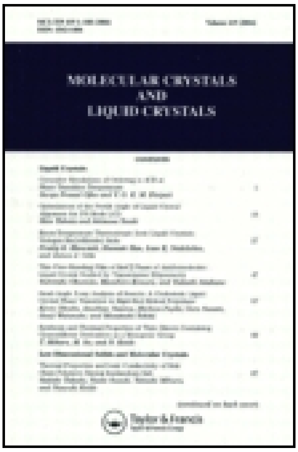

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Ion Bump in the Ferroelectric Liquid Crystal Domains Reversal Current

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Ion Bump in the Ferroelectric Liquid Crystal Domains Reversal Current

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In ferroelectric liquid crystal cells, variable electric field is applied to obtain the electro-optical switching. The transient currents through the cell show a complex behavior. A bump may appear[1] in addition to the well known bumps corresponding to the induced polarization variation and the reversal of spontaneous polarization in the bulk and at the cell surfaces. We explain different possible models for this bump. Experimental studies were conducted on the amplitude and the peak time of this bump for various compounds in different phases. From the obtained results, we conclude that this bump corresponds to the movement inside the cell of ions stuck on the electrodes. We found ionic impurities allowing to control the amount of these stuck ions.

INTRODUCTION

In electro-optical devices made with ferroelectric liquid crystal, variable electric field is applied to the compound. The transient current through the cells shows a complex behavior. A current bump may appear[1] in addition to the well known bumps corresponding to the induced polarization variation and the reversal of the spontaneous polarization in the bulk and at the cell surfaces. In thin cells ($\sim 1\ \mu m$) like those used in displays the three kinds of bump can be mixed. To investigate the real nature of this bump we use thicker cells. We measure the amplitude and the peak time of this bump for various compounds in liquid and liquid crystal phases. To test ionic effects we also add easily ionized impurities to the pure compound.

MODELS

The electrical conduction in liquids and in liquid crystals is due to ions swept along the electrical field E inside the cell. In a one dimensional cell of thickness d the

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current j per unit area of the electrode is given by:

$$j = \sum_i \int_0^d \frac{q_i n_i \mu_i E}{d}\, dx$$

n_i, μ_i, q_i are respectively the concentration, the mobility and the charge of the ions i. In this expression E and n_i are not easily obtained. E is not simply V/d because of the drop in voltage at the electrodes. n_i is not usually the thermodynamical equilibrium concentration of species i. In low conductivity liquids, Nikuradse[2] defined and interpreted three domains of conduction according to the amplitude of the applied voltage V:

i) at low voltages, the ohmic domain. The current is proportional to the field: the concentration of ions is equal to that in thermal equilibrium without a field, the drop in voltage at the electrode is negligible.

ii) at higher voltages, the saturation domain. The current is almost constant versus the voltage: the creation of ions is independent of the applied field and limits the current.

iii) at very high voltages, the current varies rapidly with V. Ions are injected by the electrodes, their density increases. The hydrodynamic motion of the liquid increases the apparent mobility simultaneously.

In ferroelectric liquid crystal cell the applied field $E \sim 10$ kV/cm corresponds to the second domain. In the first domain the field is not sufficient to reverse all the ferroelectric domains and the third domain is avoided because the injection of ions can create impurities in the cell and induce the breakdown. Hydrodynamic motion may also break the liquid crystal texture.

When a constant field is applied, the current is the saturation current. For very pure compounds, the bulk dissociation of the compound gives most of the ions present in the cell, as indicated by Nikuradse, following the J.J. Thomson model for gases. The saturation current is given by:

$$j_s = \sum_i q_i c_i d$$

c_i is the rate of creation of ion i in the bulk.

In less pure compounds a neutral impurity reaching the electrodes can give ionic radicals.[3] This radical is swept along to the other electrode where it is neutralized. The slowest step in the process is the diffusion of these neutral impurities towards the electrodes. In this case the saturation current is given by:

$$j_s = \sum_k D_k |q_k| \frac{2n_k}{d}$$

D_k and n_k are respectively the diffusion constant and the concentration of the neutral impurity k. q_k is the charge on the ionic radical made from the neutral impurity k.

