Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Conductivity, Permittivity, and the Electrode Space-Charge of Nematic Liquid Crystals. Part II

G. J. Sprokel [a]

[a] IBM System Products Division East Fishkill Laboratory, Hopewell Junction, New York, 12533

Version of record first published: 28 Mar 2007.

To cite this article: G. J. Sprokel (1974): Conductivity, Permittivity, and the Electrode Space-Charge of Nematic Liquid Crystals. Part II, Molecular Crystals and Liquid Crystals, 26:1-2, 45-57

To link to this article: http://dx.doi.org/10.1080/15421407408084822

Mol. Cryst. Liq. Cryst., 1974, Vol. 26, pp. 45-57

Printed in Dordrecht, Holland

Conductivity, Permittivity, and the Electrode Space-Charge of Nematic Liquid Crystals. Part II†

G. J. SPROKEL

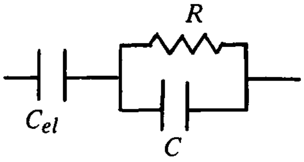
IBM System Products Division
East Fishkill Laboratory
Hopewell Junction, New York 12533

(*Received January 15, 1973*)

The molar conductivity of doped MBBA is given by Onsager's equation for electrolytic conduction. The anisotropy of the conductivity is determined largely by the anisotropy of the viscosity of the host material. Experimental values for Λ^0 and α are presented.

INTRODUCTION

In a previous communication[1] it was shown that the impedance of a liquid crystal cell can be regarded as the series arrangement of a surface capacitance C_{el} with the parallel combination of the bulk capacitance and resistance.



$$Z = R/(1 + i\omega RC) + 1/i\omega C_{el}$$

---

† Portions of this paper were presented at the Miami Beach, Florida meeting of the Electrochemical Society, 8–13 October, 1972 (Abstract No. 279).

This three parameter model fits experimental data between 0.1 Hz and 10 kHz, i.e., the range of operation of these devices. It applies to positive and negative azomethines as well as to *t*-stilbenes. At sufficiently high frequency the impedence of C_{el} is negligible and the cell behaves as a parallel RC circuit. At low frequency the cell is in essence the series arrangement of C_{el} and R. The capacitance C_{el} has been equated with a double layer capacitance assumed to arise from preferential adsorption of charge carriers. The order of magnitude of the surface charge density, the width of the double layer and the dissociation constant of the dopant were obtained from Gouy-Chapman Theory.

Thus the underlying assumption is that of ionic conduction and the liquid crystal cell is regarded as an electrolytic solution between two electrodes. However, this solution is not isotropic and the permittivity of presently known negative nematics is relatively low for efficient ionization. It is therefore, of considerable interest to establish whether existing theories of electrolytic conduction apply to doped nematics. While the previous paper dealt mainly with the electrode capacitance and the permittivity, the subject of the present discussion is the conductivity, in particular the concentration dependence of the molar conductivity of doped MBBA. Since the three parameters are closely related, some overlap is unavoidable.

The bridge used for these measurements has not been described before, hence a brief description preceeds the main part of this paper.

INSTRUMENTATION

W. E. Vaughan[2] has reviewed two recent designs of low frequency bridges. Neither of these is directly applicable to measurements on liquid crystal cells but both contain features which were adopted in our design.

The Harris bridge[3] requires two inputs, a sine wave and its quadrature. It is difficult to maintain exactly $\pi/2$ phase shift between the two inputs over a wide range of frequency. The bridge seems to work best in the 0.01–15 Hz range. The detector is an op. amp. mixer and a storage scope is used to balance for zero phase shift. The bridge was designed to measure dielectric properties of insulators and the resistance is limited to the range 10^8–10^{14} ohm. Liquid crystal cells are of the order 10^5–10^7 ohm.

The Scheiber bridge[4] employs a variety of detectors depending on the frequency of operation. All detectors are one side grounded which requires that the imput to the bridge is floating. Commercial low frequency sine wave generators (function generators) invariably produce a signal one side of which is grounded. Transformer isolation is of course impossible at very low frequencies. Introduction of a Wagner ground does not alter the requirement for a floating input.

The choice of the ground connection was all important in arriving at a design.

