from *n*-butylaniline and *p*-anisaldehyde and purified by successive fractional crystallizations and distillation under vacuum. MPT was synthetized according to J. Jacques⁽⁴⁾ and purified by several crystallizations in ethanol and by alumine chromatography. MPAB, which was kindly given by Dr. Kelker, was zone refined, and the commercial product Merck IV was just degassed and dehydrated under vacuum.

Table 1 Chemical Formula, Name and Nematic Range of the Studied Nematic Compounds

	MBBA	(21°–47°)
	MPAB	(32°–48°)
	MPT	(44°–57°)
	MERCK IV	(16°–76°)

The electrodialytic cells, which have been previously described⁽⁵⁾ are made of PTFE, and the stainless steel electrodes are separated by a fixed gap of 1 cm ; they are coated with ion exchange membranes (Ionac MA 3475 and MC 3470), which are preliminary washed with distilled water, then with ethanol and finally dried and storaged under vacuum before use.

2.2. Electrolytic Purification of Nematic Compounds

The electrodialysis which are presented correspond to the transient currents observed when the compounds are submitted to a voltage for the first time. The voltage values are chosen so that no conduction relaxation appear when the electric field is switched off. Then, the observed behaviours correspond to an irreversible purification, and not to the displacement of ionization equilibria with slow kinetics.

Figure 2 shows the current variations recorded in the isotropic phase of MBBA at 50 °C, under 250 V. The same kind of transient

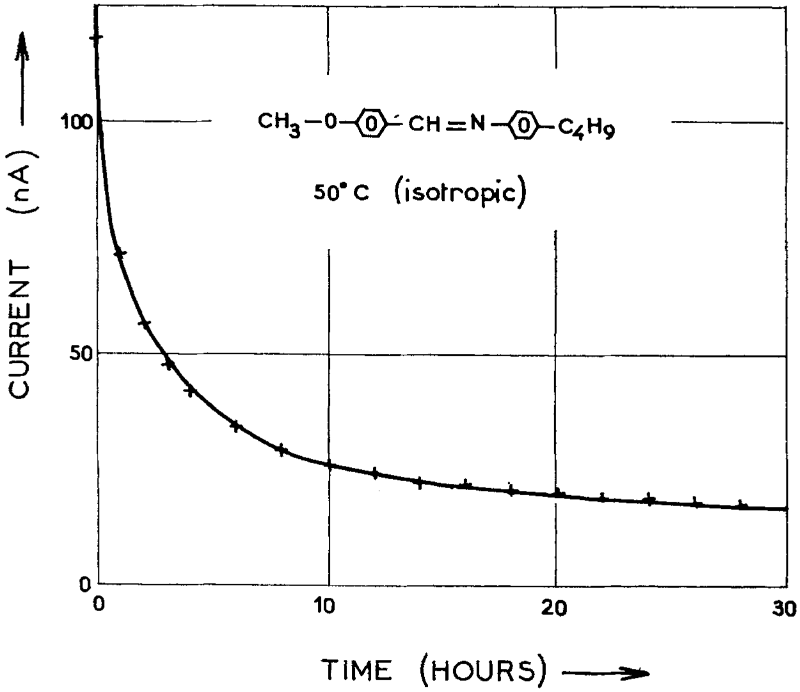


Figure 2. Current variations showing the purification of MBBA ($V = 250V$, isotropic phase = 50 °C).

current is observed for the other compounds, in both isotropic and nematic phases. Fast at first, then more and more slower, the current variations express the epuration complexity, several kinds of impurities with ions of various mobility being simultaneously eliminated. It must be noted that no linear variation has been observed, because fast kinetics are quite unlikely in weakly dissociating media such as liquid crystals.

The different results are gathered on Table 2. The initial and final conductivities (σ_0 and σ_e respectively), measured at equilibrium (that is to say when no permanent field is applied) are reported, and their ratio σ_0/σ_e give the ionic purification efficiency. This ratio varies from 2 to 10, depending on the initial purity of the samples. The resistivity increase carried out by electrodialysis is noticeable, but we must emphasize that the ratio of the initial and final conductivities is much higher in the case of more polar liquids than liquid crystals.⁽⁶⁾ The studied nematic compounds are very associating media with slow kinetics so that the electrodialytic purification efficiency is greatly reduced.