When the field is reversed the transient current corresponds to three phenomena: the reversal of the flow of ions inside the bulk, the exchange of ions or neutral compounds stuck on the electrodes and the reversal of the diffusion flow of the neutral impurities. The reversal of the ionic current gives, versus time, a parabolic bump of current. Its amplitude is half the saturation current and its peak time is half the transit time of the ions: $\tau_i = d/\mu_i E$. The exchange between the two electrodes of ions or neutral compounds stuck on them is the most complex phenomenon. If these ions are almost free e.g. in the outer Helmoltz layer the corresponding current is a rectangular bump, with duration time equal to the transit time. By contrast, if there are ions or neutral species adsorbed on the surface which are randomly ejected, the transient current is a bump made of two exponentials. The bump cusp time is the transit time.[4] The ejection can be not random but enhanced by the field[5] near the electrode in the Helmoltz layer. The time for rebuilding this layer is close to the transit time for a high field. The current shows a peak close to the transit time. The bump may correspond to the charge transfer helped by an electro-hydrodynamical transient flow.[6] There is a threshold voltage. If the voltage is higher than the threshold, the propagation speed of the electrohydrodynamical streamer is proportional to the applied voltage in the case of bipolar injection. The reversal of the diffusion flow of the neutral impurities is the slowest process. It corresponds to a current decreasing versus time. The asymptotic decay time is $\tau_k = d^2/4\pi^2 D_k$, the decay time of the lower order harmonic of the triangular equilibrium distribution of the neutral impurities.

EXPERIMENTAL TECHNIQUE

The studies on the ion bump were conducted using the experimental set up for the measurement of the spontaneous polarization.[7] The liquid crystal samples were prepared between two conducting glass plates (ITO coated, Balzers, West-G); SiO layer of thickness ~225 Å was evaporated at an angle of 60° on these glass plates, to get a good planar alignment. The surface area of the sample was 10 mm × 3 mm. The two plates were separated by the mylar spacers of thickness between 3.5 μm to 36 μm. The compound was introduced in isotropic phase by capillary action. The sample temperature was maintained by a temperature regulator.

The essential features of the experimental set up are shown in Figure 1. A symmetrical rectangular wave shape voltage having frequency less than 10 Hz is amplified by the amplifier (KEPCO BOP 500 M) in the range 0–800 V pp. This voltage is simultaneously applied to the sample cell and an adjustable capacitor. This capacitor serves two purposes. It compensates the polarization current of the sample cell and also helps suppress the noise of the power amplifier at frequencies higher than 10 KHz. The difference between the currents in the sample and the capacitor is given by a differential amplifier (Tectronix 1A7A). This difference is then digitized and accumulated by the oscilloscope (Tectronix 7306). An Apricot computer is used to integrate the required part of the current.

For these studies we have used the liquid crystal compound 90BEB05* (4-(2-

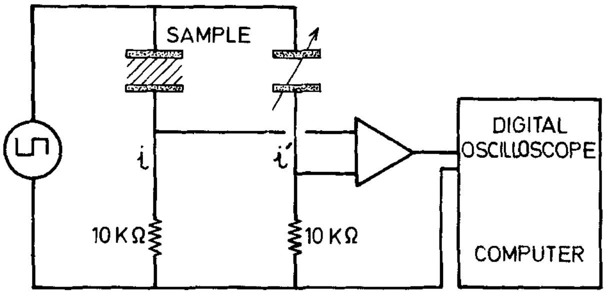
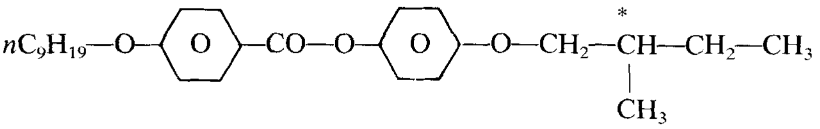


FIGURE 1 Block diagram of the experimental set-up.

