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Degradation of liquid crystal devices under d.c. excitation and their electrochemistry

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Electrochemical properties of biphenylnitriles and phenylbenzoates are given and are compared with those of other liquid crystal (LC) families. The experimental results prove that a small gap and the reversibility of the reactions occurring at the electrodes favourably influence the LC life-time during d.c. dynamic scattering.

1. Introduction

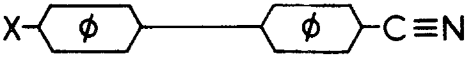
The dynamic scattering (DS) undergone by nematic liquid crystals (LCs) is one of the basic effects used in LC display devices [1]: a thin layer of nematic LC sandwiched between two electroded glass plates diffuses light and becomes opaque when a voltage is applied to the device. Both d.c. and a.c. excitations have been investigated; scattering devices operated with a.c. excitation are reliable with time, but the devices under d.c. drive gradually depart from customers' requirements: both a decrease of the active scattering area of the cell and an alteration of the LC characteristics are observed. DC excitation is, however, desirable in order to simplify the electronic circuit of the display. It has been suggested that d.c. dynamic scattering involves the creation of ions at the electrodes [2] and it seems to be generally accepted that the degradation of LCs under d.c. excitation also proceeds from electrolysis, i.e. electrochemical reactions at the electrodes [3, 4]; but a complete understanding of the involved phenomena has not been achieved.

We have investigated LCs from an electrochemical point of view, in the same way as that employed previously to investigate the electrical conduction of some more polar liquids such as nitrobenzene and propylene carbonate. Indeed, as LCs are also polar liquids and ionic conductors, our electrochemical approach [5] to the study of the conduction of resistive liquids is no doubt quite right to describe the conduction of LCs.

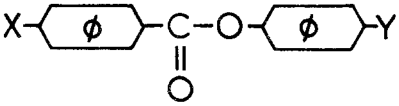
We report here some results on biphenylnitriles and phenylbenzoates. They are discussed and compared with those previously obtained with other LC families. We describe experiments proving the favourable influence of reversible electrochemical reactions on the life-times of displays and the existence of a LC regenerating process which is strongly augmented at small gaps.

2. LC electrochemical study in acetonitrile

We have investigated the electrochemical properties of biphenylnitriles (BN)



and of phenylbenzoates (PB)



These materials are chemically and thermally stable.

With regard to their oxidation and reduction, LC redox voltages on a platinum electrode have been measured in acetonitrile (CH_3CN) versus the Ag/Ag^+ reference electrode; they are compared in Table 1 with previously obtained results on other LC families [6]. The relation between these redox voltages and the LC electrical conduction can be explained as follows: if, for example, a cell is filled with a mixture of biphenylnitrile and tolane, at low current density values, the oxidation of tolane would take place at the anode and the reduction of the biphenylnitrile at the cathode; at larger current densities, biphenylnitrile (BN) oxidation would also occur at the anode. So, knowing the LC redox voltages permits us to predict the reactions occurring at the electrodes of a LC display.

It appears from Table 1 that the reduction voltage is quite similar for the various compounds; but oxidation voltage varies a lot with the LC chemical nature. It is low for *p*-methoxybenzilidene *p*-butylaniline (MBBA) and rather high for biphenylnitrile (BN).

The species formed at the electrodes by electrochemical processes were also determined. The first step of LC reduction is always $LC + e \rightleftharpoons LC^{\dot{-}}$. The LC radical formation is reversible. This was easily shown by electrochemical methods such as cyclic voltammetry and electronic paramagnetic resonance (EPR). In the latter case, we have detected the radicals electrochemically produced in the resonant cavity itself of the spectrophotometer.

LC reduction occurs in two steps. The reversible step is followed by an irreversible reaction in acetonitrile. By-products are still unidentified, but their oxidation does not give back the original LC molecule.

LC oxidation is generally irreversible; it gives protons with a faradaic efficiency of about 1 measured by controlled voltage exhaustive coulometry at the LC oxidation voltage. We met a different oxidation process only with the alkoxybiphenylnitriles (AOBN). Their oxidation occurs according to the reaction $AOBN \rightleftharpoons AOBN^+ + e^-$; the radical cations have been detected by EPR.