Not only are function generators grounded, standard variable capacitors are best operated one side grounded and finally the test cell containing the liquid crystal sample must be grounded. The test cell must be inserted between the poles of a magnet and its capacitance must be determined in two perpendicular orientations. If the cell were floating this would change the stray capacitance by a magnitude comparable with the effect of the orientation.

Floating detectors are of course undesirable but this can be avoided by using high impedance operational amplifiers and oscilloscopes with x, y and differential x–y inputs. All signals are processed one side grounded and phase and output comparisons are made by the CRT's. The circuit of the apparatus used for all measurements is shown in Figure 1. It is an equal arm bridge intended to be used by the substitution method. With the cell connected the bridge is balanced with the reference arm. Then the cell is disconnected and the bridge is balanced again with cell arm. Thus the only change in capacitance is the stray capacitance of the cell itself, about 2pF.

The resistors in the reference and cell arms are Victoreen Hi Meg 1% deposited carbon, arranged in 4 decades from 100 MΩ to 10K Ω and a 10K ten turn potentiometer. The capacitor decade boxes and the variable standard capacitor are General Radio items. The magnet is a Varian V4005 with associated power supply. The magnetic field is about 10K Gauss. The dectector circuit was built

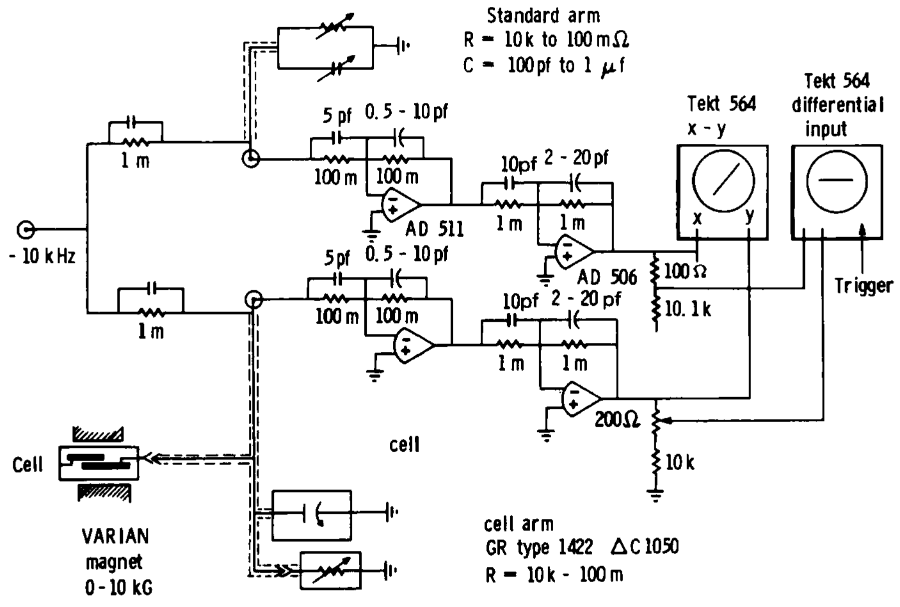


FIGURE 1. Schematic diagram of a direct coupled low frequency bridge for measuring permittivity and resistivity of liquid crystals.

around FET operational amplifiers (Analog Devices AD511, AD506) arranged as unity gain inverting amplifiers. Since the summing point is a virtual ground, the input is 100 MΩ shunted by 5pF. The detector bandwidth is 100kHz. The phase shift imbalance, measured with squarewave input is less than 0.5μs. Noise is mainly 60Hz, it is less than 5mV for the complete bridge. The generator input is adjusted to about 5V peak to peak across the cell, well below the threshold for dynamic scattering. Reproducibility of the measurement is about 1%.

EXPERIMENTAL RESULTS

Experimental data are conveniently summarized by plotting ϵ_{app} and ρ versus frequency. ϵ_{app} is the ratio of the measured capacitance of the filled and that of the empty cell corrected for stray capacitance. ρ is calculated from the measured resistance as $\rho = \epsilon_0^{-1} \cdot R \cdot C_V$. ($C_V$ is the corrected capacitance of the empty cell.) The procedure eliminates parameters pertaining to the test cell. Data are obtained with the aligning magnetic field parallel with and perpendicular to the electric field. Figure 2 shows an example for doped MBBA. Similar graphs for other dopants have been discussed. For negative as well as for positive azomethines $\rho_\parallel$ and $\rho_\perp$ are independent of frequency in the range of 0.1Hz to 10kHz. ϵ_{app} is constant at sufficiently high frequency but increases sharply at lower frequency, eventually as $\epsilon_{app} \sim 1/\omega^2$.