Methylbutyloxy)phenyl-4′nonyloxy benzoate)

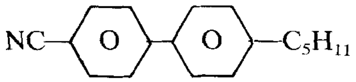


which presents the phase sequency

Cr Sb SmC* SmA Isotropic

40.6 21.5 47.2 56.4 °C

The main aim of these studies was to study the ion bump in SmC* phase but the experiments were also conducted on two nematic compounds: 5CB (5-cyano 4′-*n* pentyl biphenyl)



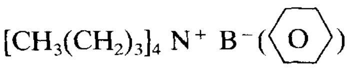
which presents the phase sequency:

Cr N Isotropic

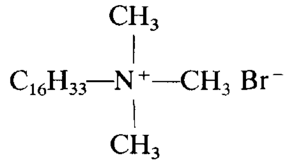
24 35 °C

and EN-38 (a liquid crystal for positive contrast display made by Chisso Corporation). The *n* tridecane was also tested.

To study the effect of additional ions, TBATΦB (tetrabutyl ammonium tetraphenyl borate) and CTAB (cetyltrimethyl ammonium bromide) were added to the above mentioned compounds and here after we refer to the obtained mixtures as impure compounds. The compounds TBATΦB and CTAB are considered to be easily dissociable into their ionic components, while TBATΦB dissociates into ions of approximately the same radius as:



the compound CTAB dissociates as:



$$C_{16}H_{33}\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}\text{—}CH_3\ Br^-$$

The addition of specific quantities of TBATΦB to the pure compound is carried out in the following four step dilution process.

1. The solution of TBATΦB having a concentration of 10^{-2}/litre is prepared in pure acetonitrile (CH_3CN). (sol. 1).
2. One ml of solution 1 is mixed with 99 ml of acetonitrile (sol. 2).
3. One ml of solution 2 is then mixed with 99 ml of methanol (sol. 3). One ml of this solution has a concentration of 10^{-9} mole of TBATΦB
4. Five ml of solution 3 are finally mixed with 10^{-3} M of the pure compound giving the concentration of the mixture as 5 10^{-6} (impurity molecule/molecule of pure compound).

A typical transient current versus time record is shown in Figure 2 for different phases of 90BEB05*. The time scale zero corresponds to the instant of the reversal of the applied electric field. In SmC* phase, the current shows two bumps "a_I" and "b_I" simultaneously. The bump "a_I" corresponds to the reversal of the spontaneous polarization. The bump b_I is the object of our present study and is named by us as the "ion bump." This bump is observable in all three phases of this compound.

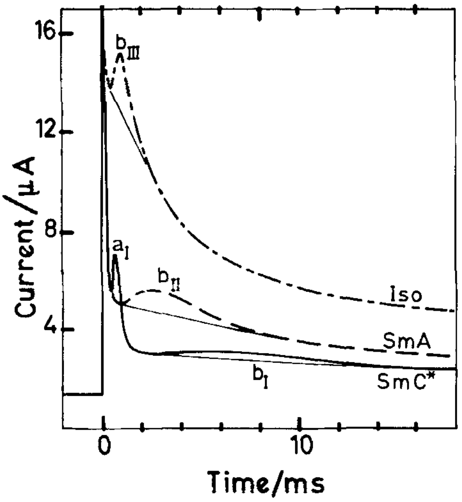


FIGURE 2 Typical transient current versus time curves for the liquid crystal compound 90BEB05* in different phases on the application of symmetrical 150 V alternate field.

In order to characterize the bump we integrate the current between the curve and its tangent as shown in the curves in Figure 2. The time of the bump or the peak time is defined as the time between the field reversal and the center of the ion bump peak.

STUDY OF THE ION BUMP PEAK TIME

For 90BE05*, the dependence of peak time on different parameters like voltage, sample thickness, temperature and phases was studied. The peak time is proportional to the voltage as shown in Figure 3. With an increase in sample thickness d, the peak time increases as d^2. From these results we can write for the peak time τ:

$$\tau = \frac{d^2}{\mu V}$$

giving $\mu = 0.95 \times 10^{-9}$ m²/Vs (isotropic); and $\mu = 0.47\ 10^{-9}$ m²/Vs (SmC*).

