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Correlation between Chemical and Electrochemical Reactivity and dc Conduction in the Isotropic Phase of a Liquid Crystalline p-Methoxybenzylidene-p-n-butylaniline

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Correlation between Chemical and Electrochemical Reactivity and dc Conduction in the Isotropic Phase of a Liquid Crystalline *p*-Methoxybenzylidene-*p*-*n*-butylaniline

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Abstract—Different mechanisms of ions generation that take place, either in the liquid volume or at a chemically inert electrode, have been distinguished by polarographic study of hydrolysis and electrochemical oxidation which characterizes the *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) molecule. In both cases, the protonated form of MBBA has been identified. The analysis of low field electrical conductivity of highly purified samples gives information on mobility values and kinetic constants of dissociation and recombination of a presumed protonic weak electrolyte in solution.

The main conclusion is that thermal dissociation of impurities is responsible for bulk residual conductivity while protonic injection plays a leading part in high field conduction in the liquid phase of MBBA.

Introduction

The low residual conductivity of aprotic solvents has been found to be the result of two main different processes depending on the electric field intensity:

In low field conditions, the electrical behaviour is due to thermal dissociation of ionic impurities always present in minute concentration, even in the purest samples.(1)

Ionic injection plays a leading part in the conduction at higher fields, and arises from electrochemical oxidation and reduction of the solvent and/or impurities, at the electrodes.(2)

These mechanisms have been studied in detail in nitro-benzene(3) and more recently found in the isotropic phase of the liquid crystal E.P.P.H.(4) This paper describes similar results, obtained through experiments performed on MBBA; it is shown that the phenomena previously described are quite general and related to chemical and electrochemical properties of the sample compound.

PART 1: ELECTRICAL BEHAVIOUR OF THE ISOTROPIC PHASE OF MBBA

Most previous conduction studies on liquid crystal were performed with metal electrodes and in high field conditions(5,6,7) which, consequently, involved strong injection phenomena. The use of ion-exchange membranes as electrodes in well defined conditions, hinders most secondary electrodes processes and injection phenomena.(3) Then it is possible to observe clearly the ionic bulk conductivity resulting from residual impurities.

1. Theory

The simplest model of a typical impurity is taken as a weak electrolyte in solution which gives rise to the following dissociation equilibrium:

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

$$\nu \qquad n^+ = n^- = n$$

ν: non-dissociated AB concentration,
$n^+ = n^- = n = A^+$ and B^- concentration
k_D and k_R are the dissociation and recombination kinetic constants respectively.

During the application of an electric field to the sample, this equilibrium is disturbed owing to electrolysis. The study of the displacement of this ionic equilibrium, for a weak electrolyte, has been developed in a previous paper.(8) Only the main conclusions are reported below for the analysis and discussion of experimental results.

1.1 Natural Equilibrium

When no cause of disturbance, such as an electric field, is present the natural ionic concentration at equilibrium is: $n_e = \sqrt{k_D\nu/k_R}$. This number of charge carriers, n_e, determines the so-called natural conductivity:

$$\sigma_e = e(\mu_+ + \mu_-)\sqrt{\frac{k_D\nu}{k_R}},$$

where μ_+ and μ_- are the ionic mobilities.

The natural conductivity is measured by means of brief low voltage pulses which do not disturb the equilibrium. This measurement is a very sensitive purity test.

1.2 Disturbed Equilibrium

When an electric field E is applied to the sample the ionic concentration can be derived from the following differential equation:

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = k_D\nu - k_R n^2(t) - \frac{E(\mu_+ + \mu_-)}{l} n(t) \tag{1}$$

where the last term corresponds to electrical elimination of ions (l = electrodes spacing).

A new form for Eq. (1) is derived by introducing the three following constants:

(i) The chemical relaxation time introduced by Langevin: $\tau_R = \frac{1}{2}(k_R k_D \nu)^{-1/2}$ which characterizes the kinetic rate of natural equilibrium

(ii) The ionic mean transit time $\tau_T = 2l/E(\mu_+ + \mu_-)$

(iii) The saturation current density: $i_s = k_D \nu e l$ (e = electron charge).

The new equation is:

$$\frac{\mathrm{d}i(t)}{\mathrm{d}t} = \frac{2i_s}{\tau_T} - \frac{\tau_T}{(2\tau_R)^2}\cdot\frac{i(t)^2}{2i_s} - \frac{2i(t)}{\tau_T} \tag{2}$$

By writing $\mathrm{d}i(t)/\mathrm{d}t = 0$ one can compute the steady state current density from Eq. (2) for any value of τ_T, i.e., for any value of the field strength. A general derivation of Eq. (2) can be made when $\tau_R \gg \tau_T$. The steady state solution leads to a value of the current which is i_s.

