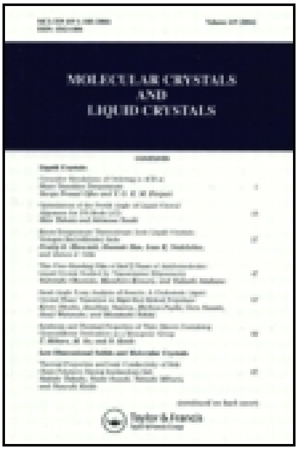

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DC Conductivity in Smectic A Phases-A Breakdown of Kohlrausch's Law

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DC Conductivity in Smectic A Phases-A Breakdown of Kohlrausch's Law

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We have combined the two cations *N*-hexadecylpyridinium and the dicyclohexyl-18-crown-6 complex of sodium with the three anions bromide, *p*-toluenesulphonate and tetraphenylborate, into six different salts, and measured their conductivity in the smectic A liquid crystal, S3. This allows us to extract mobilities for the five individual ions.

It is found that the mobility of different ions within a smectic A layer is determined by the cross section the ion presents in the direction of movement, and the law of independent movements of ions is valid. For the mobility perpendicular to the smectic A layers the mobility is critically dependent on the quality of the homoetropic alignment. This quality will be determined by the history and alignment conditions of the sample, as well as any impurities present. The movement of the individual ions can thus no longer be treated independently of other ions or undissociated salt that are present in the sample.

Keywords: ionic conductivity, smectic A

1 BACKGROUND

The movement of ions in a liquid crystal is a phenomenon of great practical and theoretical interest. In dynamically scattering nematic[1] and smectic[2,3] devices, the movement of ions is essential for the operation of the display and has to be optimized for application. In active matrix displays, the movement of ions gives a leakage current and should be minimized to achieve the best performance of the display.[4] In the surface-stabilised ferroelectric display, the inclusion of ions can be detrimental to the performance or enhance the bistability depending on the ionic concentration.[5]

The theoretical treatment of ions and ionic conductivity in liquid crystals is not straightforward. Due to the generally low dielectric constant of the liquid crystals, any added salts will only be weakly dissociated even at very low concentrations. A treatment of the problem must thus be based on the weak electrolyte theories by Ostwald[6] or Onsager.[7] The electric field strengths involved in liquid crystal devices will however affect the equilibrium between undissociated salts and dissociated ions.

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The anisotropy of the medium will not only give different conductivities parallel and perpendicular to the director of the sample, but will also lead to a breakdown of simplifying assumptions like Waldens rule.[8] Even if the rule is valid in the isotropic phase of the mesogens, the rule is no longer useful in the nematic phase, as the correct combination of the four nematic viscosities are not known.

In addition to these problems, most investigations in this field were performed more than a decade ago, when there was a very limited choice of stable liquid crystals, and thus a risk of introducing extra ions in addition to those being studied. In fact many early studies relied completely on ionic impurities present in the liquid crystals.[2,9-12]

The sparsity of recent data combined with the practical implications of this problem led us to undertake this study. During the investigation we discovered that the Kohlrausch law of independent movement of ions is no longer valid for the movement of ions along the director in smectic A phases.

2 THEORETICAL

We adopted the weak electrolyte theory[13] for determination of the mobility of the ions. Here the average time of flight for the ions (τ_T) is given by

$$\tau_T = 2d/(E[\mu_+ + \mu_-])$$

where d is the cell thickness and E is the electric field across the cell. μ_+ and μ_- are the mobilities of the positive and negative ions, respectively.

Assuming that the dissociation of the salts is a much faster process than the time of flight for the ions, the time of flight is also given by:

$$\tau_T = -2(I(t) - I_\infty)(\partial I/\partial t)$$

where $I(t)$ is the current through the cell at time t and I_∞ is the residual current at infinite time. For this current we substitute the experimentally-determined current through undoped S3.

Combining the two expressions for τ_T we obtain the following expression for the combined mobilities of the ions in the cells.

$$(\mu_+ + \mu_-) = [(\partial I/\partial t)E]/[-d(I(t) - I_{\mathrm{Back}})]$$

As ions are swept towards the electrodes charges will build up and the effective field across the cell will be reduced. To avoid this problem, values of $I(t)$ during the first few seconds of the measurement were used to calculate the mobilities of the ions.

Above 1.5 Volts/μm, electrolytic and other complex pressure processes might begin to interfere.[6] In the present work we used 1 Volt across an 11 μm cell to give a field well below this value.

It had been shown that the double layer thickness will be insignificant in nematic liquid crystals.[6] The parameters that govern the double layer thickness are not affected by the nematic-to-smectic A transition and we thus expect the same to be the case in smectic A liquid crystals.

3 EXPERIMENTAL

3.1 Cell Construction

The cells used in this study each consisted of a matrix of 32 × 32 tin oxide electrodes on glass, thus allowing many measurements on each cell. Each single electrode was 1 mm^2. The electrode spacing was 50 μm and the distance between the two substrates was 11μm, maintained over the whole area with glass fibre spacers. There were no alignment layers in the cells. The electrodes where cleaned in an ultrasonic bath with detergent solution, before rinsing thoroughly with deionized water, and finally acetone. The glass plates were dried at 120 °C before assembly. A thermosetting glue without ionic contaminant was used for the assembly. The cells were vacuum filled with the mixtures under investigation in the isotropic state through a small hole in one of the glass plates, with suction applied to another hole in the opposite corner. The cells were sealed with indium metal and UV curing glue before the measurements.

3.2 Mixtures

The smectic material used in this study is S3, a mixture of alkyl- and alkoxy-cyanobiphenyls from Merck (Poole, Dorset).

Sodium *p*-toluensulphonate, sodium tetraphenylborate, *N*-hexadecylpyridinium bromide and the crown ethers are all commercially available and were used without further purification. *N*-hexadecylpyridinium *p*-toluensulphonate was made by mixing saturated solutions of *N*-hexadecylpyridinium bromide and sodium *p*-toluensulphoate in water and extracting with chloroform. The chloroform solution was washed several times with water before the solvent was evaporated and a soft white crystalline material resulted. The phase transitions were crystal–113 °C–Smectic–165–165.8 °C–isotropic.