3. LC electrochemical reaction and its degradation under d.c. voltage

3.1. *Electrochemical reactions at the electrodes of a LC cell*

We have studied, by gas chromatography, the evolution of a 2 mm thick layer of *p*-methoxybenzilidene *p*-butylaniline between two stainless steel electrodes submitted to a d.c. voltage (5 kV); when the current began increasing with time, we observed that the *p*-butylaniline (*p*BA), a product of MBBA hydrolysis by residual water, gradually disappeared with a faradaic efficiency of about 0·5 mol Faraday^{-1}, assuming a one-electron oxidation. Later the disappearance of the *p*-anisaldehyde (*p*Ade), the other product of MBBA hydrolysis occurred, and an increasing formation of a new unidentified species [4]. But these reactions are not the only ones at the electrodes, since their faradaic efficiency is found to be lower than 1.

The occurrence of electrochemical reactions of the LC itself, or impurities or additives, at both electrodes, is also clearly demonstrated by the measurement of the electrode polarization, i.e. the voltage drop at the electrode necessary to achieve a given electrochemical reaction. Indeed, when a constant current density crosses the cell, the voltage drop between the electrodes is $U = RI + P_a + P_c$, P_a and P_c being the polarizations of the anode and the cathode respectively, and RI the ohmic drop. When the circuit is opened, RI disappears quite instantaneously and the remaining voltage $U_r = P_a + P_c$ decreases very slowly. This procedure, which we have used in liquids of resistivity up to $10^8\,\Omega$cm [7], has been applied to heptylbiphenylnitrile (Fig. 1). With pure heptylbiphenylnitrile (curve 1), no significant current crossed the cell until the total polarization $P_a + P_c$ was about 3 V. For larger applied voltages, the voltage increase mainly resulted from an increase of the ohmic drop. When easily reacting additives such as

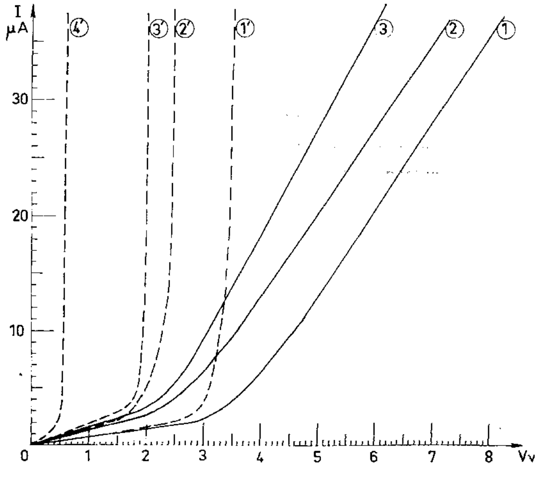


Fig. 1. Current–voltage curves as measured (1,2,3), current–polarization curves (1′,2′,3′,4′) in heptylbiphenylnitrile (HBN) 1,1′: pure HBN; 2,2′: HBN + H_2; 3,3′: HBN + tetraphenylenediamine (TMPDA); 4′: HBN + TMPDA + *p*-benzoquinone.

Table 1. Voltages of oxidation and reduction reactions of liquid crystals on a platinum electrode, in acetonitrile 10^{-1} M Et_4NClO_4, measured versus a Ag/Ag^+ reference electrode

Reaction	*LC*													
	Schiff base			*Miscellaneous*			*Tolane*			*Phenylbenzoate*			*Diphenylnitrile*	
	MBBA	*pBA*	*pAde*	*PAA*	*N_4 Merck*	*N_5 Merck*	*MPT*	*HPT*	*DOT*	*HPHB*	*BPHB*	*B(EPC)PC*	*HBN*	*HOBN*
Oxidation 1st step	+1·1	+0·50		+1·15	+1·20	+1·20	+1·05	+1·05	+0·95		+1·30	+1·35	+1·60	+1·35
2nd step		+0·80			+1·45	+1·45	+1·40			+1·70	+1·70		+2·05	+2·10
Reduction 1st step	−2·40		−2·30	−1·90	−1·85	−1·85	−2·80	−2·80	−2·85	−2·55	−2·60	−2·35	−2·40	−2·45
2nd step (Hg electrode)				−2·40	−2·40	−2·40	−3					−2·80	−2·90	−2·95