We interpret τ as the transit time of ions from one surface to the other.[9] Using

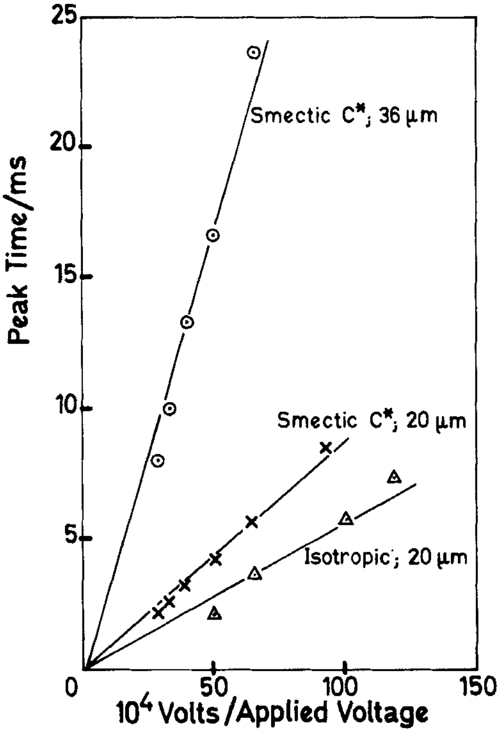


FIGURE 3 Variation in ion bump peak time on the application of the field in different phases of 90BEB05* for different sample thicknesses.

this interpretation μ is the mobility of the ions. The value of μ obtained is of the same order of magnitude as that for the nematic phase,[2] with an analogous variation with temperature.

In order to prove our hypothesis that the ion bump is due to ion movement we performed similar experiments on pure and impure C_{13}. As expected no bump was obtained in pure C_{13} but a well defined bump was observed in the impure one. The peak time variation for impure C_{13} with voltage shows similar behavior as that for pure 90BE05*. The value of μ for the component ions of TBATΦB, obtained from the experimental data for C_{13} is 4 10^{-9} m^2/Vs. Substituting this value of μ in Stokes law and taking viscosity of C_{13} = 1.55 cp at 23.3°C,[8] we get the radius of ions equal to 10 Å. This effective radius is two times larger than the theoretical value obtained from molecular bond lengths.

The effect of additional ions in 90BE05* in smectic A and SmC* phases is shown in Figure 4. The curve shows a non-linear behavior. At very low and high voltages the curve is almost linear with different slopes. The slope at high voltages resembles that for the pure compound as shown for comparison in the same figure. We interpret these curves to be the result of two types of ion. At high voltages the dissociation of the compound gives the major contribution to the total number of ions present in the sample. This explains the similarity in behavior of the curve for pure and impure compounds in this range of voltages. At low voltages the impurity

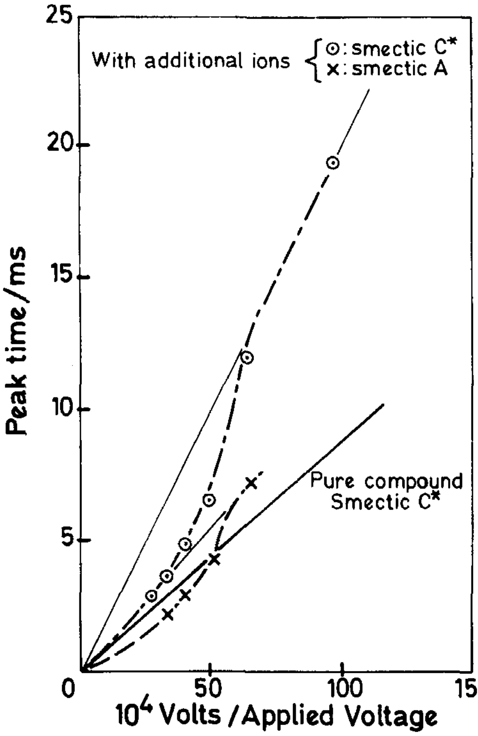


FIGURE 4 Variation in ion bump peak time for different phases of impure 90BEB05* for 20 μm cell thicknesses. Experimental curve of pure 90BEB05* is given for comparison.

ions are predominant as they are easily ionizable. The product τV of the peak-time and applied voltage is constant and gives the mobility μ of the impurity ions as $\mu = 0.2\ 10^{-9}$ m^2/Vs at 47°C. This mobility matches their mobility in nematic MBBA at 25°C[2]: thus the viscosity of 90BE05* at a given temperature is about 3 times that of MBBA.