N-hexadecylpyridinium tetraphenylborate precipitated as a white waxy compound when saturated solutions of *N*-hexadecylpyridinium bromide and sodium tetraphenylborate were mixed. The product was dissolved in hexane and washed several times with water before the hexane was evaporated and the white precipitate dried under vacuum. The melting point was 88 °C.

All solutions were made by dissolving approximately 1% of the dopants in the liquid crystal mixture S3. The solutions were heated above the clearing point and shaken several times to ensure homogenous mixing. This solution was then diluted further to the final concentrated of 0.01% (w/w). In all solutions with crown ethers there were a three- to five-fold excess of the crown ether.

The dibenzo-18-crown-6 formed a sparingly soluble complex with sodium salts and the solution was thus formed by dissolving 0.01% of the sodium salts and 0.05% of the crown ether directly in S3.

We also tried to make solutions with different picrate salts. These all turned red when heated to the isotropic phase. S3 is a mixture of alkyl- and alkoxy-cyanobiphenyls. Octylcyanobiphenyl (8CB) did not give any such colour change, while octyloxy-cyanobiphenyl (8OCB) gave a very similar colour. A solution of picrate salts in octanol also turned reddish brown when heated. These observations lead us to the conclusion that the picrate salts form a Meisenheimer complex[14] with the alkoxy part of the liquid crystals. Further tests with picrate salts were thus abandoned.

3.3 Measurement

A Keithley 617 Electrometer was used for the measurements. Above 1.5 Volts/μm, electrode processes might begin to interfere,[6] the 1 Volt used across an 11 μm cell is well below this value. When the same pixel was measured several times it gave the same initial value for the conductivity every time, when the voltage across the pixel was below 10 Volts. Above 15 Volts the pixel started to show higher resistivity for the second measurement, and the difference increased with voltage. All values in this study are for the first measurement of any pixel and voltages were kept below the 10 V limit.

The material in these cells naturally adopted a planar orientation with rather large focal conic brushes. The homeotropic alignment was achieved by heating the samples into the isotropic state and cooling with a 7.5 kHz, 110 V AC field across the sample. SnO_2 gives a planar orientation, while In_2O_3 gives homeotropic alignment.[15] This is probably the reason why most studies use tin oxide for the alignment in this kind of experiment.

4 RESULTS

In Table 1, the conductivity anisotropy ($(\sigma_{\|} - \sigma_{\perp})/\sigma_{\perp}$) at $t = 0$ is given for the different solutions.

There is clearly an effect of the shape of the ions. The salt with elongated cation and anion gave an anisotropy value that is comparable to pure S3, while all other salts give much smaller values.

The anisotropy of the conductivity is dependent both on the anisotropy of the mobility of the single ions and their relative mobilities. Since most salts also seem to have less anisotropy than the ions naturally present in S3, the dissociation constant of the salts will also influence the conductivity anisotropy.

In Table 2, mobilities of the salts in planar and homeotropic orientation are shown. These mobilities agree well with previous measurements which give values 2.8×10^{-7} cm^2/V s for cholesterol myristate,[16] 3.5×10^{-7} cm^2/V s for cholesterol erucate,[16] $10^{-6} - 10^{-7}$ cm^2/V s for *p*-cyanobenzylidene-*p*′-octylaniline,[17] $0.5 - 3 \times 10^{-6}$ cm^2/V s

TABLE I

	$\sigma_{\|} - \sigma_{\perp}/\sigma_{\perp}$
S3	−2.65
N-hexadecylpyridinium *p*-toluensulphonate	−7.01
Sodium crown tetraphenylborate	−0.37
N-hexadecylpyridinium tetraphenylborate	−3.24
Sodium crown *p*-toluensulphonate	−0.67
N-hexadecylpyridinium Bromide	−2.30
Sodium crown Bromide	−1.61

TABLE II

The sum of the ionic mobilities and the dissociation constants for the salts studied

Salt	Planar Mobility 10^{-7} cm^2/V sec	Homeotropic Mobility 10^{-7} cm^2/V sec	Dissociation constant
N-hexadecylpyridinium *p*-toluenesulphonate	4.8	0.8	1.7×10^{-4}
Sodiumtetraphenylborate + dicyclohexyl-18-crown-6	4.5	3.9	1.9×10^{-4}
N-hexadecylpyridinium tetraphenylborate	2.9	3.8	5.8×10^{-5}
Sodium *p*-toluenesulphonate + dicyclohexyl-18-crown-6	5.3	5.3	5.6×10^{-5}
N-hexadecylpyridinium bromide	4.0	1.8	4.8×10^{-6}
Sodium bromide + dicyclohexyl-18-crown-6	5.2	2.8	1.5×10^{-5}

for *p*-*n*-butoxybenzylidene-*p*-octylaninline[17] and $10^{-5} - 10^{-7}$ cm^2/V s for cholesterol esters[17] without specifying any ionic species, and also with the value of 5×10^{-7} cm^2/V s for the charge-transfer complex TMTTF-ODTCNQ in the smectic C phase.[18] The anisotropy ratios are also in good agreement with earlier reports.[19]

From the mobilities in the planar orientation together with the values for the initial conductivity, the concentration of ionic species can be calculated from the equation:

$$I_o = E(\mu_+ + \mu_-)N_o$$

With the concentration of the ionic species and the initial concentration of the salt known, it is easy to calculate the dissociation constant for the different salts, and this is given in the last column in the table.

5 DISCUSSION

5.1 Conductivity Anisotropy

The conductivity anisotropy given in Table 1 is a function of the shape of the ions. The salts with liquid-crystal-like ions, such as *N*-hexadecylpyridinium show larger anisotropy, while salts with more spherical ions show much smaller anisotropy. The salt with both ions somewhat elongated thus shows the largest anisotropy for the conductivity, while the salts with both ions near spherical shows the smallest anisotropy. This is in agreement with what have been found earlier for the nematic phase.[20] In most cases, the salts give solutions with lower anisotropy than the undoped S3, this shows that the ions naturally present in the liquid crystal, not surprisingly, are liquid crystal like. As most ions have less anisotropy than the background, it is also easy to see that increased concentrations of the salts would seemingly give lower conductivity anisotropy. This have been observed in several cases.[10,21]

5.2 Planar Orientation

An example of how the current through the cell decays with time is shown in Figure 1. All samples showed similar behaviour to this with a smooth decrease of the current through the cells for the planar orientation. We have five different ions combined into six different binary salts, it is thus in principle possible to extract the mobilities for every single ion. This is done for the planar alignment in Table 3. We expect the values have an experimental error of +/−15%. In Table 4 the calculated and measured values for the salts are compared, assuming independent migration of ions. As can be seen the values are well within experimental error.

