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The Electro-Optical Kerr Effect of Optically Active Liquids

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The electro-optical Kerr effect of optically active liquids has been studied theoretically, applying the lamellar model of Jones, and experimentally, by measurement of the solution Kerr constant B_{12} of a series of solutions of d- and dl-camphor in carbon tetrachloride. Equations are presented which allow the intrinsic phase retardation, δ, associated with the Kerr effect to be determined using the Sénarmont method in conjunction with either dc or pulsed electric fields. The method of determining δ, using pulsed electric fields is particularly useful for solutions having an appreciable electrical conductivity. The time-dependent behaviour of a relaxing system, measured using quadratic detection of the optical transient resulting from the application of a pulsed rectangular electric field, is predicted to be essentially unaffected by optical activity over a wide range of δ and optical rotation.

INTRODUCTION

The electro-optical Kerr effect is well established as a useful and sensitive technique for studying the molecular structure and rotational motion of molecules in the liquid state. Extensive investigations, recently undertaken in this laboratory, have involved the application of dielectric and Kerr-effect relaxation techniques to the study of molecular rotational diffusion in a variety of systems: supercooled viscous molecular liquids (fluorenone/O-terphenyl[1], tritolyl phosphate[2] and 2-methyl-2,4-pentanediol[3]), rod-like macromolecules in solution (poly(n-butyl isocyanate)[4] and poly(n-octyl isocyanate)[4]), bulk amorphous polymers (polypropylene oxide[5] and poly-phenylmethyl siloxane[6]) and liquid-crystals (4,4-n-heptylcyanobiphenyl[7] and cholesteryl oleyl carbonate[8]). During the course of these detailed studies we have established that correlations between Kerr-effect and dielectric relaxation times may best be rationalised through the use of two different models for molecular rotational diffusion:[9] the small-step diffusion model and the "fluctuation-relaxation" model. The electro-optic behaviour of the optically active liquid-crystal cholesteryl oleyl carbonate, which initiated the present theoretical study, indicated that it was necessary to understand how optical activity influenced the Kerr effect.

De Mallemann was one of the first investigators to study the electro-optic behaviour of an optically active solution and to analyse the results using a theory which includes the effect of optical activity on the Kerr effect.[10,11] However, the equations presented by De Mallemann are somewhat cumbersome and are not ideally suited to our present optical technique. Suitable basic equations for this purpose have been derived by Jones[12] and others,[13–15] but relatively little has been published concerning the practical aspects of studying the electro-optic behavior of optically active systems.[16–18] In this paper we wish to describe a simple practical approach for the determination of the intrinsic electro-optical Kerr constant of an optically active liquid using the Sénarmont method of detection for both dc and pulsed electric fields. In addition we will consider how the time-dependent behaviour of the Kerr effect of a relaxing system, measured using quadratic detection of the optical transient, is affected by the presence of optical activity.

THEORY

Although the propagation of plane-polarised light through an optically transparent body can be rigorously described using standard electromagnetic theory the algebraic form of the final expressions is often complicated and may offer little physical insight. Partly for these reasons and because we will be chiefly concerned with the practical aspects of determining the intrinsic electro-optical solution Kerr constant of chiral molecules, we have adopted a simple macroscopic description of the optical system, as given by Jones.[12]

The optical properties of an optically active liquid in a uniform electric field are assumed to be accurately represented by a sufficiently large number of equivalent linearly retarding elements arranged in an alternating sequence with an equal number of equivalent circularly birefringent elements. Figure 1 shows the orientation of the optical components and the electric vectors of plane-polarised light entering and leaving the Kerr cell in the absence of an applied electric field. The electric vector of the incident light is fixed at 45° relative to the x and y axes of the reference Cartesian coordinate system and the direction of propagation is parallel to the z-axis. A uniform electric field may be applied along the y-axis.

The electric vector of the light emerging from the Kerr cell, after traversing N pairs of optical elements, can always be resolved into two components,

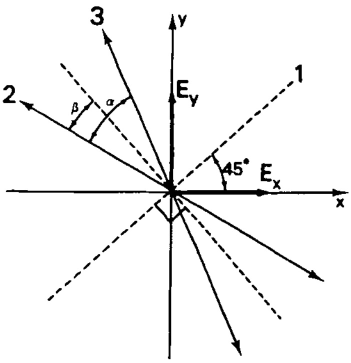

FIGURE 1 Orientation of optical components and electric vectors. (1) Electric vector of plane-polarised light incident on Kerr cell. (2) and (3) are positions of plane of transmission of analysing prism for quadratic and Sénarmont modes, respectively. The slow axis of the quarter-wave retarder is fixed along (2).