At high frequency ϵ_{app} represents the permittivity, ϵ, of the dielectric while at low frequency ϵ_{app} is given by the equation:

$$\omega^2 \rho^2 \epsilon_0^2 (\epsilon_{app} - \epsilon) \frac{C_{el}}{C_V} = 1 \tag{2}$$

The approximation is valid for $(\omega\rho\, \epsilon_0 \epsilon_{app})^2 \ll 1$.

C_{el} can be obtained from Eq. (2) as it contains only observed quantities. C_{el} was found to depend primarily on the dopant and its concentration. It is a weak function of frequency and invariant to the direction of the aligning field.

It follows that for a particular sample ϵ_{app} is approximately proportional to $1/\omega^2$ at frequencies well below the knee in the $\epsilon_{app}(\nu)$ curve. Furthermore, on comparing the curves for the two orientations it follows from (2) that

$$\frac{\epsilon_{app\perp}}{\epsilon_{app\parallel}} = \left(\frac{\rho_\parallel}{\rho_\perp}\right)^2 \tag{3}$$

for constant ω, well below the knee in the ϵ_{app} curve. Since for negative as well as for positive azomethines $\rho_\parallel < \rho_\perp$ it follows from (3) that $\epsilon_{app\perp} < \epsilon_{app\parallel}$ for frequencies below the knee in the curve. For negative nematics at frequencies beyond the knee, one has $\epsilon_{\parallel} < \epsilon_{\perp}$ and thus the $\epsilon_{\text{app}}(\nu)$ curves for crossed and parallel orientation must intersect. For positive nematics $\epsilon_{\parallel} > \epsilon_{\perp}$ and the curves do not intersect. Examples of this behavior have been given.

At high frequency the ϵ_{app} curves reflect the anisotropy of the permittivity, at low frequency the anisotropy of the conductivity.

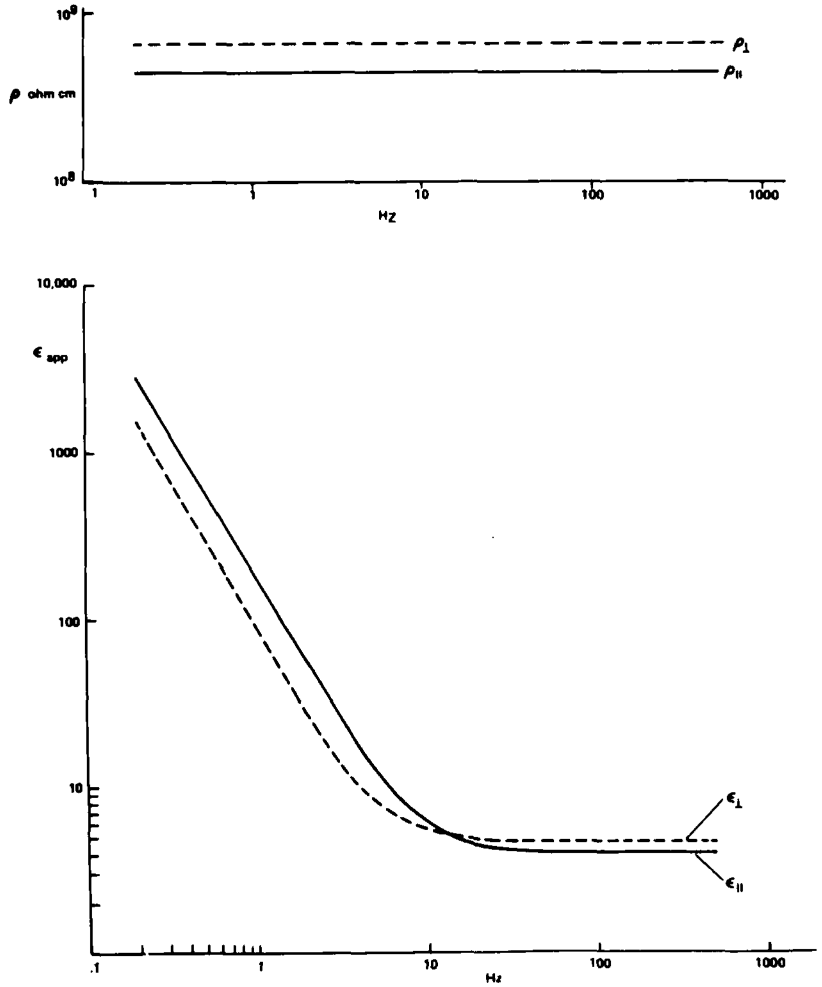


FIGURE 2. ϵ_{app} and ρ versus frequency for crossed and parallel E and H field for negative nematics. Figure included to summarize general features, more detailed information in Part I.