The inverse mass and cross section of the ions are given in Table 3. The cross section is defined as the area projected by a rectangle with the sides of the longest axis and shortest axis for the three elongated ions. For the tetrahedral tetraphenylborate we take the triangle covered when projected onto a plane, for bromide the area is the projected circle with radius equal to the ionic radius. Figure 2 clearly shows the excellent agreement between the size of the ions and the mobilities. The inverse mass of the ions shows much poorer correlation. The movement of the ions parallel to the layers seems to be determined by their chances of colliding with a liquid crystal molecule and is determined by their cross section orthogonal to the direction of movement.

Ions will always appear in pairs. Any measurement of conductivity or mobility will thus give the added contribution from both the positive and negative species. The two different species will move in opposite directions, but they also carry opposite charges, thus both will give a positive contribution when mobilities are determined. Kohlrausch's law assumes that the mobilities of the ions can be treated independently. The mobility of a cation in a given solvent is independent of which anions that might be present. It is therefore meaningful to determine contributions from single ions to the overall conductivity of the sample. The mobilities of single ions have been determined for unoriented nematic samples by assuming that the two ions tetraphenylborate and tetra(isopentyl)ammonium which have the same radius and shape also will have the same mobilities.[22] This is disregarding the differences between the fully saturated tetra(isopentyl)ammonium and the highly aromatic tetraphenylborate ions.

Another way of obtaining values for different single ions is to combine the ions into enough different salts to have at least as many salts as ions. This will give a solvable set of equations. We have combined the two cations *N*-hexadecylpyridinium and the dicyclohexyl-18-crown-6 complex of sodium with the three anions bromide, *p*-toluenesulphonate and tetraphenylborate into six different salts. We thus end up with a system where we have one measurement more than unknowns, this allows us not only to solve the equations to find mobilities for every single ion, but also gives a check of how good the determination is. The results are given in Table 3 together with the cross section and inverse mass of the ions. Not unexpectedly our values for mobilities are somewhat lower than those found in the less ordered

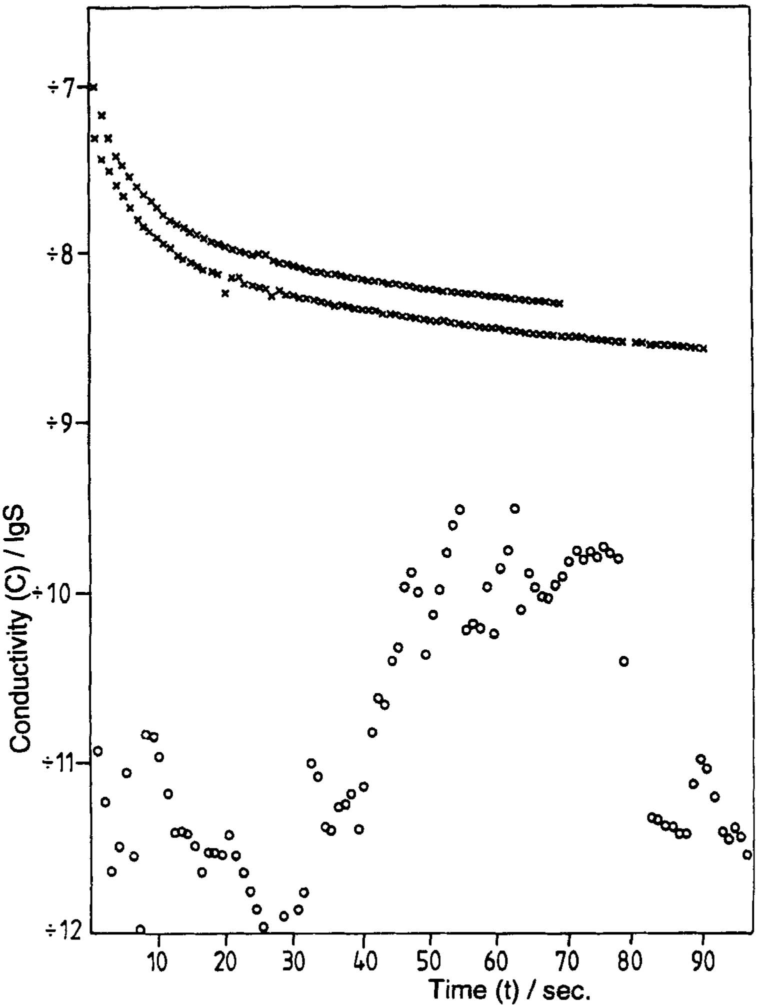

FIGURE 1 Current through a cell doped with sodium-dicyclohexyl-18-crown-6 *p*-toluensulphonate as a function of time, for three different textures, top to bottom planar (focal conics), homeotropic and sanded (random). The applied voltage is 1 Volt.

nematic phase. Table 4 compares the calculated and experimental values for the mobilities of the different salts. Over a wide range of structures the mobilities seem to depend only on the size of the ions. The simplifying assumption that tetra(isopentyl)ammonium and tetraphenylborate have the same mobilities[22] thus appears to be justified.