In the SmA phase the curve shows similar behavior with the mobility of the impurity ions increasing to $0.42\ 10^{-9}$ m^2/Vs. Comparing the results of pure and impure 90BE05*, we have the radius of intrinsic ions to be half the radius of impurity ions. Assuming that the impurity ions are not solvated, the radius of the intrinsic ions comes out to be 2.5 Å and corresponds to half the molecular short axis.

From these studies in the smectic phase and in the ordinary liquid phase we get the ion bump time as the ion transit time from one electrode to the other. The obtained mobility in the smectic phase of the pure compound indicates an ion radius close to that of the compound molecules. This allows the hypothesis that ions are made by dissociation of the compound molecules.

STUDY OF THE AMPLITUDE OF THE ION BUMP

The bump charge per unit area for different sample thickness at various voltages is shown in Figure 5. The bump charge density has a voltage threshold beyond which it increases to a saturation value. This saturation value shows a linear dependence on the sample thickness. For a given sample thickness, the bump charge

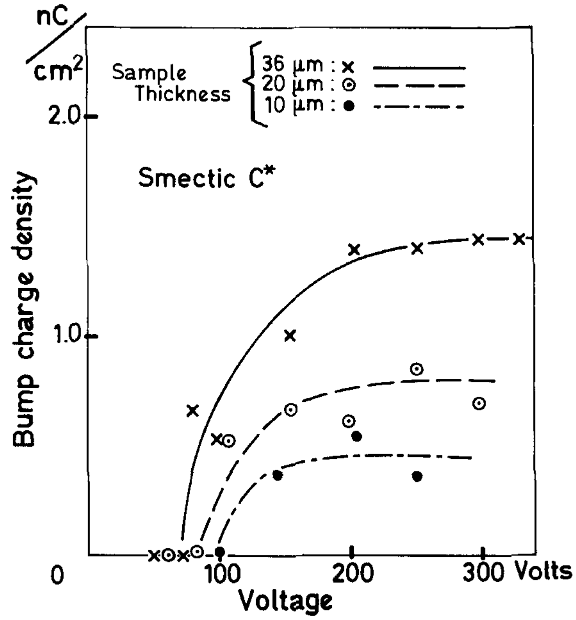


FIGURE 5 Variation in ion bump charge density on the application of alternate voltage for 90BEB05* for different sample thicknesses at 47°C.

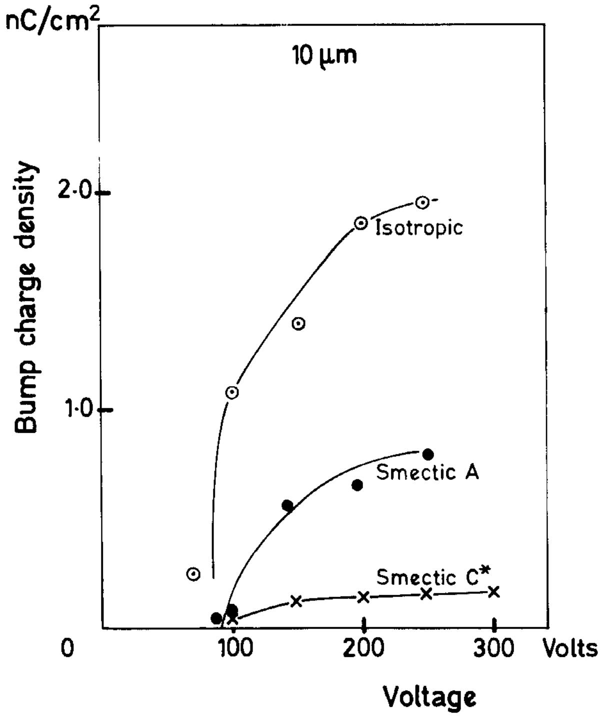


FIGURE 6 Variation in ion bump charge density with voltage for different phases of 90BEB05*.

density increases with the increase in temperature, Figure 6. Thus the amplitude of the bump does not depend on any interface effect between the liquid crystal and the electrodes but on the volume of the sample cell.