MBBA: *p*-methoxybenzilidene *p*-butylaniline; *p*BA: *p*-butylaniline; *p*Ade: *p*-anisaldehyde; *p*AA: *p*-anisole; N_4, N_5: Merck liquid crystals; HBN: heptylbiphenylnitrile; HOBN: heptoxybiphenylnitrile; MPT: *pp*′-methoxypentyltolane; HPT: *pp*′-heptylpentyltolane; DOT: *pp*′-dioctoxytolane; HPHB: 4-*n* hexyloxyphenyl 4′-*n* hexanoyloxybenzoate; BPHB: 4-*n* Butoxyphenyl 4′-*n* hexoxybenzoate; B(EPC)PC: Butyl *p*-(*p*-Ethoxyphenoxycarbonyl) phenylcarbonate.

H_2 (curve 2) or tetraphenylenediamine (TMPDA) (curve 3) or both TMPDA and *p*-benzoquinone (*p*BQ) (curve 4) were added to heptylbiphenylnitrile, the total polarization became constant at about 2·1, 2 and 0·6 V respectively. The values (3; 2·1; 2 and 0·6 V) agree respectively with the voltage drops between reduction and oxidation of heptylbiphenylnitrile (HBN), HBN reduction and H_2 oxidation, HBN reduction and tetraphenylenediamine oxidation, *p*-benzoquinone reduction and tetraphenylenediamine oxidation, which we have measured by electrochemical methods (see Table 1).

3.2. *Liquid crystal degradation and the reversibility of their electrochemical reactions*

The liquid crystal degradation is related to the reversibility of the electrochemical reactions. This was observed in comparing the electrical behaviour of *p*-methoxybenzilidene *p*-butylaniline (MBBA) and heptoxybiphenylnitrile (HOBN). For the same electric field in the sample, the current density through HOBN is 10 times higher than through MBBA; indeed, the higher dielectric constant of HOBN increased its residual conduction. However, 0·33 F mol^{-1} of HOBN decreased its phase transition temperature by about 1·3°C; 0·28 F mol^{-1} of MBBA decreased its transition temperature by 4·6°C. The variation of the transition temperature which is related to the amount of impurities in the LC, indicates a smaller degradation of HOBN. This is confirmed by a faradaic efficiency of about 0·1 mol F^{-1} obtained by gas chromatographic analysis of the sample during the experiment.

A very low faradaic efficiency of the LC electrolysis has also been found when materials such as tetrachlorobenzoquinone, tetracyanoquinodimethane and tetraphenylenediamine were added to the LC [8, 9]. These compounds are electrochemically well known; for example, they are very easily oxidized or reduced, their reactions are reversible and they form stable radical ions. So, the LC displays seem to degradate more slowly when the electrochemical reactions are reversible.

3.3. *Influence of the cell gap on liquid crystal degradation*

The faradaic efficiency of the LC electrolysis strongly depends on the gap between the electrodes. It has been pointed out by Sussman that the life-times of displays, although too short for customers, correspond to a very low degradation rate of the materials, far from the value expected by Faraday's law of electrolysis [3]. Indeed, a common operating time of a LC device using dynamic scattering is about 10^4 h with a current density of 1 μA cm^{-2} and a gap of 10 μm. The quantity of electricity which has passed through the cell before the device failed, is thus more than 70 F mol^{-1} of liquid crystal. So, the amount of material altered by any mechanism whatever must be less than 10^{-2} mol F^{-1}.

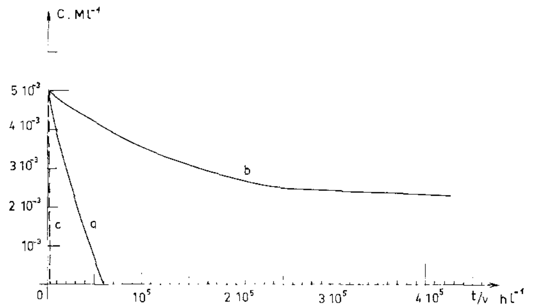


Fig. 2. Tetraphenylenediamine concentration in propylene carbonate as a function of time *t* per volume *v* of the liquid in the cell. Current intensity: 50 μA; curve (a) gap: 1 mm; volume of liquid $v = 1{\cdot}9 \times 10^{-3}$ l; curve (b) gap: 0·1 mm; $v = 0{\cdot}5 \times 10^{-3}$ l; curve (c) is given by Faraday's law, which applied to both experiments (a) and (b).