The smectic phase can be regarded as a sandwich structure with alternating layers of cyanobiphenyl cores and alkyl chains. The molecules form dimers with overlapping pairs of cyanobiphenyl units and as the diameters of the alkyl chains are less than the phenyl part, the density will show a corresponding alternation. There will be smaller

TABLE III

The mobilities of individual ions together with their cross section and inverse mass

Ion	Mobility 10^{-7} cm^2/V. sec	Cross Section Å^2	Mass$^{-1/2}$ a.u.$^{-1/2}$
N-hexadecylpyridinium	0.7	51.9	0.0574
Sodium dicyclohexyl-18-crown-6	1.8	45.2	0.0503
p-Toluenesulphonate	3.9	17.9	0.0764
Tetraphenylborate	2.6	28.1	0.0439
Bromide	3.4	12.1	0.1119

TABLE IV

A Comparison between the calculated and measured mobility of the different salts

Salt	Mobility Measured 10^{-7} cm^2/V sec	Planar Calculated 10^{-7} cm^2/V sec
N-hexadecylpyridinium *p*-toluenesulphonate	4.8 + / − 0.2	4.6
Sodiumtetraphenylborate + dicyclohexyl-18-crown-6	4.5 + / − 1.9	4.4
N-hexadecylpyridinium tetraphenylborate	2.9 + / − 0.7	3.3
Sodium *p*-toluene-sulphonate + dicyclohexyl-18-crown-6	5.3 + / − 1.1	5.7
N-hexadecylpyridinium bromide	4.0 + / − 0.4	4.1
Sodium bromide + dicyclohexyl-18-crown-6	5.2 + / − 1.0	5.2

interactions between the alkyl chains, and their more isotropic fluid-like behaviour will make it easier for neutral molecules to fit in here. Moseley and Loewenstein showed that small neutral molecules will preferably be found among the alkyl parts of smectic[23] structures. Later investigations have however come to different conclusions as they find no changes in order parameters between the different parts of the mesogen with inclusion of small hydrocarbons.[24]

The group at STC also assumed that the ions were situated among the alkyl chains[25] and thus relatively free to move parallel to the layers. Heppke and co-workers studied the dielectric constants of the core parts and alkyl chains of alkoxyazobenzenes and found it much more likely that the ions would be among the cores which had a higher dielectric constant and thus were more favourable to ionic dissociation. It was also found that the salts they used were 10^4 times more soluble in azobenzene than in hexane.[21] Our measurements shows that only

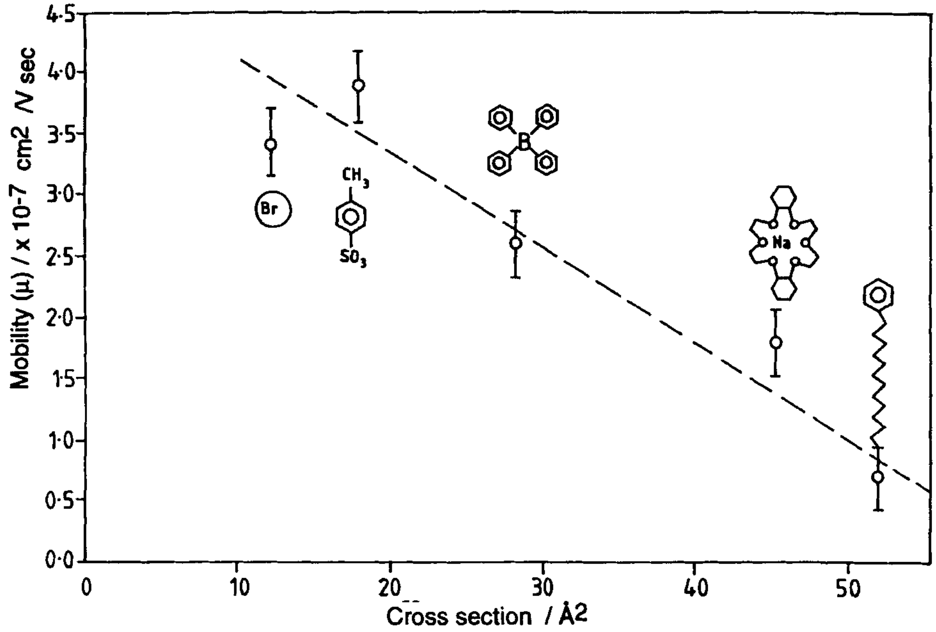

FIGURE 2 Mobilities of the five ions as a function of their cross section orthogonal to the direction of movement.

the cross section of the molecules and not their shape determine the mobility. This indicates an environment that more closely resembles an isotropic fluid, and the ions thus probably reside most of the time among the less densely packed alkyl chains.

The low concentration of dopants used in this study did not affect the phase transition temperatures. The more concentrated solutions made during the mixing procedure did however show interesting trends. *N*-hexadecylpyridinium *p*-toluensulphonate depressed both the smectic A–nematic and nematic–isotropic by about the same amount. The other salts depressed the nematic–isotropic transition far more than the smectic A–nematic. The sodium complex of bicyclohexyl-18-crown-6 with tetraphenylborate depressed the smectic A–nematic transition so much that there was a transition directly from smectic A to isotropic when the concentration was above ~ 1.5% (w/w). It is clear that the elongated salts have relatively little effect on the stability of the nematic phase while the more spherical ions strongly disrupts the nematic order, while leaving the smectic ordering relatively intact. This can be explained by the ions being preferably situated among the alkyl chains in the smectic A phase. The alkyl chain are flexible and can relatively easily accommodate the bulky ions without severely disrupting the parallel ordering of the biphenyl cores in regular layers. In the nematic phase there are no corresponding hiding places for the ions, and the ordering is more severely disrupted. It was also found that S3 doped with *N*-hexadecylpyridinium *p*-toluensulphonate gave a very strong tendency for homeotropic orientation on glass. The other dopants, the sodium complex of bicyclohexyl-18-crown-6 with tetraphenylborate in particular, gave many small round droplets decorated with a maltese cross in otherwise homoetropic samples. As Figure 3 shows this texture can be explained by a bending of the layers.[26] Having bulky ions among the alkyl chains would of course force them somewhat apart and induce a layer bending, or at least make it easier.

Similar effects of the shape of non-ionic additives on the relative stabilities of the nematic and smectic phases have been observed earlier.[23,24]

5.3 Random Orientation—Sanded Texture

It has been found[6] for the nematic phase that an average ionic mobility controls the current in the turbulent scattering state.