TABLE 2 Irreversible Purification of Nematic Liquid Crystals by Electrodialysis. Comparison of the Initial and Final Conductivities

Compound	Temperature (°C)	Initial conductivity σ_0 ($\Omega^{-1} \times \text{cm}^{-1}$)	Final conductivity σ_e ($\Omega^{-1} \times \text{cm}^{-1}$)	$\frac{\sigma_0}{\sigma_e}$
MBBA	50° (Isotropic)	10^{-10}	1.5×10^{-11}	7
	80° (Isotropic)	4.6×10^{-10}	10^{-10}	4.6
Merck IV	50° (nematic)	3×10^{-11}	1.8×10^{-11}	1.7
	25° (nematic)	5×10^{-11}	10^{-11}	5
Tolane MPT	50° (nematic)	1.4×10^{-11}	0.4×10^{-11}	3

2.3. DC CHARACTERISTICS AFTER ELECTRODIALYSIS

The steady current-voltage curves which can be drawn after electrodialysis are defined by the electrolytic impurities which have not been removed by the electrical purification, that is to say by weak electrolytes with slow kinetics. On Fig. 3, the stationary current versus the applied voltage is reported for MBBA in the isotropic phase at 50 °C. Three parts are to be distinguished:

—first, for voltages lower than 300 V, the current increases linearly with the stress; this part corresponds to a field range where the ionic transit time is higher than the chemical relaxation time of the ionic equilibrium; the ionic depletion by electrolysis is slow compared to the ionic depletion by natural recombination; the electrolyte is always at equilibrium and the ionic charge carriers number remains constant over all the field range.

—the second part is observed between 700 and 1500 V, where a pseudo-plateau is observed. The current is quasi independent of the applied voltage. In this field range, the ionic transit time is lower than the chemical relaxation time, so that the ions are removed from the liquid as soon as they are created by natural dissociation; consequently recombination can be neglected and a current saturation is obtained. This last one is proportional to the ionic formation speed, which is the product of the dissociation rate constant by the

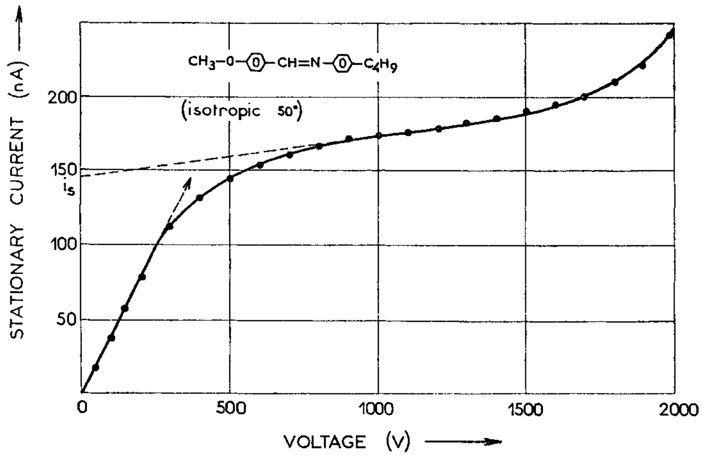


Figure 3. Stationary current vs. applied voltage curve for MBBA (isotropic phase $T = 50$°C).

molecular concentration of the impurity.

—for higher voltages than 1500 V, the faster increase of the current gives evidence of injection phenomena. Their coming out may be responsible for the weak slope of the saturation plateau.

A similar curve Fig. 4 is obtained in the isotropic phase of MPAB at 50 °C. The main three behaviours may also be distinguished; however, injection phenomena appears for lower voltages (probably due to the easy oxidation of the azo-group), and consequently, the slope of the saturation current is more important than in the case of MBBA. Nevertheless, in both cases of MBBA and MPAB, the saturation current is reached for relatively low voltages, giving evidence of the slow kinetics of the involved dissociation equilibria.

Figure 5 shows the stationary characteristic observed for MBBA in the nematic phase; two different curves can be drawn with the electric field parallel and perpendicular to the magnetic field which orients the sample; these curves point out the anisotropy of conductivity. No well-defined saturation current is obtained, just like it was with the nematic *p*-ethoxyphenyl azo phenyl heptanoate EPPH:(7) this seems to indicate that the kinetics of the ionization equilibria are affected by the order of the nematic phase.