When $\tau_R \gg \tau_T$ the electrolysis rate is much faster than the recombination rate and all the ions formed from dissociation are collected by the electrodes and there is no more recombination. This is the high field behaviour for a weak electrolyte. (Neglecting field enhanced dissociation effect).

On the other hand, in the low field condition, the opposite borderline case is $\tau_R \ll \tau_T$. The electrolysis rate is slow and equilibrium is only scarcely disturbed by the electric field. Then the ionic concentration and conductivity are not different from the natural equilibrium value n_e and σ_e.

1.3 RELAXATION OF EQUILIBRIUM

Providing that $\tau_R \gg \tau_T$, one can compute from Eq. (2) the variations of the current which follow a change in field condition. The ionic concentration and related current follow the equilibrium relaxation. Three cases are to be investigated:

(i) A field is applied to the sample, which was in natural equilibrium. The current is initially $i_0 = \sigma_e \times E$ and obeys the law:

$$i(t) = i_s\left[1 + \left(4\frac{\tau_R}{\tau_T} - 1\right)e^{-2t/\tau_T}\right] \tag{3}$$

(ii) The sample is in the steady state under a voltage V_1 and a different voltage V_2 is applied. The variation law is similar to Eq. (3):

$$i(t) = i_s\left[1 + \left(\frac{V_2}{V_1} - 1\right)e^{-2t/\tau_T}\right] \tag{4}$$

(iii) When the electric field is switched off chemical relaxation takes place. The ionic concentration grows from its displaced steady value to the natural equilibrium value with the time constant τ_R. The ionic concentration can be tested by means of low voltage pulses or with a steady low voltage. Then the observed current follows the law:

$$i(t) = i_e\frac{e^{t/\tau_R} - \beta}{e^{t/\tau_R} + \beta} \quad \text{where } \beta = \frac{i_e - i_0}{i_e + i_0} \tag{5}$$

(i_e = current at natural equilibrium, i_0 = initial current.)

Experimental studies of these three transient behaviours allow the determination of τ_R and τ_T and from the steady state current vs voltage characteristic curve i_s can be derived. From these three constants k_R, $k_D\nu$ and the ionic mean mobility $\frac{1}{2}(\mu_+ + \mu_-)$ can be calculated. It is not possible to compute separately k_D and ν nor μ_+ and μ_- from these experiments.

2. Experimental

The room temperature nematic liquid crystal MBBA is synthetized by condensation of *p*-*n*-butylaniline with *p*-anisaldehyde. Purification is carried out by several crystallizations from alcohol, drying on molecular sieves and distillation under reduce N_2 pressure (0.05 mmHg at 170 °C). Samples are stored under vacuum in order to provide degassing and to prevent oxidation. The natural conductivity of the sample is then $2 \times 10^{-10}\,(\Omega \times \mathrm{cm})^{-1}$ at 50 °C. Further purification by electrodialysis reduces this value to

$$5 \times 10^{-11}\,(\Omega \cdot \mathrm{cm})^{-1}.$$

Nematic range is found to be 21–47 °C.

The electrodialytic cells have been previously described.(4) They are made of P.T.F.E. The plane stainless steel electrodes are coated with ion exchange membranes (IONAC MC 3470 and MA 3475), their spacing is generally 1 cm. Mechanical stirring provides homogeneity of ionic concentration. The cell is placed in a thermostated box with circulation of temperature controlled nitrogen. Temperature stability inside the cell is about 1/50 °C. Experiments were performed on the isotropic phase, at 50 °C.

The chemical kinetics are very slow and when equilibrium is disturbed it is generally necessary to wait 20 hours in order to obtain a steady state. We assume that the steady state is reached when the current variation is less than 1% during the last hours. Before an experiment is performed the sample is at first electrodialysed for two days in order to obtain a reproductive conduction level.

3. Results

3.1 THE STATIONARY CURRENT *vs* VOLTAGE CURVE

This characteristic, studied by successive changes of voltage shows three parts (Fig. 1):

(i) Above 1500 V injection phenomena take place and the current

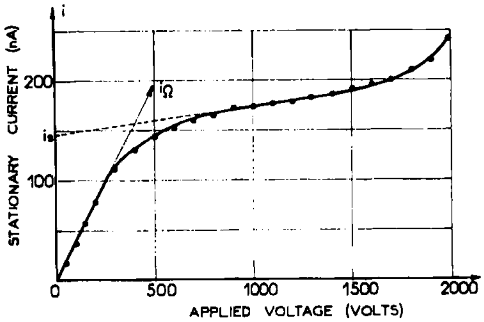


Figure 1. Stationary current vs applied voltage. Characteristic curve of electrodialysed MBBA ($T = 50\,°\mathrm{C}$). (1) Low field Ohm's law region ($\sigma_e = 5.10^{-11}\,\Omega^{-1} \times \mathrm{cm}^{-1}$); (2) Saturation plateau ($i_s = 145.10^{-9}$ A); (3) Injection region.

rapidly increases with voltage. This is the result of electrochemical behaviour of MBBA or of impurities.