Table I gives the dc and ac resistances of 90BE05* samples for various thicknesses at a fixed temperature 47°C. The ac resistance is obtained with a Wayne and Kerr bridge. The frequency is 1,6 kHz and the applied voltage 4 volts peak to peak. The dc resistance is given by a Keithley electrometer for an applied voltage of 1 volt. In the case of pure compound the dc resistance is proportional to the sample thickness. This indicates conduction due to ions created in the bulk by thermal dissociation. We found that the amplitude of the ion bump keeps proportionality, i.e. the amount of ions stuck on the electrodes is also proportional to the thickness. It corresponds to a cloud of ions created in the bulk by thermal dissociation and

TABLE I

S. No.	Sample thickness (μm)	Resistance (dc) (GΩ)	Resistance (ac) (MΩ)
1	20	0.8	10.0
2	10	1.5	7.3
3	5	2.5	3.3

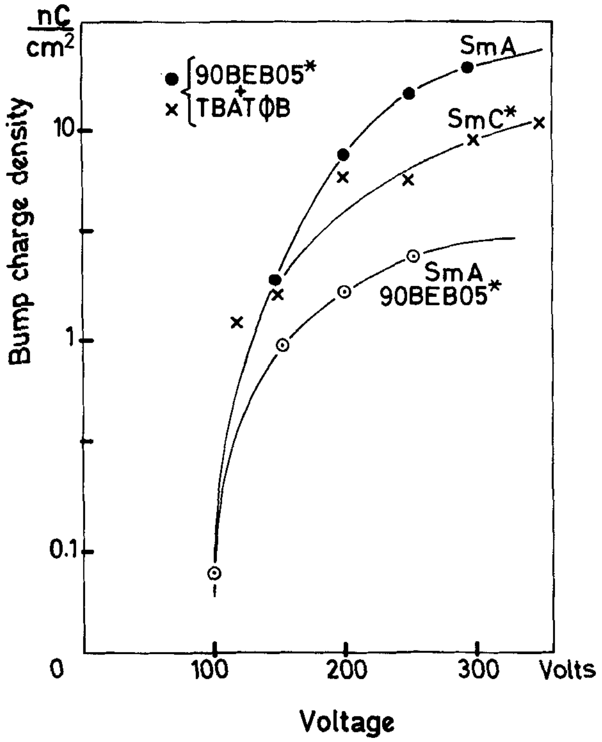


FIGURE 7 Variation in ion bump charge density with voltage for pure and impure 90BEB05* in different phases for 20 μm cell thickness.

waiting a given time near the electrode before being neutralized. The temperature dependence of the ion bump amplitude gives an activation energy of 0,86 eV which is of a good order of magnitude for a stable compound.

The impurity ions increase the amplitude of the bump. Figure 7, drawn for pure and impure 90BE05* shows the effect of additional ions on the amplitude. The voltage threshold stays the same. At a given temperature, the amplitude is about 6 times larger than that for the pure compound. Increase in temperature do not change the general behavior of the curve but the variation with temperature is less pronounced for the impure compound than for the pure one. On Table II the ion bump amplitude and the total ionic charge crossing the sample during half a period is plotted. The addition of TBAΦB increases the ion bump more than the total ionic charge. The effect of the TBAΦB impurity is obvious: it increases the amount of free ions in the bulk, but it increases the number of ions stuck on the electrodes more.