$E_x^{(N)}$ and $E_y^{(N)}$, parallel to the x and y axes, respectively. We define $\Delta\delta$ to be the phase retardation incurred by the Y component relative to the X component during their passage through a single linear retarder element, and $\Delta\beta$ to be the angle through which the X and Y components are rotated about the z axis during their passage through a single rotator element. We may also write $\Delta\delta = 2\delta/N$ and $\Delta\beta = 2\beta/N$, where δ is the total phase retardation of the Y component relative to the X component which would occur in the absence of natural optical activity, and β is the total rotation of the plane of polarisation of the light in the absence of electrically-induced birefringence. By performing retardation and rotation operations on the X and Y components emerging from each successive pair of optical elements it can readily be shown that the final X and Y components leaving the Kerr cell may each be represented by a series of N time-dependent sine functions, $\sin(\omega t - k\Delta\delta)$, whose arguments differ only in their phase, $k\Delta\delta$; where k is an integer. The coefficients associated with each of these sine functions may be conveniently calculated using a digital computer. In the appendix we use this approach to derive expressions for the intensity of light transmitted by the analysing prism for both quadratic and Sénarmont detection, and we examine the validity of the lamellar model as a function of the number of optical elements for the case of quadratic detection.

Since a physically acceptable representation of the waveforms leaving the Kerr cell will be obtained only when the number of elements is very large we will use the concise matrix method of Jones in which the number of optical elements approaches infinity and the optical properties of the Kerr cell are represented by a single 2 × 2 matrix. Using this method the amplitudes of the X and Y components of light leaving the Kerr cell, denoted by $\mathscr{A}_x$ and $\mathscr{A}_y$ respectively, may be represented by the column vector

$$\mathscr{S} = \begin{bmatrix} \mathscr{A}_x \\ \mathscr{A}_y \end{bmatrix} = \frac{\mathscr{A}}{2} \begin{bmatrix} \cos\varphi + \dfrac{i\delta}{2\varphi}\sin\varphi & -\dfrac{\beta}{\varphi}\sin\varphi \\ \dfrac{\beta}{\varphi}\sin\varphi & \cos\varphi - \dfrac{i\delta}{2\varphi}\sin\varphi \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{1}$$

where $\mathscr{A}$ is the amplitude of the light incident on the Kerr cell. φ is equal to $(\beta^2 + \delta^2/4)^{1/2}$ and $i = (-1)^{1/2}$.

We will now consider how various analyser arrangements modify the X and Y components leaving the Kerr cell.

A Quadratic detection using DC electric fields

The optical arrangement used for quadratic detection consists of an analysing prism adjusted for extinction of the light with no electric field present in the Kerr cell. Referring to Figure 1 it can be readily seen that the amplitude of light transmitted by the analysing prism, during the application of an electric field, will be given by

$$\mathscr{A}_Q = \mathscr{A}_y \sin\Theta - \mathscr{A}_x \cos\Theta \tag{2}$$

where $\Theta = \pi/4 - \beta$. The intensity of light transmitted by the analysing prism is equal to

$$I_Q = \mathscr{A}_Q \cdot \mathscr{A}_Q^* \tag{3}$$

where $\mathscr{A}_Q^*$ is the complex conjugate of $\mathscr{A}_Q$. By straightforward substitutions, involving Eqs. 1–3, we obtain the relationship

$$I_Q = \frac{\mathscr{A}^2}{2}\left(\sin^2\beta\cos^2\varphi + \cos^2\beta\sin^2\varphi - \frac{\beta}{2\varphi}\sin 2\beta\sin 2\varphi\right) \tag{4}$$

for the intensity of light transmitted by the analysing prism during the application of an electric field to the Kerr cell.

B Sénarmont detection using DC electric fields

In this mode of detection a quarter-wave retarder is placed between the Kerr cell and the analysing prism. The orientation of the retarder is fixed, with its slow axis either parallel or perpendicular to the electric vector of plane-polarised light leaving the Kerr cell in the absence of an applied electric field.