(ii) Between 750 and 1500 V a saturation plateau is observed. For these voltages the equilibrium is entirely displaced ($\tau_R \gg \tau_T$). According to the theory this plateau should be horizontal. However, its slope can be explained by the beginning of injection phenomena. The saturation current is found by extrapolation: $i_s = 145.10^{-9}\,A$. This leads to the value of $k_D\nu = 2.3 \times 10^{11}\,(\mathrm{cm}^3 \times s)^{-1}$.

(iii) Below 300 V the behaviour is ohmic; the equilibrium is only weakly distributed by the field. The measured natural conductivity is

$$\sigma_e = 5 \times 10^{-11}\,(\Omega \times \mathrm{cm})^{-1}.$$

3.2 TRANSIENT BEHAVIOUR, CHEMICAL RELAXATION

The equilibrium is displaced by a 10^3 V × cm^{-1} electric field and a steady state is reached. Then the field is switched off and a low voltage (15 V) is applied. The current shows an exponential-like relaxation during the first 20 hours but no stationary value is reached. The current always increases slowly. This behaviour may be explained by slow chemical degradation. Figure 2 shows the linearized experimental plot according to Eq. (5). From this result $\tau_R = (2.7 \pm 0.2) \times 10^4$ s is computed.

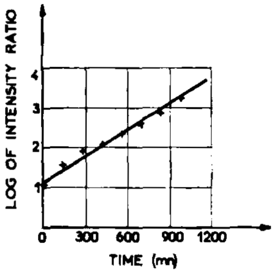


Figure 2. Chemical relaxation of MBBA ($T = 50\,°C$). Linearized graph $\ln(i(t) + i_e/i(t) - i_e) = f(t)$ according to Eq. (5).

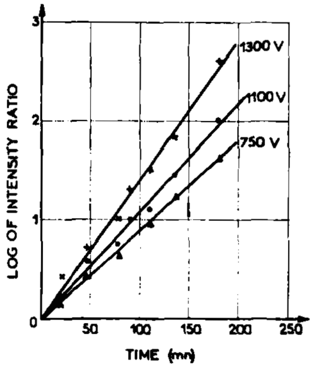


Figure 3. Electrical relaxation of MBBA ($T = 50\,°C$). Linearized relaxation curves $\ln(i(t) - i_\infty/i_0 - i_\infty) = f(t)$ under different applied voltages (1300, 1100 and 750 V).

3.3 ELECTRICAL RELAXATION

Any change of the applied voltage in the range 750–1500 volts leads to electrical relaxation. Linearized relaxation curves are shown on Fig. 3 and their interpretation leads to the following data:

Applied voltage	750	1100	1300	Volts
τ_T	13.6	10.9	8.5	$\times 10^3$ s
$\frac{1}{2}(\mu_+ + \mu_-)$	9.8	8.3	8.2	$\times 10^{-8}\,\mathrm{cm}^2\cdot\mathrm{V}^{-1}\cdot\mathrm{s}^{-1}$

Kerr effect experiments show that the electric field remains uniform between the electrodes up to several kV × cm^{-1}. Consequently the measured mobilities are ionic mobilities and not the result of an hydrodynamic flow. The agreement with theory is not perfect, because of the non-constant mean mobility. However, these results give an average value of the mean ionic mobility:

$$\frac{\mu_+ + \mu_-}{2} \simeq 9 \times 10^{-8}\ \mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$$

Results obtained with other liquids (nitrobenzene and E.P.P.H.) are summarized for comparison in the following table:

	$k_D \nu$ $\mathrm{cm}^{-3} \cdot \mathrm{s}^{-1}$	k_R $\mathrm{cm}^3 \cdot \mathrm{s}^{-1}$	$\bar{\mu}$ $\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1}$	R_s Å Stockes' radius
Nitrobenzene(1) (25°)	$3.4 \cdot 10^9$	$2.6 \cdot 10^{-17}$	10^{-4}	7
E.P.P.H.(4) (124°)	$3.8 \cdot 10^{11}$	$1.3 \cdot 10^{-19}$	3.10^{-6}	40
MBBA (50°)	$2.3 \cdot 10^{11}$	$1.5 \cdot 10^{-21}$	9.10^{-8}	400