In Figure 1, the current through a cell in homeotropic orientation, planar orientation and the highly scattering sanded texture are shown. As expected for smectic phases the

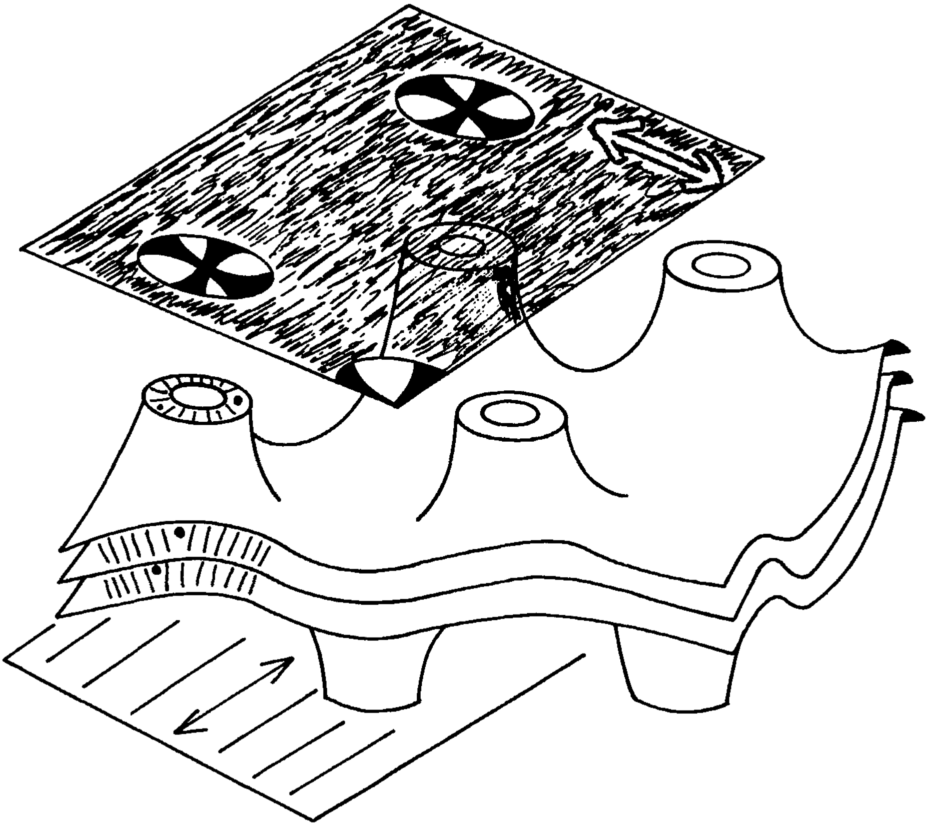

FIGURE 3 Schematic view of deformed homeotropic textures showing small birefringent droplets between crossed polarisers.

current through the cell in the homeotropic orientation where ions have to move from one layer to the next is slightly smaller than in the planar texture where ionic movements take place within the layer. In the sanded texture there are probably small fragments of smectic A layers randomly oriented with numerous defects. Two effects are immediately seen from the figure. The current through the cell is much smaller than for both the planar and the homeotropic state and clearly not an average of the two. The sanded texture was introduced in these cells by mechanical treatment, and the difference is thus not due depletion of ions during any electrical scattering process. While the curves for the current through the cells over time in the two more well ordered states show a smooth decline the current through the cell in the sanded texture varies widely, although there is a general decline over the first 20–30 seconds and a slight increase after this. This increase was first thought to be due to an electrical ordering of the material, although no changes to the texture could be seen under the microscope. Reducing the voltage across the sample to 0.1 Volts did however give the same increase after the same time. The very low conductivity and the large variations over time for the sanded texture clearly show the difficulties for the ions in passing over the defect from one microdomain to the next. This behaviour is quite different from the dynamic scattering texture of the smectic A display where the current through the cell increases markedly due to the turbulent motion.[2]

5.4 Homeotropic Alignment

Most of samples showed similar behaviour to the planar cases with a smooth decrease of the current through the cells. For undoped S3 and S3 doped with *N*-hexadecylpyridinium-*p*-toluenesulphonate, there was a different behaviour with the same general trend, but a series of small steps on the curve. It seems as if the *N*-hexadecylpyridinium *p*-toluenesulphonate ion pair (and whatever ions are naturally present in S3) have much the same difficulty in passing from one smectic layer to the next as the ions of sodium crown complex and *p*-toluenesulphonate have in crossing the borders between different domains.

For *N*-hexadecylpyridinium tetraphenylborate, the steps might be present, but are much smaller and cannot be clearly seen with the resolution our experiment gives.

These steps could only be seen the first (few) times the cells were oriented homeotropically. After a series of heating and reorientation processes the curves were smooth, and the mobilities of the ions were found to be much higher. This is very reminiscent of the "burn-in" process that takes place in electrically addressed smectic A devices.[3]

The observations made so far led us to conclude that the mobilities of the ions perpendicular to the layers are very dependent on the quality of the alignment, and that defects present seem to lower the barriers for the ions to move from one layer to the next. We thus tested the cell with *N*-hexadecylpyridinium *p*-toluenesulphonate with several different conditions for the homeoptropic alignment of the liquid crystal.

Figure 4 shows the effect of the frequency used for 110 volt peak-to-peak sine and square waves, applied for 18 minutes. The mobility is fairly independent of the frequency up to about 10–12 kHz for the sine waves. At this stage the mobility increases and the alignment also visually deteriorates as the cross-over frequency where $\Delta\varepsilon$ becomes negative is approached.