Using the matrix method of Jones the components of light impinging on the analysing prism may be represented by the column vector

$$\begin{bmatrix} \mathscr{A}_{\parallel} \\ \mathscr{A}_{\perp} \end{bmatrix} = \mathscr{P}\mathscr{Q}\mathscr{R}\mathscr{S} \tag{5}$$

where $\mathscr{A}_{\parallel}$ and $\mathscr{A}_{\perp}$ are the amplitudes of components of light parallel and perpendicular to the transmission plane of the analysing prism, respectively. $\mathscr{S}$ is a column vector, representing the effect of the Kerr cell and has been defined earlier (see Eq. 1). Matrix $\mathscr{Q}$ is defined by

$$\mathscr{Q} = \begin{bmatrix} 1 & 0 \\ 0 & e^{\pm i\pi/2} \end{bmatrix} \equiv \begin{bmatrix} 1 & 0 \\ 0 & \pm i \end{bmatrix} \tag{6}$$

and represents the effect of the quarter-wave retarder on components of light, projected by matrix $\mathscr{R}$ (see below), along directions parallel and perpendicular to its slow axis. The double sign in the exponential term denotes the orientation of the quarter-wave retarder. When the sign of the exponential is negative the slow axis of the retarder is parallel to the electric vector of plane-polarised light leaving the Kerr cell when no electric field is present. $\mathscr{P}$ and $\mathscr{R}$ are rotational transformation matrices given by

$$\mathscr{P} = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \mathscr{R} = \begin{bmatrix} \cos\Theta & -\sin\Theta \\ \sin\Theta & \cos\Theta \end{bmatrix} \tag{7}$$

where α is the azimuthal angle of the analysing prism, relative to its zero-field position of extinction. Matrix $\mathscr{R}$ transforms the X and Y components of light emerging from the Kerr cell, into components parallel and perpendicular to the slow axis of the quarter-wave retarder. Matrix $\mathscr{P}$ performs a similar function to that of $\mathscr{R}$ by resolving the components of light leaving the retarder plate along directions parallel and perpendicular to the transmission plane of the analysing prism.

Equation 1 may be rewritten in shorthand form as

$$\mathscr{S} = \frac{\mathscr{A}}{2} \begin{bmatrix} K - L + iM \\ K + L - iM \end{bmatrix} \tag{8}$$

where $K = \cos\varphi$, $L = (\beta/\varphi)\sin\varphi$ and $M = (\delta/2\varphi)\sin\varphi$. After substituting Eqs. 6-8 into equation 5, and premultiplying by the row vector [1 0] to extract the amplitude of the component parallel to the transmission plane of the analysing prism, we obtain

$$\mathscr{A}_{\parallel} = \frac{\mathscr{A}}{2}\{[(K - L)\cos\Theta - (K + L)\sin\Theta]\cos\alpha \pm M(\sin\Theta - \cos\Theta)\sin\alpha$$
$$\mp i[(K - L)\sin\Theta + (K + L)\cos\Theta]\sin\alpha + iM(\sin\Theta + \cos\Theta)\cos\alpha\} \quad (9)$$

for the amplitude of light transmitted by the analysing prism. Multiplying Eq. 9 by its complex conjugate and simplifying using well known trigonometrical identities we eventually obtain the relationship

$$I_s = \frac{\mathscr{A}^2}{4}\left[1 - \left(\cos 2\beta\cos 2\varphi + \frac{\beta}{\varphi}\sin 2\beta\sin 2\varphi\right)\cos 2\alpha \mp \frac{\beta}{2\varphi}\sin 2\varphi\sin 2\alpha\right] \quad (10)$$

for the intensity of light transmitted by the analysing prism when an electric field is present in the Kerr cell.

The angular position of the analysing prism, defined by $\alpha = \alpha_{\min}$, which gives minimum transmission of light when an electric field is applied, is obtained by differentiating equation 10 with respect to 2α, equating the derived function to zero, and solving for α. We thus find

$$\alpha_{\min} = (1/2)\tan^{-1}\left(\frac{\pm(\delta/2\varphi)\sin 2\varphi}{\cos 2\beta\cos 2\varphi + (\beta/\varphi)\sin 2\beta\sin 2\varphi}\right) \quad (11)$$

C Sénarmont detection using pulsed electric fields

Pulsed electric fields are generally employed when the rotational diffusion of the molecules is of interest and when it is necessary to minimise the effects of Joule heating and turbulence in samples which possess appreciable electrical conductivity. The arrangement of the optical components is the same as that used for the Sénarmont method described in Section B above.