CONDUCTIVITY AS A FUNCTION OF DOPANT CONCENTRATION

In Figure 3, ϵ_{app} is plotted for 5 levels of dopant concentration. The two orientations are plotted separately to avoid intersecting curves. It is seen that ϵ does not depend on the doping level in this concentration range. Table I lists the dopant concentration, the ratio $\sigma_{\parallel}/\sigma_{\perp}$, and the molar conductivity. The molar conductivity decreases sharply as the dopant concentration increases.

The data apply to solutions of dibenzyl dimethyl ammonium chloride in MBBA. Solutions of other quaternary ammonium salts show qualitatively the same behavior.

In view of the low dielectric constant of the solvent, it is expected that the strong electrolyte is highly associated. Thus, the molar conductivity is expected to be given by the Onsager equation:

$$\Lambda(c) = \alpha\,(\Lambda^0 - S_\lambda\sqrt{\alpha c}) \tag{5}$$

where α is the fraction present as ions.
Assuming mass equilibrium, α is determined by the ionization constant K:

$$K = \frac{\alpha^2 c}{1-\alpha} \tag{6}$$

The terminology adopted here is that used in the monograph by Harned and Owen[7]. S_λ is given by the expression

$$S_\lambda = \frac{5.802 \times 10^5 \Lambda^0}{(\epsilon T)^{3/2}} + \frac{58.32}{\eta(\epsilon T)^{1/2}} \tag{7}$$

The permittivity of these MBBA samples is:

$$\epsilon_{\parallel} = 4.61 \qquad \epsilon_{\perp} = 5.12$$

Numerical values for η are taken from Martinoty and Candau:[8]

$$\eta = 0.27 \qquad \eta = 0.42$$

Inserting these values Eq. (7) becomes:

$$\begin{aligned} &\parallel = \text{orientation} \quad S_{\lambda\parallel} = 16.1\,\Lambda^0_{\parallel} + 8.22 \\ &\perp = \text{orientation} \quad S_{\lambda\perp} = 13.8\,\Lambda^0_{\perp} + 5.03 \end{aligned} \tag{8}$$

Combining Eqs. (5), (6) and (8), it is seen that $\Lambda(c)$ contains two constants: Λ^0 and K:

$$\Lambda(c) = \alpha\,(\Lambda^0 - \Lambda^0 A\sqrt{c\alpha} - B\sqrt{c\alpha}) \tag{9}$$

$$\alpha = \tfrac{1}{2}\cdot\frac{K}{c}\left(-1 + \sqrt{1 + 4\frac{c}{K}}\right)$$

A and B are the numerical constants in Eq. (8).