A linear characteristic is also obtained in the nematic phase of Merck IV (Fig. 6) oriented by a 7000 G magnetic field. No saturation is reached in the field range which have been studied: the residual impurities in this compound behave like electrolytes with faster kinetics than electrolysis speed, so that the ionization equilibrium is not appreciably perturbed by the electric field.

All these current–voltage curves show that in the conditions of electrodialysis, the electrical characteristics of nematic liquid crystals are mainly determined by the ionization equilibria of dissolved impurities which are always present in the purest samples, whatever the purification process may be. In the same way, it appears clearly that the high values of the resistivity measured under a permanent electric field which corresponds to a saturation range are senseless because they refer to a displaced equilibrium, when no effective elimination of ions origin occurs. Thus, the only significant values of the conductivity are those deduced from the linear part of the dc characteristic which is always observed in low field conditions.

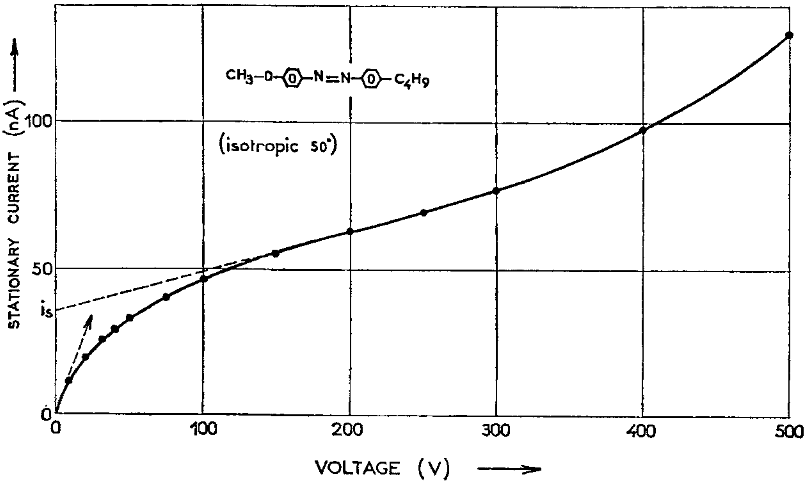


Figure 4. Stationary current vs. applied voltage curve for MPAB (isotropic phase $T = 50\,^{\circ}\mathrm{C}$).

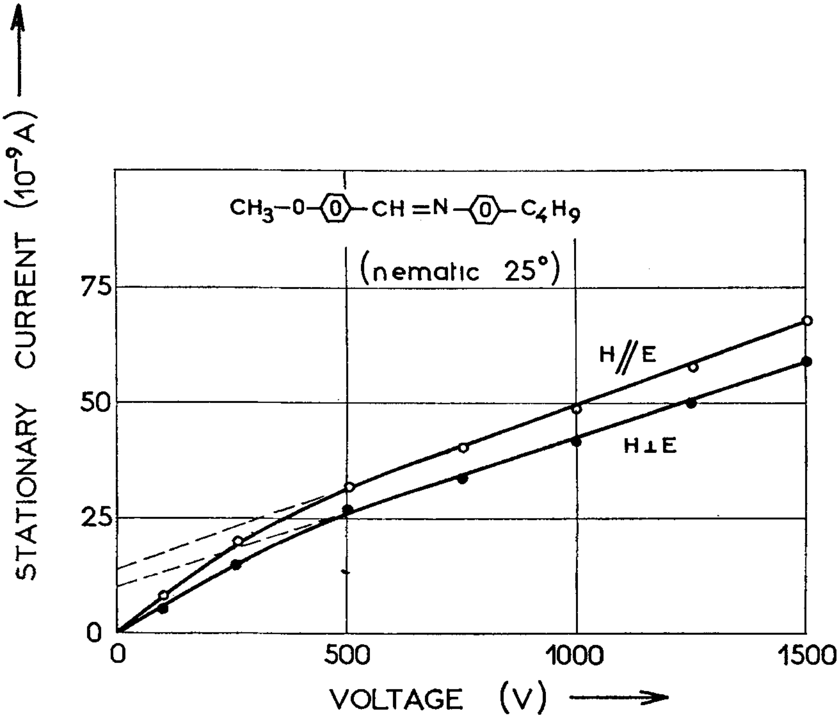


Figure 5. Stationary current vs. applied voltage curve for nematic MBBA (nematic phase $T = 25\,^{\circ}\mathrm{C}$, magnetic field $H = 7000$ G).