The magnitude of the optical pulse depends on I_s (given by Eq. 10), which is the steady intensity of light transmitted by the analysing prism during the application of the electric field, and on $I_{E=0}$, which is the steady intensity of transmitted light when the electric field is removed. By rotating the analysing prism, during a sequence of rectangular electric pulses, it is possible to find a position, $\alpha = \alpha_{\min}$, where $I_s = I_{E=0}$. When this condition is achieved the magnitude of the optical pulse is zero and it can easily be shown, using Eq. 10 and the relationship $I_{E=0} = (\mathscr{A}^2/2)\sin^2\alpha$, that

$$\alpha_{\min} = (1/2)\tan^{-1}\left[\frac{(\beta/\varphi)\sin 2\beta\sin 2\varphi + \cos 2\beta\cos 2\varphi - 1}{\mp(\delta/2\varphi)\sin 2\varphi}\right] \quad (12)$$

When β equals zero Eq. 12 reduces to the simple form

$$\alpha_{min} = (1/2)\tan^{-1}\left(\frac{\cos\delta - 1}{\mp\sin\delta}\right) \tag{13}$$

which may be simplified still further to give

$$\alpha_{min} = \pm\delta/4 \tag{14}$$

RESULTS AND DISCUSSION

A Theoretical calculations

I Quadratic detection The intensity of light transmitted by the analysing prism for quadratic detection was calculated as a function of δ and β using Eq. 4. The results of these calculations are presented in graphical form in Figure 2. The graphs of I_Q vs. $\sin^2\delta/2$ are essentially linear over the range $0 < \delta < \pi/2$ for values of β not exceeding 30°. As β is increased above 30° the range over which I_Q varies linearly with $\sin^2\delta/2$ decreases. However, even when δ and β are both large the departure from linearity may still be quite small. For example, when $\beta = 60°$ and $\delta = 70°$ ($\sin^2\delta/12 \simeq 0.33$) the calculated intensity is only 5% higher than that predicted from a straight line fitted to the points calculated for small values of δ. The major effect of

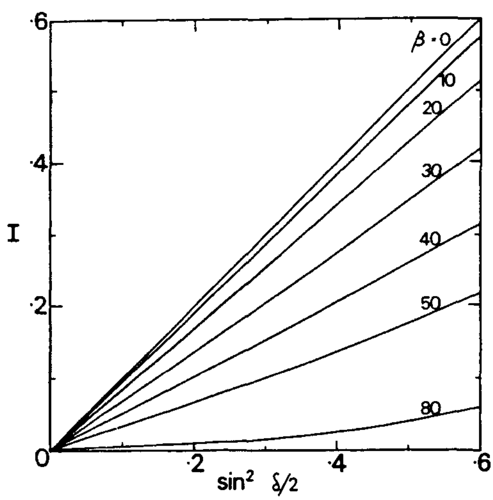

FIGURE 2 Normalised intensity of light, I, calculated (using Eq, 4) for quadratic detection vs. $\sin^2\delta/2$, for different values of optical rotation β.

optical activity on quadratic detection is that it decreases the intensity of light transmitted by the analysing prism in a manner that is independent of the value of the phase retardation, δ, subject to the constraints discussed above. Since graphs of the intensity of light, I_Q, as a function of $\sin^2 \delta/2$ are predicted to be linear over a wide range of combinations of phase retardation and optical rotation we may conclude that the time-dependent behaviour of the Kerr-effect of a relaxing system, measured using quadratic detection of the optical transient, is essentially unaffected by optical activity.