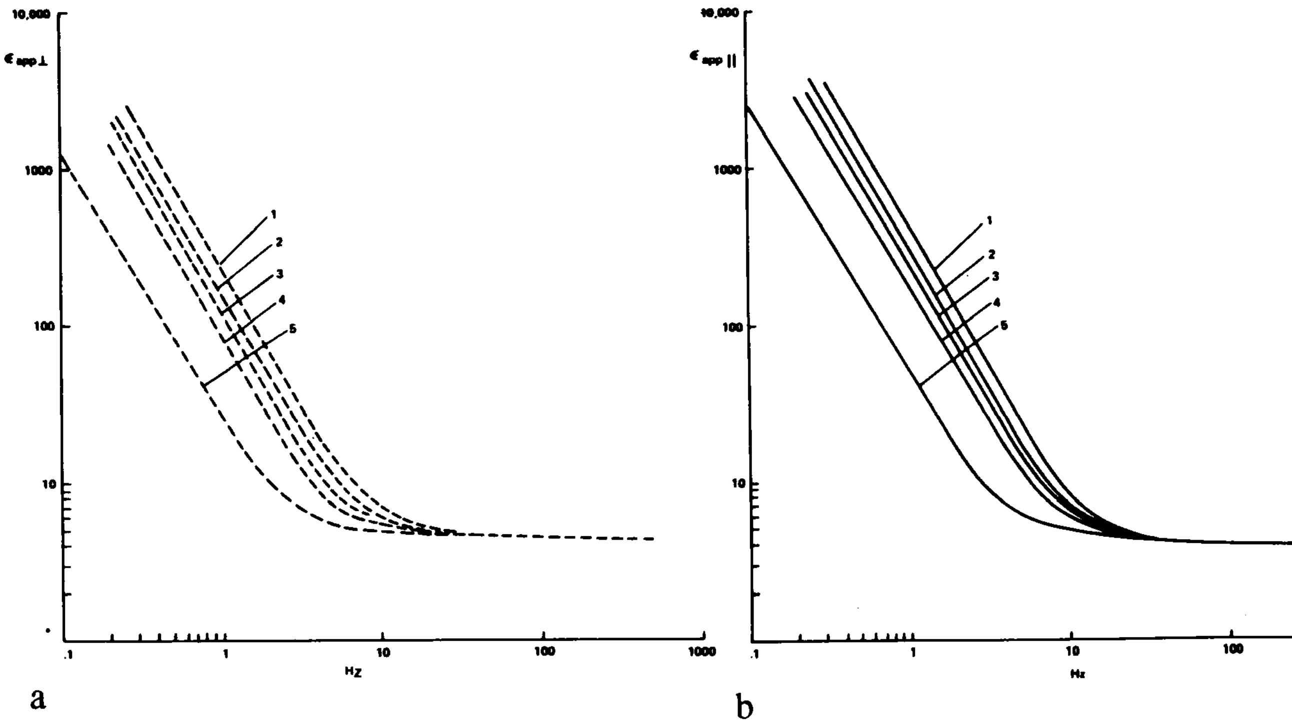


FIGURE 3. Apparent permittivity for 5 levels of dopant concentration (a) crossed *E* and *H* field; (b) parallel *E* and *H* field: dopant concentration (1) 1.09×10^{-5}, (2) 0.57×10^{-5}, (3) 2.85×10^{-6}, (4) 2.28×10^{-6}, (5) 0.56×10^{-6} gmol/ml. The corresponding conductivity is given in Table I.

TABLE I

Conductivity at 5 levels of dopant concentration
Molar conductivity

C gmol/ℓ	$\sigma_{\parallel}/\sigma_{\perp}$	$\Lambda_{\perp}$	$\Lambda_{\parallel}$
1.09×10^{-2}	1.48	0.19×10^{-3}	0.28×10^{-3}
0.57×10^{-2}	1.46	0.40×10^{-3}	0.58×10^{-3}
0.285×10^{-2}	1.48	0.62×10^{-3}	0.92×10^{-3}
0.228×10^{-2}	1.45	0.76×10^{-3}	1.10×10^{-3}
0.56×10^{-3}	1.48	1.18×10^{-3}	1.76×10^{-3}

Λ^0 and K are the solutions of a set of simultaneous equations $\Lambda(n), c(n)$ $n = 1, \ldots. 5$. However the algebraic form of these equations precludes direct calculation of Λ^0 and K. Fuoss[9] developed a method (nearly 40 years ago) to obtain their values. The method is essentially graphical and relies on extrapolation of Λ (c) to infinite dilution to obtain starting values for Λ^0. Using modern numerical techniques such extrapolation is no longer necessary. The equations contain their own starting values and furthermore as the iteration proceeds one can follow its convergence. The numerical approach is described in some detail in the appendix. The results are:

‖ orientation

$K = 7 \times 10^{-7}$ $\qquad$ $\Lambda^0_{\parallel} = 0.133$ cm² ohm⁻¹ gmol⁻¹

⊥ orientation

$K = 7 \times 10^{-7}$ $\qquad$ $\Lambda^0_{\perp} = 0.083$ cm² ohm⁻¹ gmol⁻¹

As noted in the appendix, the numerical values obtained for K are the same in the two orientations, although the numerical values for Λ, A and B are different. This lends considerable support to the model since the degree of dissociation should be invariant to the orientation of the magnetic field.