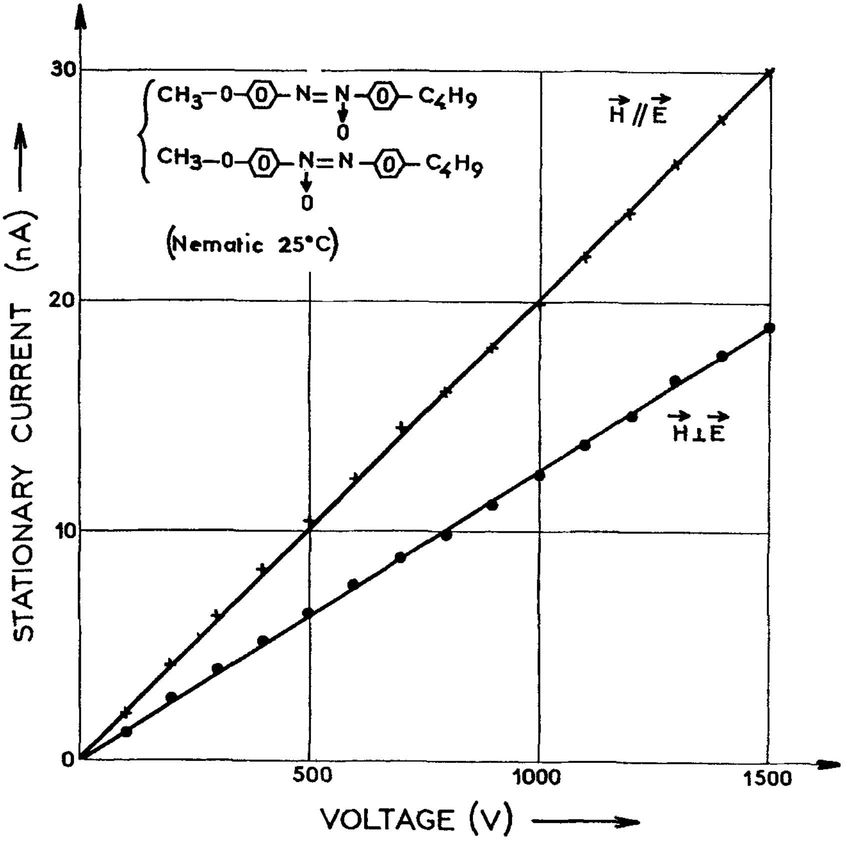


Figure 6. Stationary current vs. applied voltage curve for nematic Merck IV (nematic phase $T = 25$ °C, magnetic field $H = 7000$ G).

3. Temperature Dependence of the Residual Conductivity of Nematic Liquid Crystals

3.1. Results

Figure 7 shows the current variations recorded for MPAB in both isotropic and oriented nematic phases. A super cooling phenomenon is observed at the nematic–solid transition, and a singularity appears near the clearing point. This singularity is reproducible and observed in both cases of decreasing and increasing temperature. These variations are linearized on Fig. 8, where the log of the steady current is plotted versus the inverse of the absolute temperature. The slopes of the linear parts represent the activation energy of conductivity. We can notice that the activation energy of the super cooling range is different from the nematic one; this fact leads to think that this last part could rather correspond to a monotropic smectic phase. Similar variations are observed in the case of MBBA (Fig. 9), for which the same kind of singularity is observed near the nematic–isotropic transition. The conductivity of Merck IV is also governed by the same temperature dependence in the nematic phase, but the isotropic phase has not been studied because of the high temperature involved.

These curves lead to the determination of the activation energies of conductivity, which are gathered on Table 3. We notice that the activation energy is quite the same in the two orientations of the nematic phase.