II *Sénarmont detection using DC electric fields* The Sénarmont method of detection using dc electric fields was evaluated with the aid of Eqs. 10 and 11. Figure 3 shows graphs of α_{min} as a function of β, for various values of δ, calculated using Eq. 10. Since α_{min} and β may both be measured experimentally it is in principle a straightforward procedure, using interpolative and extrapolative methods and the graphs shown in Figure 3, to determine the intrinsic phase retardation δ. However, it is evident, from the calculated intensity data

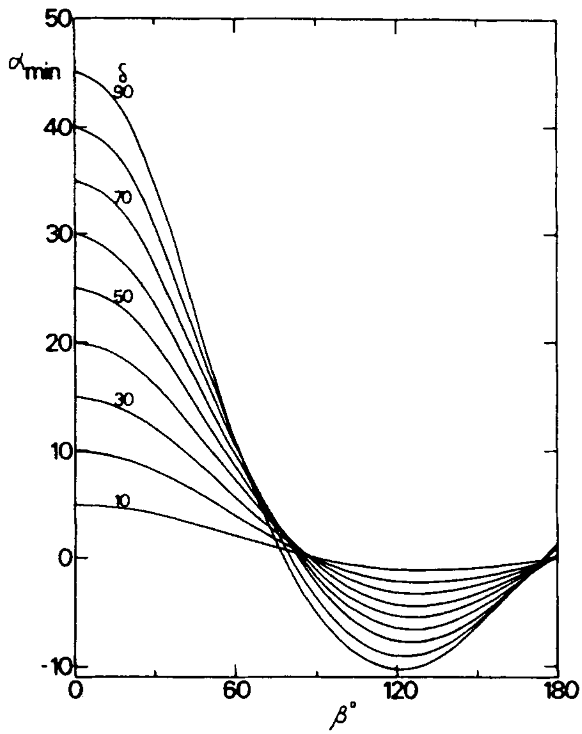

FIGURE 3 Azimuthal angle, α_{min}, of analysing prism for minimum transmission of light, as a function of δ and β, for Sénarmont detection using dc electric fields.

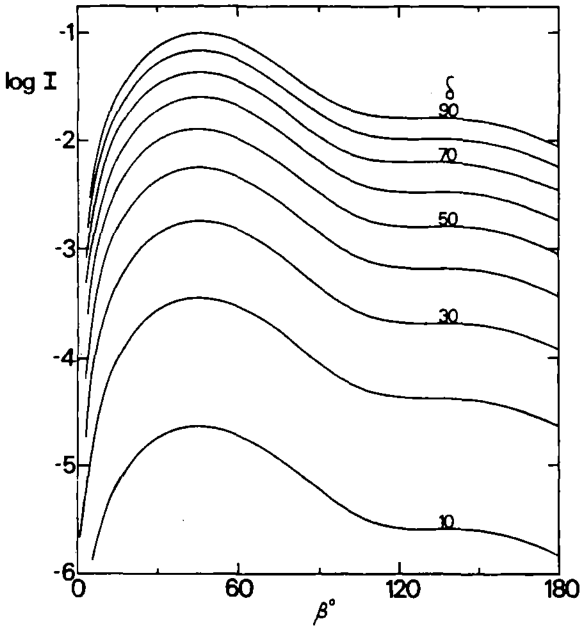

FIGURE 4 Logarithm of the normalised intensity of light, I, (calculated using Eq. 10) as a function of δ and β for Sénarmont detection and dc electric fields, with the analysing prism oriented for minimum transmission.

shown in Figure 4, that an appreciable intensity of light may be transmitted by the analysing prism when it is set for minimum intensity (i.e., when $\alpha = \alpha_{min}$). Referring to Figure 4 it is clear that the intensity of transmitted light, not extinguishable by the analysing prism when $\alpha = \alpha_{min}$, rapidly increases as δ increases and that the intensity is greatest when β equals $\pi/4$. For the case where δ and β are both large this residual light will be quite high and signal-to-noise ratios would be expected to be poor. This problem may usually be overcome in practice by employing Kerr cells with short optical paths or by using dilute solutions.