In Figure 4, $\Lambda(c)$ is plotted versus c for both orientations and the experimental data points are superimposed. The agreement is considered satisfactory. Also plotted in Figure 4 is the Ostwald dilution function using the same value for Λ^0 (only the ‖ case is shown). This serves to indicate the magnitude of the Onsager "correction" terms. Of the two terms in Eq. (9), the term containing B has the larger effect. It is recalled that the first term in the expression for S_{λ}, sometimes called the relaxation term, accounts for the shielding effect of the ion cloud on the central ion. The second term, the electrophoretic term, accounts for the motion of the ion cloud in accordance with Stokes law. Thus, these results indicate that the electrophoretic term dominates and the values for the mobilities are different in the two directions principally because the viscosity is different in the two directions. The dielectric anisotropy enters only as a square root. The numerical values for the sum of the mobilities of both ions calculated from the Λ^0's are:

$$\parallel = \text{orientation} \quad \Sigma\mu = 1.39 \times 10^{-6}\,\text{cm}^2\ \text{sec}^{-1}\ \text{volt}^{-1}$$

$$\perp = \text{orientation} \quad \Sigma\mu = 0.86 \times 10^{-6}\,\text{cm}^2\ \text{sec}^{-1}\ \text{volt}^{-1}$$

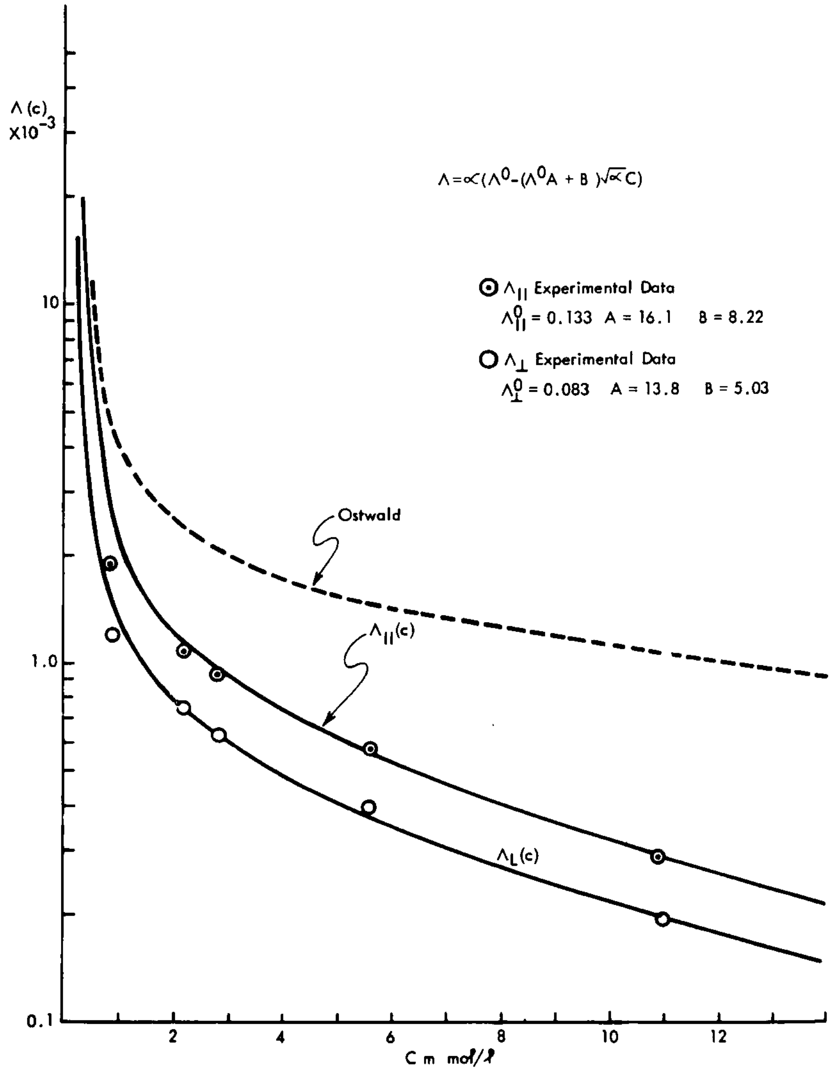


Figure 4. Calculated molar conductivity as function of concentration for parallel and crossed fields, graphs $\Lambda_{\parallel}(c)$ and $\Lambda_{\perp}(c)$. The curve marked "Ostwald" is $\Lambda(c) = \alpha\Lambda^0$. Data points ● for parallel orientation and o for crossed fields.