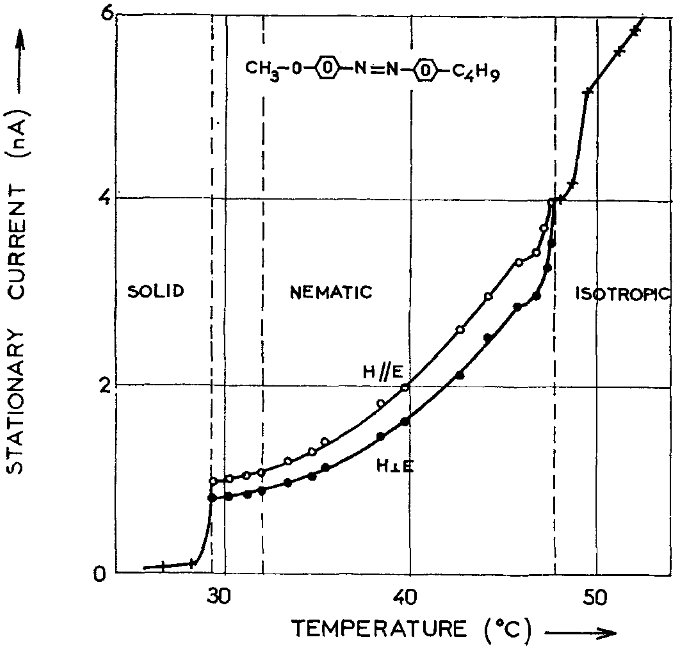


Figure 7. Temperature dependence of the residual conductivity of MPAB (permanent voltage $V = 10$ V, magnetic field $H = 7000$ G).

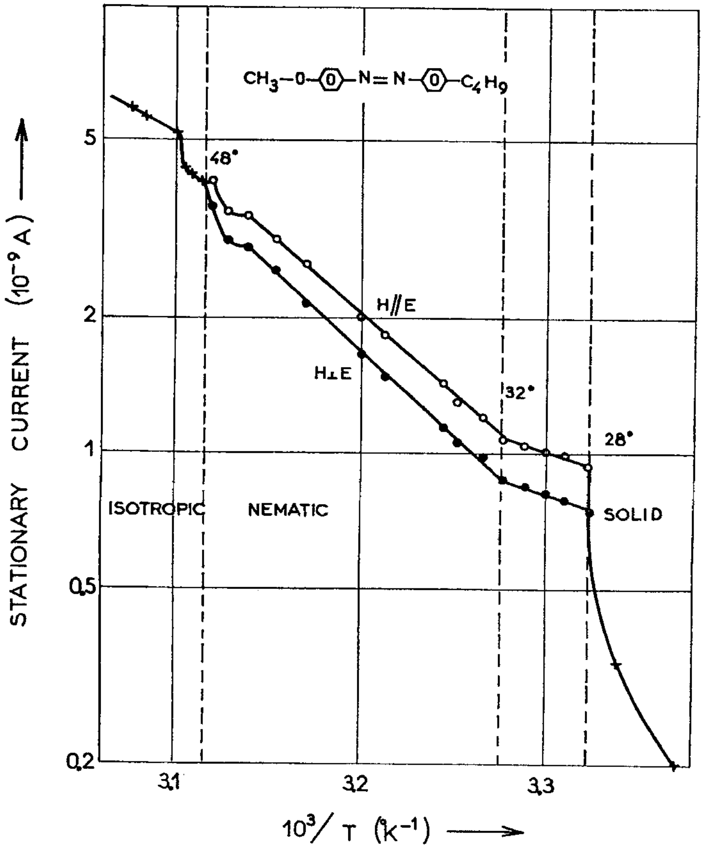


Figure 8. Linearized temperature dependence of the residual conductivity of MPAB, according to

$$\operatorname{Log} i = -(W/RT)$$

TABLE 3 Comparison of the Activation Energies of Conductivity for 3 Different Compounds in Both Isotropic and Nematic Phases

Compound	Activation energy of conductivity (Kcal × mole^{-1} × °K^{-1})		
	Isotropic	Nematic (E‖H)	Nematic (E⊥H)
MPAB	11 ± 2	16.6 ± 0.5	16.8 ± 0.5
MBBA	6.4 ± 0.5	13.8 ± 0.5	14.8 ± 0.5
Merck IV		11.6 ± 0.5	12.0 ± 0.5