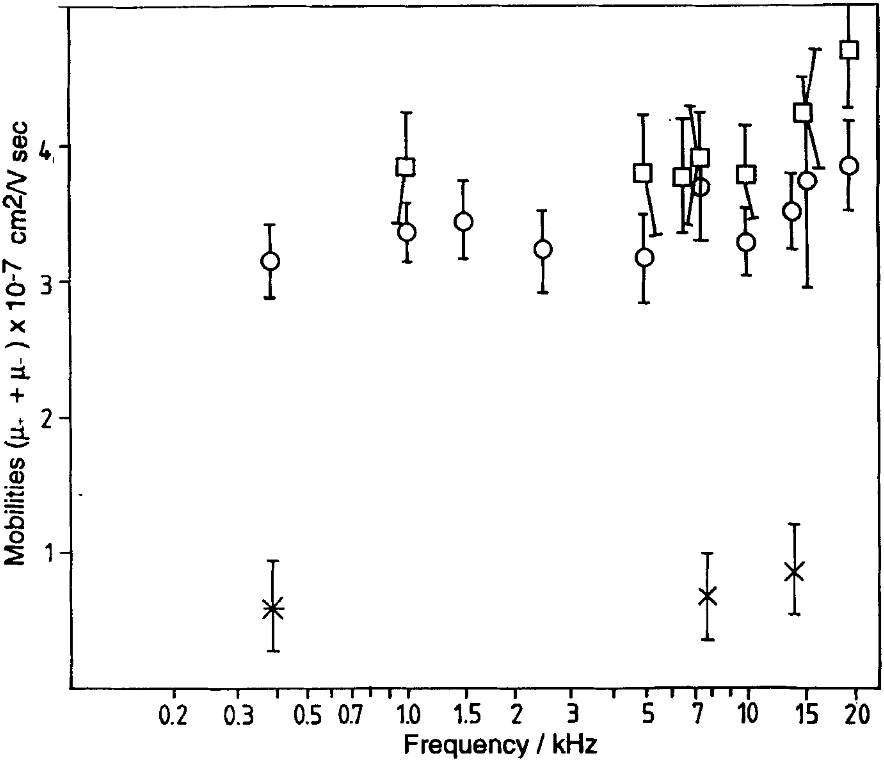

FIGURE 4 Mobilities for *N*-hexadecylpyridinium *p*-toluensulphonate in the homeotropic alignment as a function of the frequency used for alignment. The voltage is 110 V (10 V/μm). ☐ square waves, ○ sine waves, × initial sine wave treatment (see 5.4 for discussion).

For square waves, the mobility increases at lower frequencies, probably an effect of the higher harmonics already being above the cross over frequency. The sample aligned by square waves also shows a higher mobility at all frequencies. This will be explained later.

Figure 5 shows the effect of the time the field is applied for 110 V sine waves. Three minutes is the shortest time that could be used with the liquid crystal still having time to cool down from the isotropic into the smectic A phase. To align our cell homeotropically the cell was heated to the isotropic state and brass electrodes were connected. These electrodes were so wide that an area of 100–400 pixels (out of the total of 1024) were aligned at the same time. Although we made sure that no single pixels were measured more than once, to avoid any possible depletion of ions over the pixel, most pixels had been aligned several times with slightly different conditions before they eventually were measured. The total number of times a pixel was addressed seems to influence the mobility of the ions. In Figure 4 with the mobility of the ions as a function of the time, different waveforms are applied; the lower curve was the initial experiment where the cell only been addressed 10–15 times earlier. As is clearly seen, the mobility decreases as the time increases up

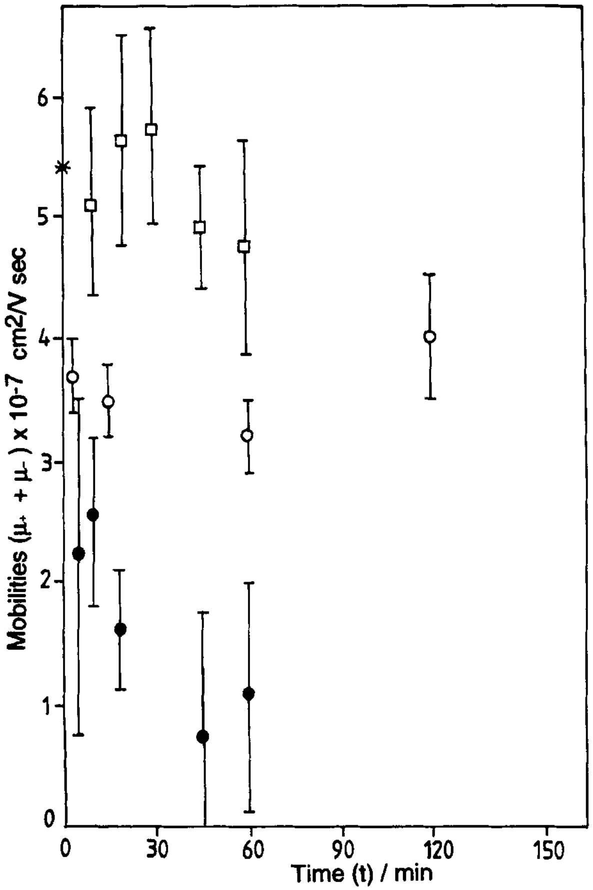

FIGURE 5 The ionic mobilities as a function of time for achieving homeotropic alignment. □ *N*-hexadecylpyridinium-*p*-toluensulphonate 110 V/17 kHz square wave. ○ *N*-hexadecylpyridinium-*p*-toluensulphonate 110 V/14 kHz sine wave. ● *N*-hexadecylpyridinium-*p*-toluensulphonate 110 V/5 kHz sine wave. × give the value for *N*-hexadecylpyridinium-*p*-toluensulphonate without field, after the "burn-in".

to about one hour. We take this as evidence of an improved alignment, which was confirmed by optical microscopy. The upper curve was a repetition made after the cell had been addressed 25–30 times, and also with some of the longer lasting experiments. Again we see the a decrease in the ionic mobilities as the time increases, but at all times the mobility is much higher than during the earlier series of experiments. The same effect can also explain why the alignment by sine wave, which was performed first, gave lower ionic mobilities than later alignment by square waves. This effects very similar to the reported "burn-in" that takes place with electrically addressed smectic A displays. It should also be noticed that after 15–20 homeotropic alignment processes, the pixels in this area adopted a permanently homeotropic alignment, even when cooled without field. The conductivity did however still also show the influence of the last treatment.

The *N*-hexadecylpyridinium tetraphenylborate was also studied in some detail, this time using a slightly modified connecting electrode and taking care to address every area only once. The effect of applying a 5 kHz sine wave is shown in Figure 5. As can be seen the effect of increasing the time is very similar to that for the *p*-toluenesulphonate analog.