The ratio of the mobilities, 1.61, agrees quite well with the ratio of the viscosities 1.55.

A final remark, Onsager's theory, developed for isotropic solutions, yields satisfactory results for nematic liquid crystals. For an isotropic liquid, the central ion is displaced from the center of charge of the Debye shpere in the direction of the field. The charge distribution still has rotational symmetry about the field axis. In an anisotropic system there must be an additional radial displacement but this is not accounted for in Eq. (9). Since the viscosity term dominates, the effect might be too small to be observed experimentally.

SUMMARY

The conductivity of nematic liquid crystals can be described by the Onsager equations for electrolytic conduction. The two constants in the Onsager equations viz the limiting molar conductivity, Λ^0 and the mass equilibrium constant, K, are determined from a set of experimental data using a simple numerical technique. It is found that the conductivity parallel to the direction of molecular alignment is larger than that perpendicular to the molecular axis. Of the two interaction terms in the Onsager equation, the electrophoretic term dominates. Thus the mobility of charge carriers is governed more by the hydrodynamic anisotropy than it is by the dielectric anisotropy. Since the hydrodynamic anisotropy ia a property of the solvent the ratio of $\Lambda_\parallel/\Lambda_\perp$ is independent of the concentration of the dopant for dilute solutions generally employed although each of the terms decreases sharply with increasing concentration.

Acknowledgement

The author wishes to thank P. J. Burkhardt of this laboratory for his help in programming and the use of his APL terminal.

APPENDIX

NUMERICAL SOLUTION OF EQS. (9) AND (10).

Write Eq. (9) in the form

$$\Lambda^0 = \frac{\dfrac{\Lambda}{\alpha} + B\sqrt{c\alpha}}{1 - A\sqrt{c\alpha}} \tag{A1}$$

$$\alpha = \frac{-1 + \sqrt{1 + 4\frac{c}{K}}}{2\frac{c}{K}} \tag{A2}$$

A value of K must be found such that if α, calculated from $A2$ is substituted in $A1$, the resulting Λ^0 is independent of c. Five data points are available for the calculation.

To determine the range of permissible K values note that:

$$A\sqrt{c\alpha} < 1$$

for any value of c. Using the smallest concentration available one has:

$$0 < K < 10^{-3}$$

Starting with $K = 10^{-3}$, the APL program iterates downward until Λ^0 is constant. It is illustrative to follow the convergence by plotting $\Lambda^0(c)$ for the chosen values of K (see Figure A1). If K is large $\Lambda^0(c)$ is in a strongly increasing function, for sufficiently small K $\Lambda^0(c)$ changes to a decreasing function of c. The data in Figure A1 are those for the parallel orientation. It is seen that between $K = 1 \times 10^{-6}$ and $K = 1 \times 10^{-7}$ the slope of the $\Lambda^0(c)$ curve changes. The computer program iterates further in this range. Since the resolution becomes too fine for graphical presentation some representative data are collected in Table TA1.

Further iteration is meaningless because of the accuracy of the input data. Thus for parallel orientation $K = 7 \times 10^{-7}$ and $\Lambda^0 = 0.133$. Similarly for the crossed orientation the program yielded $K = 7 \times 10^{-7}$ and $\Lambda^0 = 0.083$. The two values for K are the same as it should be.

Once the convergence of the method has been established it is of course unnecessary to print out intermediate data. However such details of the program need not be discussed.

TABLE TA-1

Second iteration for Λ^0 Concentration in m mol/ℓ

K \ C	2.28	5.70	10.9
1×10^{-7}	0.212	0.195	0.154
3×10^{-7}	0.150	0.149	0.131
5×10^{-7}	0.135	0.139	0.129
7×10^{-7}	0.128	0.135	0.131
9×10^{-7}	0.124	0.139	0.144