We have studied the influence of the gap on the faradaic efficiency in doping an organic solvent (propylene carbonate) with tetraphenylenediamine (TMPDA). The concentration decrease of the additive when a constant current density (50 μA cm^{-2}) flowed through samples of different thickness is shown in Fig. 2. Propylene carbonate is very difficult to oxidize or reduce whereas TMPDA is easily oxidized and gives cation radicals. In a 1 mm thick sample, TMPDA disappeared with a faradaic efficiency of 0·04 mol F^{-1}; in a 0·1 mm thick sample, TMPDA did not disappear, although no new compounds appeared in PC which kept the purple colour of the TMPDA$^+$ cation radical. So, we can conclude that the thin cell geometry enhances phenomena which regenerate the liquid crystal or its additives and are related to the formation of ion radicals.

We can also state that the contribution of electrolytic dissociation to current, and consequently to dynamic scattering, must be negligible. If this is not so, a corresponding amount of

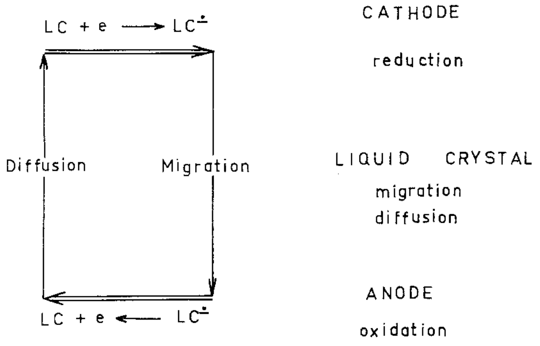


Fig. 3. Cyclic process involving the liquid crystal and its anion radical.

matter will be irreversibly decomposed. The same is true for mechanisms other than dissociation that entail irreversible deterioration: polymerization, creation of dissociated compounds for instance.

D.C. dynamic scattering occurs through electrohydrodynamic phenomena resulting from electrochemical reactions on one or both electrodes. There is indeed evidence that liquid crystal devices only work if ionic impurities are added to the systems, which is consistent with the well known fact that charge injection by electrochemical reactions at the electrodes is controlled by the amount of residual ions and not by the electric field alone. Generally the higher the initial resistivity of the liquid, then the smaller is the injection.

3.4. *Liquid crystal degradation and the cyclic processes*

Voïnov and Dunnet [10] who first proposed the term ‘cyclic process’, have explained the liquid crystal property as to be able to sustain without failure d.c. excitation for a long time, by the following scheme of cell reactions: radical ions LC^+ and LC^- are formed on the electrodes, meet in the centre of the cell and regenerate the LC molecule by reaction of LC^+ with LC^-. Such a cyclic process is not a general one in liquid crystals since LC oxidation is irreversible and does not form LC^+; the only exception we have met is the oxidation of alkoxybiphenylnitriles.

Another cyclic process has to be considered (Fig. 3). A radical ion forms on one electrode, crosses the cell by electrical migration, discharges and gives back the initial molecule which is driven by diffusion forces to the centre of the cell. This cyclic process which insures an electronic transport through the material without any net mass transport, will give rise to a long operating life if losses from side-reactions are low enough. So, the radical ions must have a life-time much longer than their transit time. This condition is fulfilled in a display cell: with 20 V applied, the transit time of radical ions between electrodes 10 μm apart is about 5 ms, the ionic mobility in LC being about 10^{-5} cm^2 V^{-1} s^{-1} [11]; the half life-time of LC radicals we have studied by EPR, is higher than 5 s. Also the radical ions must not chemically react with materials formed by electrochemical reactions on the opposite electrode. For instance, radical anions are particularly sensitive to protons which are formed at the anode by oxidation reactions. Lastly migration of radical ions and diffusion must maintain a sufficient concentration near the anode to preclude competing processes such as the oxidation of the LC itself. In a LC device, the very low losses from cyclic processes by side-reactions are explained by the small gap (10 μm), the high electric field (20 kV cm^{-1}) and the turbulence caused by ion injections decreasing the diffusion layer thickness.

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