ION BUMP IN NEMATIC COMPOUNDS

Experiments were also performed on nematic compounds to study the ion bump. The compounds chosen were 5CB and EN-38, as it was easy to add different types

TABLE II

Compound	Temp. °C	Voltage (V)	Time of integ. ms	Ion bump nc/cm^2	Total ionic charge nc/cm^2
5CB	32	20	45	120	4000
5CB$^+$ TBATΦB	32	20	45	750	4000
5CB$^+$ CTAB	32	20	45	40	1400
90BEB05*	47	200	90	0.9	70
90BEB05*$^+$ TBATΦB	47	200	90	5.4	192

of impurities to these compounds while retaining their nematic phase. In both these compounds, ion bumps with larger amplitudes were obtained. Figure 8 shows the variation of the bump charge density with voltage for pure and impure 5CB. The variation for pure 5CB is similar to the variation for pure 90BEB0S* with amplitude approximately 100 times more for the former. The bump appears at much lower voltages for 5CB. The voltage threshold is independent of the impurities. The addition of TBAΦB in 5CB in the same proportion as in 90BEB05* gives an

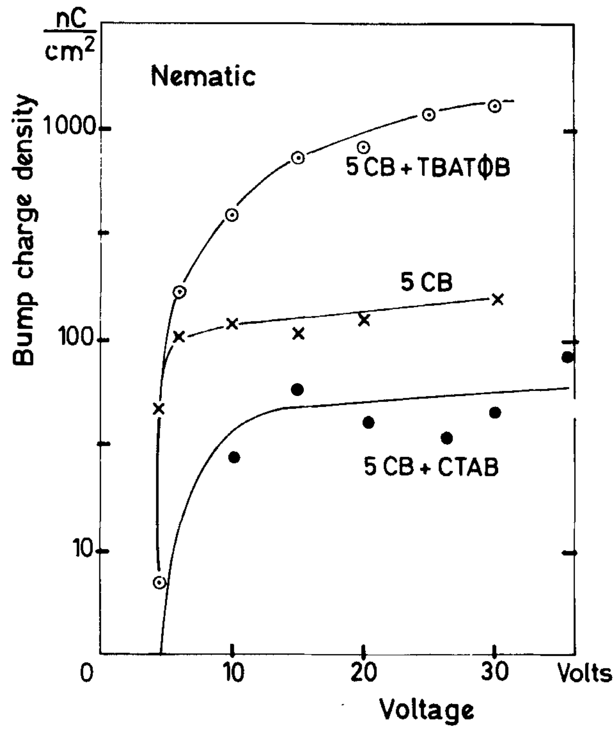


FIGURE 8 Bump charge density for pure and impure nematic 5CB compound with voltage for 20 μm sample thickness at 56°C.

amplitude about 6 times larger than for the pure parent compound. By contrast, for CTAB (cethyltrimethyl ammonium bromide) in 5CB the bump charge density is reduced. The saturation value is three times lower than that for the pure compound.

In order to estimate the total number of ions present in the sample, we integrate the total current through the sample just after the reversal of the field. The integration time is about 10 times larger than the transit time for the ions between the two electrodes. The results are shown in Table II. Addition of TBAΦB does not change the total ionic charge. Addition of CTAB divides by three the total ionic charge. We can interpret these results by the following model. CTAB acts as a retarding catalyst, lowering the dissociation speed of the pure compound. Thus the total number of ions present in the bulk at any time is decreased. The amplitude of the bump decreases in the same proportion as the decrease in the total number of ions. On the other hand TBAΦB gives additional ions that get stuck to the surfaces so that the bump charge density is increased. The rest of ions for impure 5CB do not show any observable change as the number of ions obtained by the dissociation of the pure compound is much larger than those given by the dissociation of TBAΦB.

CONCLUSION

We have measured the bump which appears in the transient current in liquid crystal cells, when a square wave field is applied. These measurements have been made in ferroelectric smectic C* liquid crystal, in other phases of the same compound and in the nematic phase of another compound.

The bump of current may exist in all the liquid phases above a given threshold voltage. It corresponds to a fast transport of ions stuck on the electrodes from one to the other. The speed of this transport is proportional to the applied field. The corresponding mobility is that of the ions in absence of any hydrodynamic motion. In pure compound the ions are produced by thermal dissociation of the compound. We can increase and decrease the amount of these stuck ions by adding different impurities to the cell.

Acknowledgments

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