Stockes' formula derived from viscosity resistance to motion of a sphere in a liquid ($\mu = e/6\pi\eta R_s$) is valid for nitrobenzene and not too bad for E.P.P.H. since Stockes' radii are consistent with molecular size. Stockes' model seems to be inadequate in the case of MBBA. Other forces, stronger than viscous friction forces are to be considered. A calculation due to de Gennes(10) using Boyd(11) and Zwanzig's(12) theory of dielectric friction, with parameters compatible with MBBA leads to the value of the mean mobility:

$$\bar{\mu} = 10^{-7}\ \mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1},$$

which is in good agreement with our result.

With regard to kinetic constants, $k_D \nu$ is not very different for the two liquid crystals; the dissociation kinetics shown by electrodialysis are also similar. Further investigations concerning the correlation between recombination constants and mobilities may be undertaken, by the above method, in the nematic phase. Measurement upon anisotropic effects should be of great interest.

In brief, the kinetic study of residual conduction in MBBA gives results which are not in as good agreement with theory as those obtained with E.P.P.H.(4) Nevertheless, this work shows that the same kind of ionic process controls the conduction in these two nematic compounds, as in nitrobenzene.

PART 2: CHEMICAL AND ELECTROCHEMICAL PROPERTIES OF MBBA

The difficulties met in the study of the electrical behaviour of MBBA can be explained by the chemical stability and the electrochemical properties of the compound, which have been studied by the methods of organic electrochemistry.

1. Experimental Section

We have studied MBBA in solution (2×10^{-3} M/l) in acetonitrile (supporting electrolyte was 0.1 M/l $LiClO_4$ or Et_4NClO_4). Two different methods were used:

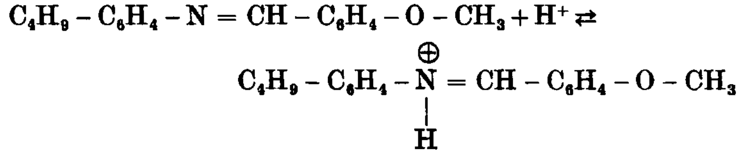
Current intensity-potential curves were drawn in order to determine the half-wave potentials of the compounds and to follow the changes of the chemical composition of the solution.

Controlled potential electrolysis was performed for selective oxidation of compounds. The number of charge exchanged was measured with an integrator.

The polarograms and coulometry measurements were obtained with a three electrodes electrolysis apparatus. The indicator electrode was a platinum electrode, rotating at 600 rpm, and an Ag/AgCl reference electrode was employed throughout all experiments and all potentials are reported with respect to this reference electrode. Acetonitrile was carefully dried on molecular sieves after distillation.

2. Hydrolysis of MBBA

It can be recalled that all stages in the preparation of imines like MBBA from carbonyl compounds and amines are reversible.(14) Consequently the hydrolysis of MBBA leading to the starting components is easy, and the first stage is the formation of the protonated imine:



$$C_4H_9-C_6H_4-N=CH-C_6H_4-O-CH_3+H^+ \rightleftarrows C_4H_9-C_6H_4-\underset{\displaystyle H}{\overset{\oplus}{N}}=CH-C_6H_4-O-CH_3$$

so, the hydrolysis is an acid-catalysed reaction.

The UV spectra of the protonated imine and of the MBBA are different (Fig. 4) and make possible the differentiation of the two forms by spectroscopy. On the other hand, in the experimental conditions previously described, MBBA in solution in anhydrous acetonitrile has an oxidation wave with a half-wave potential of 1.08 V, while the protonated form does not present any wave in the investigated potential range.

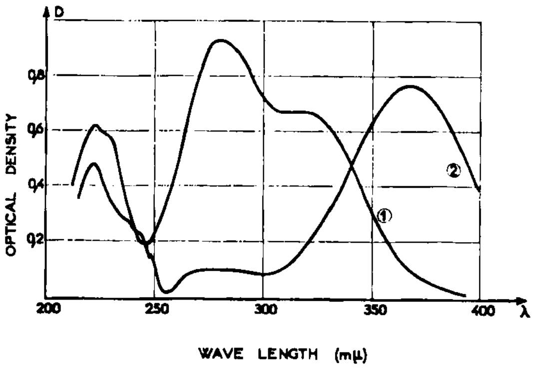


Figure 4. UV Spectra of MBBA (1) and of protonated MBBA (2)

The protonation of MBBA was carried out by adding a solution of perchloric acid (0.85 M/l in acetonitrile), and the polarograms of Fig. 5 are drawn just after each addition. These curves show the gradual vanishing of the wave of MBBA, which is protonated into the immonium salt characterized by its UV spectrum. If a polarogram is drawn one hour after adding the perchloric acid, a double oxidation wave appears ($E^a_{1/2} = 0.51$ and $E^b_{1/2} = 0.76$ V), which shows that a new compound has been formed. The study of n-butylaniline allows us to impute this new wave to this amine.