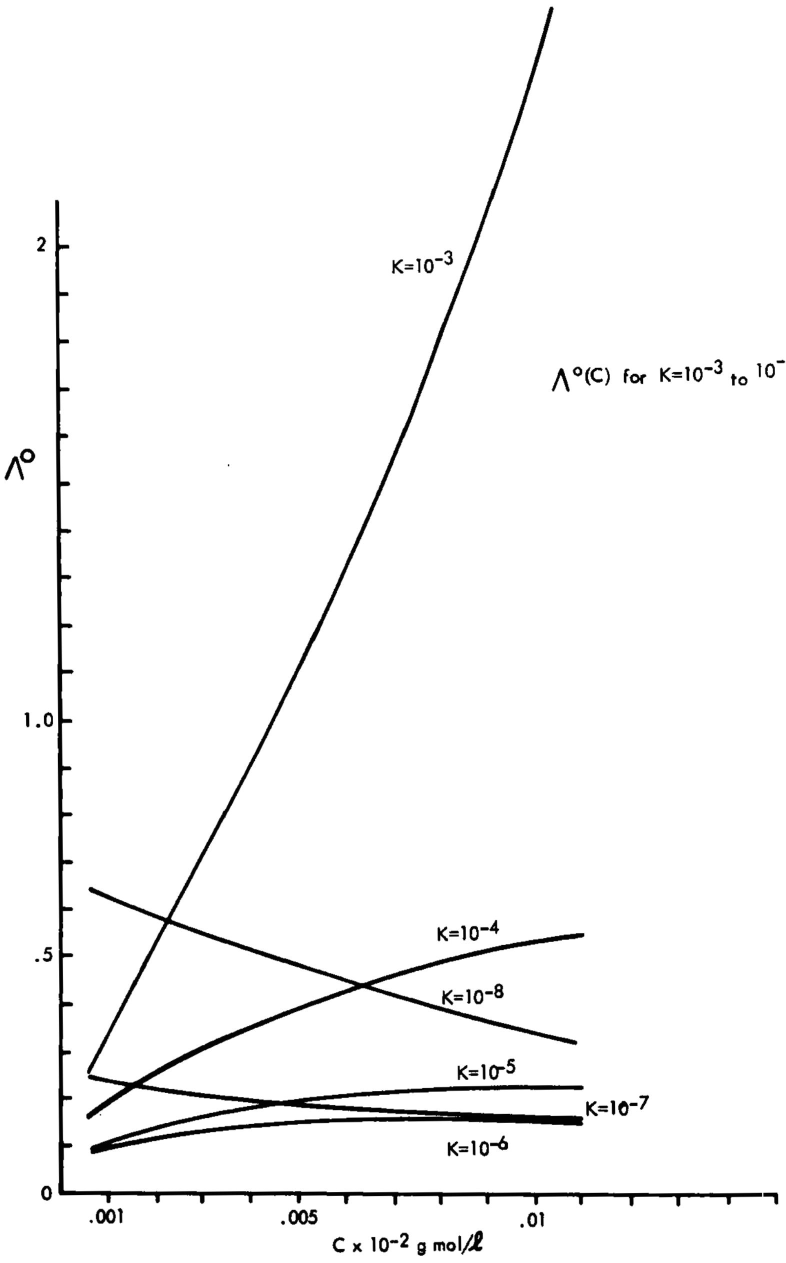


FIGURE A1. Values of $\Lambda^0(c)$ calculated from Eq. A1 for $K = 10^{-4}$, 10^{-5}, 10^{-6}, 10^{-7} and 10^{-8}.

References

1. Sprokel G.J., paper presented at Fourth International Liquid Crystal Conference, Kent, Ohio, 1972. *Mol. Cryst. and Liq. Cryst.*, **22**, 249 (1973).
2. Vaughan W. E., in *Dielectric Properties and Molecular Behavior*, N. E. Hill, Ed., Van Nostrand, 1969.
3. Harris W. P., Conference on Electrical Insulators and Dielectric Phenomena, National Academy of Science, N.R.C., Washington, 1966, p. 72.
4. Scheiber D. J., quoted from Vaughan.
5. O'M Bockris J., and Reddy A. K. N., *Modern Electrochemistry*, Vol. 1, Plenum Press, 1972.
6. Harned H. S., and Owen B. B., *Physical Chemistry of Electrolytic Solutions*, Reinold, 1964.
7. Equations (5) and (6) are identical with Eqs. 7-2-3 and 7-2-10 in Harned-Owen.
8. Martinoty P., Candau S., *Mol. Cryst. and Liq. Cryst.* **14**, 1971, 243.
9. Quoted from Harned-Owen, Chapter 6-2.