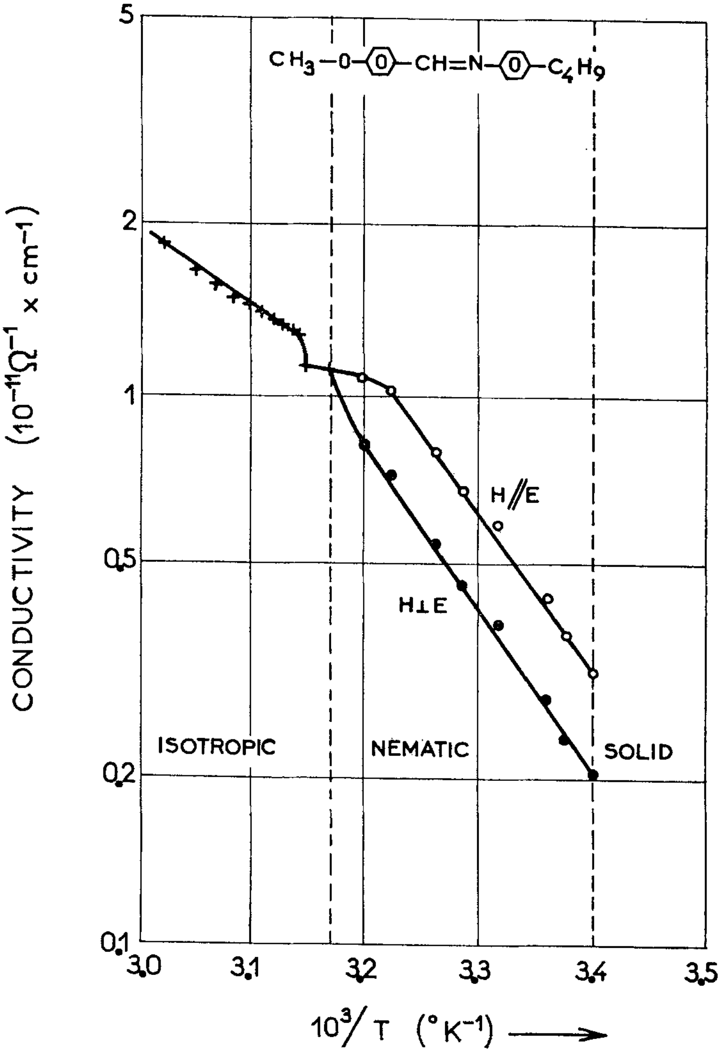


Figure 9. Linearized temperature dependence of the residual conductivity of MBBA.

However, for all the compounds, the highest value is obtained in each case for the perpendicular geometry. On the other hand, the values in the isotropic phase are much lower than those of the nematic phase.

3.2. DISCUSSION

If we suppose that the temperature dependence of the drift mobility and the charge carriers number are given by Arrhenius laws:

$$\mu = \mu_0 \exp\left(-\frac{E_1}{RT}\right) \quad \text{for mobility}$$

$$n = n_0 \exp\left(-\frac{E_2}{RT}\right) \quad \text{for charge carriers number}$$

The measured activation energy of conductivity W is a direct function of the activation energy of mobility E_1 and charge carriers number E_2:

$$W = E_1 + E_2$$

If we consider that the temperature dependence of viscosity⁽⁸⁾ is also governed by a similar law $n = n_0 \exp(-E/RT)$ and if we suppose that Walden's rule is valid for liquid crystals $\mu\eta = c^{st}$, we conclude that the activation energies of viscosity and mobility are equal $E_1 = E$.

This leads to the activation energy of the charge carriers number as a function of the activation energies of conductivity and viscosity: $E_2 = W - E$.

Our measurements show a great difference in the activation energy of conductivity between the nematic and isotropic phase. The number of charge carriers is only defined by the thermodynamical equilibrium, and the kinetic rates probably do not show a great difference in their activation energies between the two phases. Thus a great difference in the activation energy of mobility may be expected between the nematic and isotropic phases. Assuming that Walden's rule is suitable for liquid crystals, the activation energy of viscosity should then present the same difference between the isotropic and the nematic phase.

4. Conclusion

The present study has shown that electrodialysis purification of nematic compounds increases the resistivity by a factor which varies from 2 to 10, depending on the samples. The purification efficiency is lower in liquid crystals than in more polar liquid because the ionization kinetics are slower in media of low dielectric permittivity.

The observed saturation plateau gives evidence of the presence of weakly dissociated impurities with slow kinetics, and the transient currents which follow any voltage variations are explained by reversible displacements of the ionic equilibrium by the electric field.

However the complete study of these equilibria requires to take into account that a double equilibrium takes place: molecule–ion pair and ion pair-free ions. We hope that a more elaborate theory, actually on hand, will lead, from the transient and stationary electrical characteristics of the compounds, to the determination of the kinetic constants of the equilibrium and of the ionic mobilities.

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