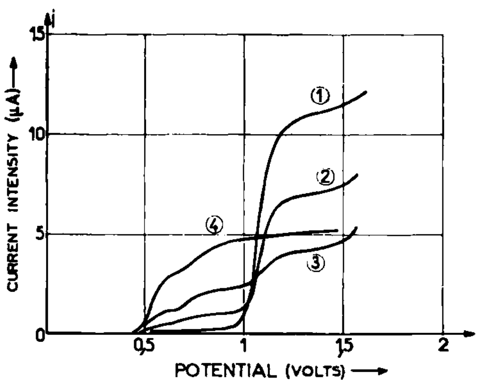


Figure 5. Protonation of MBBA by addition of perchloric acid. Polarographic curves for (1) pure MBBA (2) MBBA (2×10^{-3} M/l) + $NClO_4$ (10^{-3} M/l) (3) MBBA (2×10^{-3} M/l) + $NClO_4$ (2×10^{-3} M/l)—Curves (2) and (3) are drawn just after the addition of acid, and curve (4) is obtained from the same sample as (3) but drawn one hour later.

Therefore, the immonium cation has been hydrolysed by the residual water of the solvent (100 ppm), according to:

$$R-\phi-CH=\underset{H}{\overset{\oplus}{N}}-\phi-R'+H_2O \rightarrow R-\phi-CH=O+R'-\phi-\overset{\oplus}{NH_3}$$

but, as *p*-anisaldehyde is not electroactive in the studied potential range, we can only give evidence of the formation of *n*-butylaniline through electrochemistry. Nevertheless, these results show that residual water is able to hydrolyse the compound if protons are present.

3. Oxidation of MBBA

The chemical oxidation of imines is quite easy, and although the normal oxidation product of C=N is the nitrile group, several different oxidation compounds can be formed according to the oxidizer.(14) The voltametric oxidation must involve the same group C=N, unless electronic effects of substituents change the electrochemical reaction.

3.1 Localization of Oxidation

If electronic effects of substituants are effective on the electrochemical oxidation, the half-wave potentials of similar aromatic imines, with different substituent groups must be quite different. In order to specify these electronic effects we have prepared the following compounds:

(A) $CH_3 - \phi - CH = N - \phi - n\,Bu$

(B) $CH_3 - O - \phi - CH = N - \phi$

The half-wave potentials of these two compounds are very close to the one of MBBA, whereas the difference is larger for more electroactive substituents (see Table 1). These results show that the butyl and methoxy groups are not involved in the oxidation of MBBA, which takes place on the C=N group.

TABLE 1 Half-wave Potentials of Compounds $X_1—C_6H_4—CH=N—C_6H_4—X_2$

	MBBA	A	B	C†	D†
X_1	$CH_3—O$	CH_3	$CH_3—O$	—OH	—Cl
X_2	$n—C_4H_9$	$n—C_4H_9$	H	H	H
$E_{1/2}$(V.)	1.08	1.10	1.12	0.86	1.36

† Results from Ref. 15

3.2 CONTROLLED POTENTIAL OXIDATION

The oxidation of MBBA was performed at a potential of 1.2 V, in order to specify the feature of the electrochemical reaction. Figure 6 shows the polarograms drawn at different degrees of oxidation; it can be computed from these curves that one electron per molecule is involved in the oxidation. Nevertheless, the curve drawn a long time after complete oxidation of the solution shows the characteristic wave of *n*-butylaniline, which is the result of the hydrolysis of MBBA. On the other hand, the UV spectroscopy oxidation control (Fig. 7) gives evidence of the gradual rising of the characteristic band of protonated MBBA. Then, when magnesia is added to the solution in order to collect the protons, part of the MBBA is regenerated, and this can be seen by UV spectroscopy (Fig. 7).

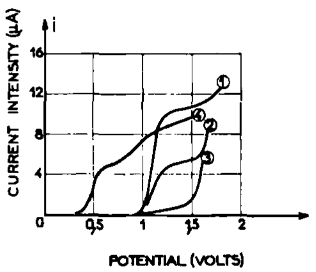


Figure 6. Oxidation of MBBA. Polarographic curves at different stages of oxidation: (1) unaltered MBBA; (2) after 0.5 electron/molecule transfer; (3) after 0.8 electron/molecule transfer; (4) same as (3), but drawn 24 hours later.