Figure 6 shows the effect of applying sine waves of different frequencies. The curve is again very similar to that found for the *p*-toluenesulphonate salt. That the conductivity increases at lower frequency and the conductivity generally is somewhat higher compared with the bottom curve of Figure 4 can probably be attributed to tetraphenylborate being much bulkier than *p*-toluenesulphonate and thus disturbing the structure to a larger extent. Even for these samples which have been oriented only once and for the same time there are rather large standard deviations.

A positive correlation was found between the number of spacers on the individual pixels and the mobility measured. As the glass fibres are cut to different lengths, the number of glass fibres only gives a very rough estimate of the sizes of the defects introduced, and one long fibre may possible improve the conductivity as much as two or three shorter ones. Figure 7 shows this trend.

Although it has not been possible to give definite and meaningful values for the mobilities in the homeotropically aligned samples, the mobilities seems to have the

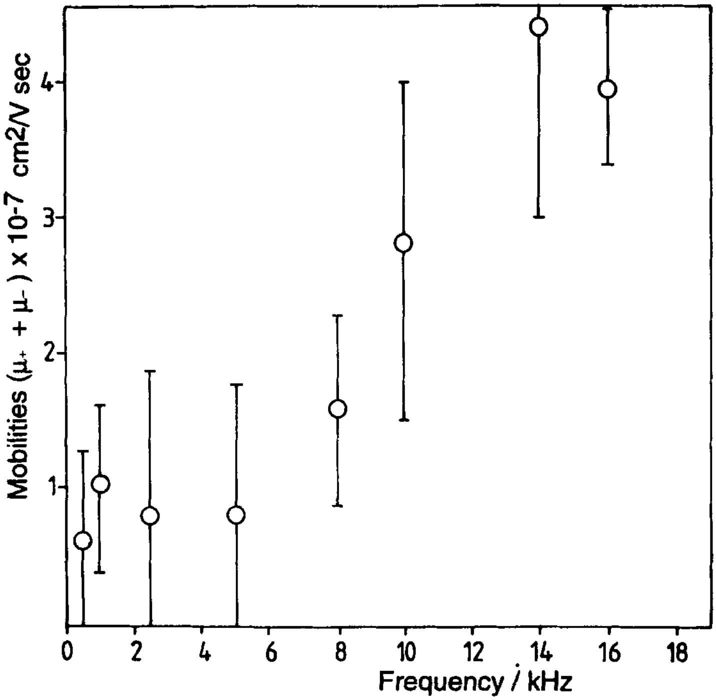

FIGURE 6 The mobilities of the ions from *N*-hexadecylpyridinium tetraphenylborate as a function of frequency used for obtaining homeotropic alignment. The voltage used is 110 V (10 V/μm) sine wave.

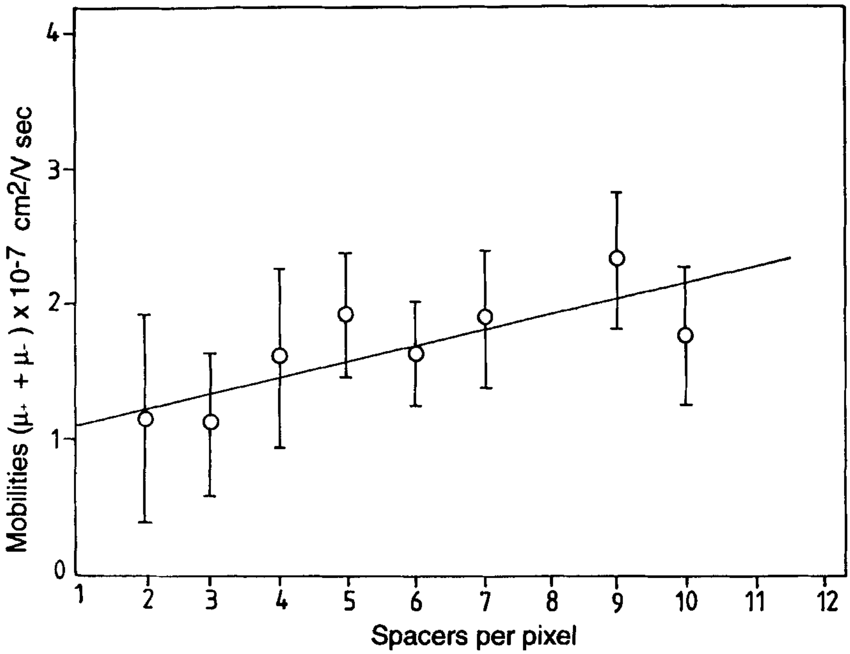

FIGURE 7 Mobilities of the ions from *N*-hexadecylpyridinium tetraphenylborate as a function of the number of spaces per pixel (square mm).

following order: *N*-hexadecylpyridinium << Tetraphenylborate ~ Bromide < Sodium crown complex ~ *p*-toluenesulphonate. This list does not bear any obvious resemblance to molecular properties.

Heppke and co workers[21] give the variation in conductivity along a smectic structure as

$$\sigma(z) = \sigma_o[1 + B\sin(2\pi z/d)]$$

where d is the layer thickness and B is a function of the amplitude of the density, the proportion of alkyl chains to the total mesogen length and the relationship between the dielectric constant and the conductivity. The average conductivity in the z direction will be:

$$\sigma = \sigma_o\sqrt{(1 - B^2)}$$

To understand how imperfectly aligned samples give higher ionic mobilities it is thus necessary to understand how imperfect alignment decreases the factor B. In Figure 8 are shown different types of defects in the smectic layering. Common for all these are areas where the smectic layers are frustrated; one way of relieving part of the stress is by adopting a more nematic-like ordering. This will obviously decrease the amplitude of the density and thus the B factor. These measurements clearly show that the mobility of ions perpendicular to the layers in smectic A (and probably most smectic structures) is