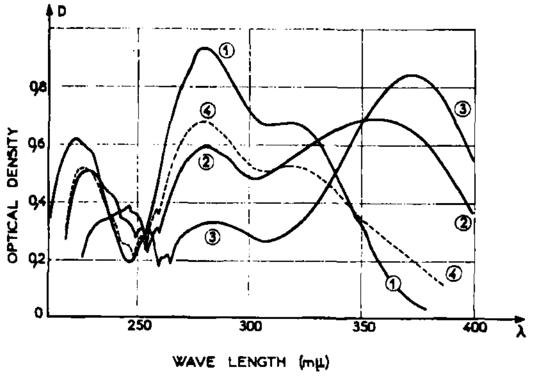


Figure 7. UV evidence of MBBA oxidation by reference to (1) unaltered MBBA after (2) 0.5 and (3) 0.8 electron/molecule transfer, followed by addition of magnesia (4).

Therefore, the oxidation does release protons which form with other molecules of MBBA the protonated form which cannot be oxidised at the controlled potential of 1.2 V. Then, the protonated imine is slowly hydrolysed with the residual water of the solvent to the starting components *n*-butylaniline and *p*-anisaldehyde. Consequently, all the MBBA molecules cannot be oxidised, and probably, the number of electrons involved in the oxidation is larger.

In order to oxidise the whole MBBA in solution, controlled potential electrolyses were performed in basic conditions (i.e. with magnesia) to inhibit the compound from being protonated. In these conditions, the polarograms show a two-electron oxidation wave (Fig. 8). The gradual vanishing of MBBA during the oxidation can be seen by UV spectra (Fig. 9) which show that no protonated imine is formed in these conditions.

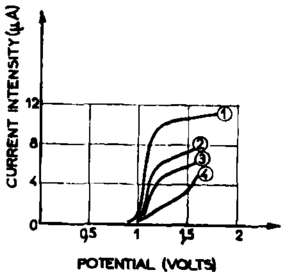


Figure 8. Polarographic curves during the oxidation of MBBA in presence of magnesia, by reference to (1) unaltered MBBA, after 0.6 (2), 1 (3), 2 (4) electron/molecule transfer.

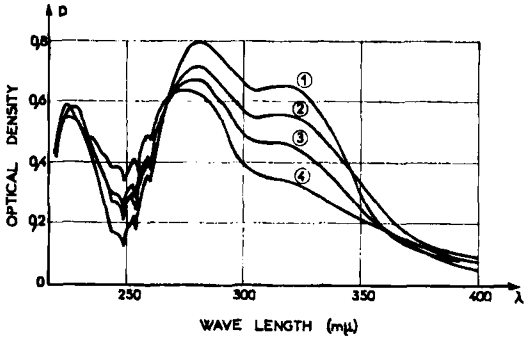


Figure 9. UV evidence of MBBA oxidation in presence of magnesia by reference to (1) unaltered MBBA, after 0.6 (2), 1 (3), 2 (4) electron/molecule transfer.

These different results lead to the following electrochemical reactions, according to Martinet, Simonet and Tendil.(15)

$$R-\phi-\mathrm{CH}=\mathrm{N}-\phi-R' \rightarrow 1\bar{e}+R-\phi-\overset{\oplus}{\mathrm{CH}}-\dot{\mathrm{N}}-\phi-R'$$

$$R-\phi-\overset{\oplus}{\mathrm{CH}}=\dot{\mathrm{N}}-\phi-R \leftrightarrow R-\phi-\mathrm{C\dot{H}}-\overset{\oplus}{\mathrm{N}}-\phi-R'$$

$$\leftrightarrow R-\phi-\mathrm{CH}=\dot{\mathrm{N}}-\phi-R'$$

$$\overset{\oplus}{R}-\phi-\mathrm{CH}=\underset{\oplus}{\dot{\mathrm{N}}}-\phi-R' \rightarrow \mathrm{H}^{+}+\bar{e}+\mathrm{R}-\phi-\mathrm{C}\equiv\overset{\oplus}{\mathrm{N}}-\phi-R'$$

The cation can later react with the solvent or with residual water. Nevertheless, the lifetime of the formed radical is not long enough to be detected by E.S.R. No signals have been detected during the electrolysis of MBBA in the cavity of an E.S.R. spectrometer.

Further experiments are on hand to bear out that mechanism, such as proton titration during the oxidation and identification of the yield of oxidation in different pH conditions.

Nevertheless, it can be concluded that the previously established facts explain the difficulty often met in the study of MBBA,[13] mainly due to acid-catalysed hydrolysis of the compound and electrical oxidation, which give rise to protons thus making the hydrolysis reaction easier.

PART 3: CONNECTION WITH ELECTRICAL BEHAVIOUR

1. Origin of Charge Carriers

The study of residual conduction in MBBA leads to the assumption that, like in nitrobenzene(1) or E.P.P.H.,(4) stationary and transient conduction phenomena are due to the dissociation of electrolytic impurities. Owing to their minute concentrations the identification of these species and the ionic equilibrium cannot be determined by classical analytic chemistry. The charge carriers density n, calculated from the equation $j = 2ne\bar{\mu}E$ (e: ion charge, $\bar{\mu}$: mean ionic mobility, E: field strength), is about 10^{15} carriers per cc, corresponding to an ionic concentration of 10^{-6} M/l. Conductivity measurements are the only way to detect and study such small concentrations. In addition, the dissociation equilibrium of impurities may be only the determinative step of a more complex kinetic mechanism which can occur through acid-base equilibria of different species introduced along the synthesis of MBBA.

Furthermore, significant alteration of the purity level is observed during the application of an electric field to the sample. After a long time under a moderate field (in the range of 10^2 V/cm) the current slowly increases instead of being quasi-constant at the end of electrodialysis. At higher fields the current increases quickly, and this increase is not reversible; a further electrodialysis under lower voltage does not reduce conductivity. An electrochemical study of the altered sample leads to identification of the new species introduced when applying the high electric field.

2. Residual Conduction

2.1 POLAROGRAPHIC BEHAVIOUR

In order to identify the species responsible for the residual current, polarographic curves have been drawn with a sample raised to a high conductivity level (10^{-8} ($\Omega \times$ cm)$^{-1}$ at 50 °C) by a three-week application of a 200 V/cm field. The drawing (Fig. 10) shows the oxidation wave of *n*-butylaniline with a weak amplitude which indicates that residual water (about 200 ppm) is in sufficient quantity to cause the hydrolysis of a little quantity of MBBA. As the first stage in hydrolysis is the protonation, we now discuss how protons may appear during an experiment.

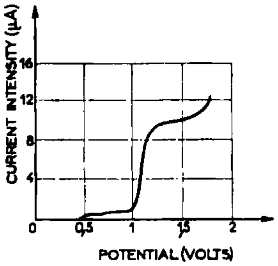


Figure 10. Polarographic curve obtained with a sample of MBBA left 3 weeks in a steady electric field.

2.2 ORIGIN OF HYDROLYSIS: PROTONIC DISSOCIATION

A low electric field does not enhance equilibrium dissociation and cannot be involved in new carrier generation but protonic dissociation can take place in the bulk solution. The first possibility is the equilibrated dissociation of residual water ($H_2O \rightleftarrows H^+ + OH^-$), protons being immediately collected by the MBBA molecules. That is yet not likely because MBBA is not a dissociating solvent, owing to its low dielectric constant ($\epsilon \simeq 5$). Moreover, addition of water to the sample (from 500 to 4000 ppm) changes only weakly the conductivity and does not induce any further degradation. Thus, it is likely that residual water is not dissociated and plays no role in MBBA protonation. A second hypothesis is based on chemical action of ion-exchange membranes. Membranes are made of an inert matrix (polyamid or polyester) on which are grafted ion exchange resins. The cationic membrane contains the acidic resin (RSO^-_3, H^+) which can release ions by partial dissolution or chemical reaction in the liquid phase. This has been observed with AMF membranes (polyamid matrix). After a long stay of some weeks in MBBA, the membrane lost its flexibility and under a 200 V/cm field, the current becomes 50 times greater during a ten-day experiment. Lastly, protons may have an accidental origin, such as traces of acid or contamination of the sample by the walls of the cell, recalling that a very small quantity of protonic impurities is enough to have a considerable effect on conductibility.

2.3 NATURE OF THE IONIC EQUILIBRIUM INVOLVED

The over-simplified model, set upon the dissociation of only one impurity ($AB \rightleftarrows A^+ + B^-$), is in the case of MBBA too elementary and the experimental observations are the result of superimposed ionic equilibria which can explain the differences between theory and experimental results. Particularly, the hydrolysis of MBBA may give rise to other equilibria, similar to that which has been characterized by the residual conduction studies. The first one, clearly shown by the electrochemical study is the protonation of MBBA:

$$\mathrm{R} - C_6H_4 - CH = N - C_6H_4 - R' + H^+ \rightleftarrows$$

$$R - C_6H_4 - CH = \overset{\oplus}{N}H - C_6H_4 - R'$$

The protonated form of MBBA is most likely one of the positive charge carriers involved in residual conduction. The *n*-butylaniline, ultimate product of the hydrolysis, also gives rise to similar equilibrium which yields another charge carrier:

$$R' - C_6H_4 - NH_2 + H^+ \rightleftarrows R' - C_6H_4 - \overset{\oplus}{N}H_3$$