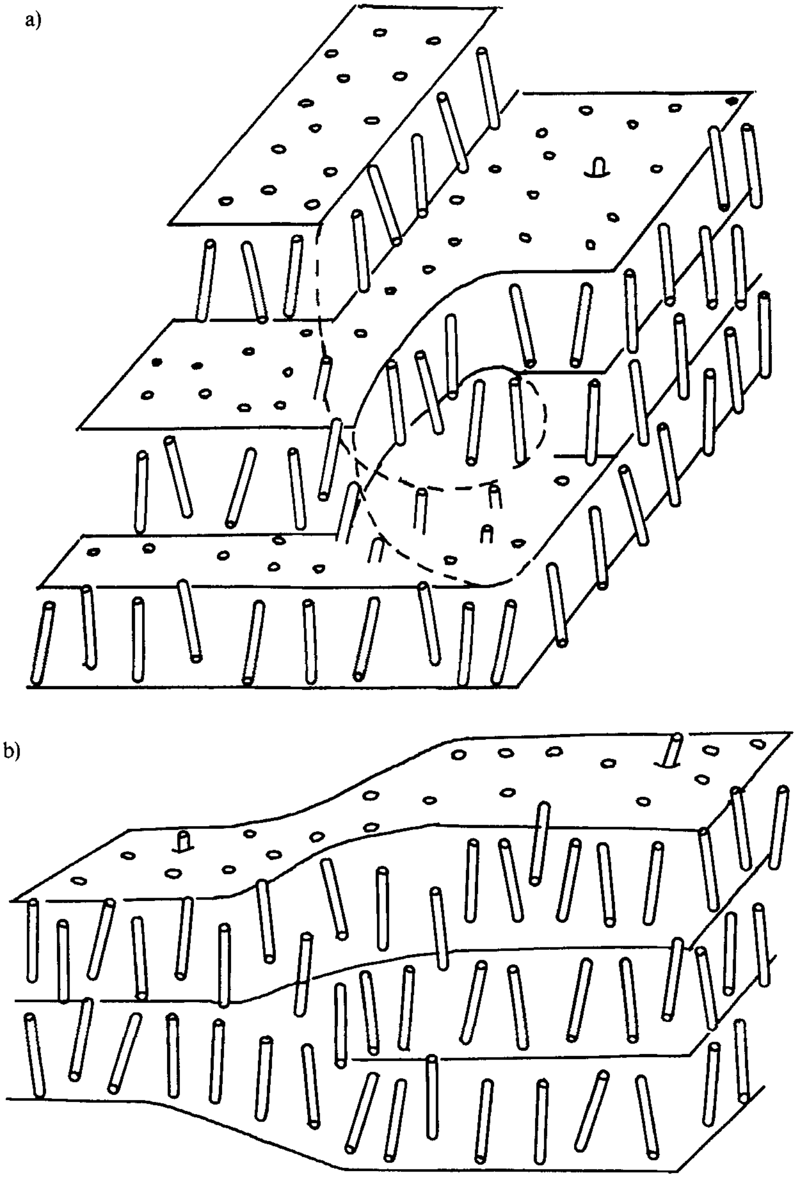

FIGURE 8 Different defects in the homeotropic smectic A alignment. A) Screw dislocation. B) Edge dislocation. C) Two disclinations. In all cases the defect or "singularity" encompasses a breakdown of the smectic layered structure, and thus also a lowering in the constant B. This gives increased conductivity of the structures. *Warning* These are simplified schematic drawings of a frozen smectic A structure, where the molecules are drawn as rigid rods while they certainly are neither rods or rigid. Also the ordering in the smectic A mesophase is a long range ordering, which is not truly represented by the small number of molecules drawn here. On this short length scale there will be a much stronger correlation between neighbouring molecules. The drawn rods can better be looked upon as average directors for groups of a few hundred molecules at one instant in time.

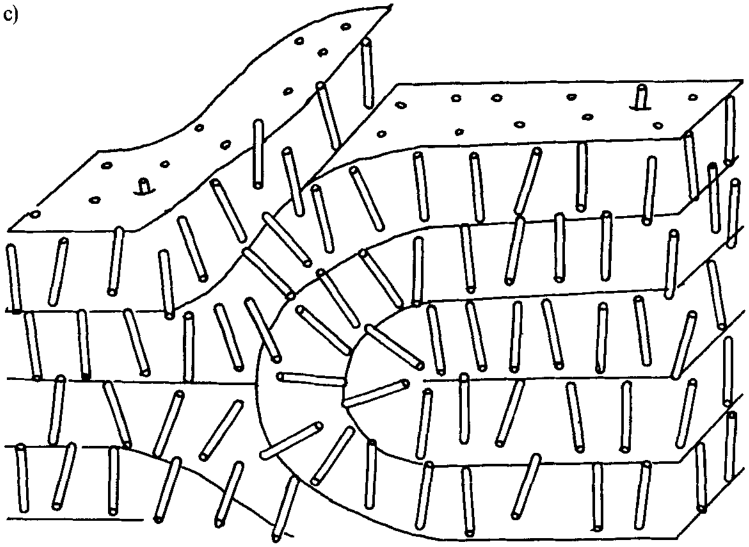

FIGURE 8 *(Continued)*

extremely dependent of the quality of the alignment and that defects in the structure make it easier for the ions to migrate. On the other hand, the density of defects is critically dependent on the preparation of the sample, and it's history. As the ions and undissociated salts present will disturb the smectic structure to different degrees, the defect density and thus mobilities of any given ion will also depend on the counter-ion present. Thus the law of independent movements of ions is no longer valid for movements along the director in the layered smectic phase.

For the electrically addressed smectic A display, it has been found that the roughness of the glass surface influences the threshold voltage for the scattering texture.[3] Rougher surfaces gave a lower threshold voltage. This observation is consistent with our observation that defects in the smectic layer structure influences the conductivity.

5.5 The Dissociation Constant

The dissociation constants for the different salts are given in Table 2. Our values are slightly higher than the ones found earlier which range from 2.2×10^{-6},[16] 2×10^{-6},[6] to $7\ 10^{-7}$.[22] On the other hand we also use larger ions than these studies, thus the work in separating the ions is less and the dissociation constant will be larger.

6 CONCLUSION

The mobility of different ions within a smectic A layer is determined by the cross section the ion present orthogonal to the direction of movement, and the law of independent movements of ions is valid . For the mobility perpendicular to the smectic A layers the mobility is critically dependent on the quality of the homoetropic alignment. This quality will be determined by the history and alignment conditions of the sample, as well as any impurities present. The movement of the individual ions can thus no longer be treated independently of which other ions or undissociated salt that are present in the sample.

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