The two previous reactions are connected by a proton exchange reaction:

$$R' - C_6H_4 - \overset{\oplus}{N}H_3 + R - C_6H_4 - CH = N - C_6H_4 - R' \rightleftarrows$$
$$R' - C_6H_4 - NH_2 + R - C_6H_4 - CH = \overset{\oplus}{N}H - C_6H_4 - R'$$

The identity of negative charge carriers yet remains unknown, but it can be assumed that these ionic species, like the positive ones, participate in equilibrated reactions. Therefore, the low-field residual conduction model must be understood in an extended sense, and the involved species may be either fully different from the compound or produced through a chemical alteration of the compound, eventually enhanced by the electric field.

3. Protonic Injection Current

In addition, in high field conditions creation of new carriers occurs at the electrodes. Two different kinds of ionic injection are to be considered: unipolar (positive or negative) injection if only one electrode is active, or ambipolar injection when electrochemical reactions take place at both electrodes, leading to the possibility of bulk ionic recombination. In a medium free of traps, a pure space charge limited current is injected by ohmic contact electrodes.(16) The opposite case corresponds to negligible space charge, injected current is then limited by the emission process. The intermediate case, generally observed, has been described recently as space charge influenced emission.(17) Two reactions mentioned above can contribute in MBBA to protonic injection from the anode:

(i) Anodic oxidation of residual water:

$$H_2O \rightarrow 2e^- + 2H^+ + O$$

(ii) Electrochemical oxidation of MBBA:

$$R - C_6H_4 - CH = N - C_6H_4 - R' \rightarrow 2\bar{e} + H^+$$
$$+ R - C_6H_4 - C \equiv \overset{\oplus}{N} - C_6H_4 - R'$$

These two reactions induce positive injection of protons, immediately collected by MBBA molecules and are stabilized; on the other hand the unstable cation created by oxidation reacts afterwards with residual water or MBBA itself. These electrode reactions induce unipolar injection of charge carriers identified as molecular ions. In concordance with this, homocharge invading the electrode gap from the anode to the cathode has been observed by measuring the Kerr electro-optic birefringence of MBBA submitted to a mean field of about 10 kV/cm.

One must emphasize that positive injection enhances further chemical degradation by proton-catalysis of MBBA, hydrolysis inducing a large increase of the conduction level. The chemical concomittant pollution is demonstrated by a decrease of the clarification temperature, probably due to a noticeable amount of *n*-butylaniline.

These facts are fringing phenomena in electrodialytic conditions; under a high field only, accidental injection may take place at the membrane-liquid interface, normally working as an open electrode. On the other hand, there is no doubt that injection from metal or metal oxide electrodes plays a leading part, even at lower voltages, and completely hides residual conduction of the compound. Particularly one must infer that the mentioned(18,19) fast changes of the liquid crystal conductivity and clarification point are due to strong ionic dc injection.(6,20)

The electric field distribution between metallic electrodes shows large distortions near the electrodes(20) and the rise time of hydrodynamic flow(21) is in agreement with $t_r = C \cdot (\eta/\epsilon E^2)$, in the same manner as in isotropic liquids submitted to unipolar injection.(22)

Conclusion

The overall conductivity of MBBA is the result of combined physico-chemical and electrochemical ionic processes, as for homogeneous bulk conduction and for electrode injection conduction. Generally, these two basic mechanisms take place simultaneously but with an erratic relative part in a given fluid, and hitherto they have never been well separated. The use of membranes allows one to distinguish between them and to put forward the idea that the weak residual conductivity of most liquids has, after electrodialysis, reproductive feature due to displaced ionic dissociation equilibria. In the case of MBBA the determination of species involved in these equilibria is suggested by taking into account the chemical reactivity of the purest samples. Another point is that electrochemical reactivity at the anode gives information on the oxidation mechanism equivalent to the observed unipolar positive injection. De Gennes(11) has called forth the problem of the relative importance of injected and residual currents, especially in order to explain electro-optic phenomena in the nematic phase. This work shows that low field conductibility is not specific and may be reduced by further purification and that a strong protonic injection has to be considered. The determination of electrochemical properties of liquids seems to be the only way to clarify the origin of injection and degrading phenomena. It can be concluded from this study that MBBA is not the best nematic material to understand the complex electrical behaviour of liquid crystals, owing to its great chemical and electrochemical reactivity; this indicates, in contrast, the way for future investigations.

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