III *Sénarmont detection using pulsed electric fields* The Sénarmont method of detection using pulsed electric fields was evaluated using Eq. 12 to calculate α_{min}(the value of α when the optical pulse is nulled) as a function of β for various values of phase retardation δ. The results of these calculations are shown in Figure 5. The graphs are discontinuous with points of singularity occurring whenever φ $(=(\beta^2 + \delta^2/4)^{1/2})$ equals an integral multiple of $\pi/2$. At these points of singularity the light leaving the Kerr cell is plane-polarised and $\alpha_{min} = \pm\pi/4$. Apart from this behaviour the graphs shown in Figure 5

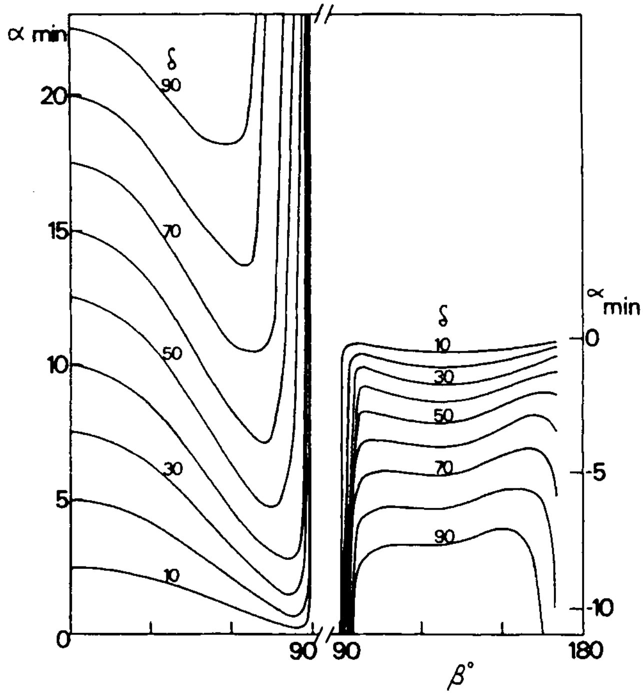

FIGURE 5 Azimuthal angle, α_{min}, of analysing prism set for minimum transmittion of light, as a function of δ and β, for Sénarmont detection using pulsed electric fields.

are qualitatively similar to those (Figure 3) obtained for Sénarmont detection using dc electric fields, for small values of β.

B Interpretation of experimental results

The electro-optical Kerr constants of a series of solutions of dl-camphor and d-camphor in carbon tetrachloride were measured using optical apparatus described previously.[4] The Kerr cell had an optical path, l equal to 7.45 cm and an electrode separation of 0.114 cm. The purity of the camphor was checked by recrystallisation and by determination of its melting point. The electro-optical phase retardations induced in solutions of dl-camphor were measured in the normal way using the Sénarmont method and dc electric fields. For solutions of d-camphor the azimuthal angles, α_{min}, of the analysing prism at extinction was measured using the Sénarmont method described in Section B above. The strength of the applied electric field was adjusted so that the rotation of the analysing prism between the field-on and field-off positions of extinction never exceeded 1.5 degrees. Plots of α_{min}(for d-camphor)

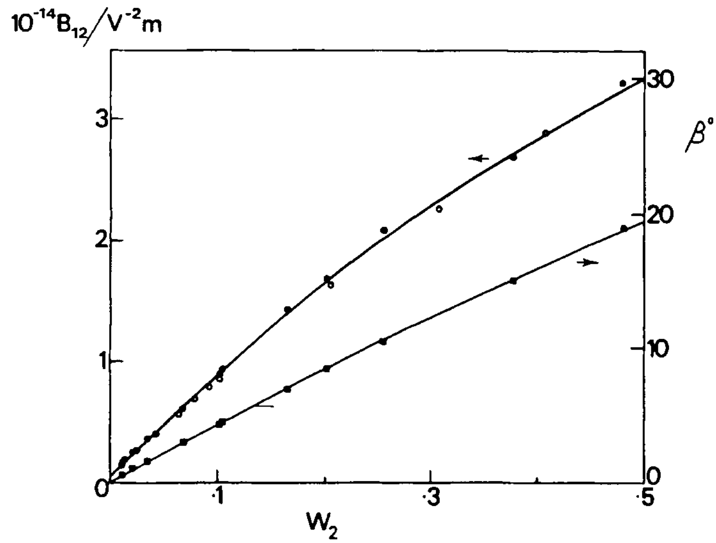

FIGURE 6 Solution Kerr constant, B_{12}, and optical rotation, β, for solutions of d- and dl-camphor vs. weight fraction of solute, w_2. Temp. $= 295$ K. (d-camphor ●, ■).

and $\delta/2$ (for dl-camphor) against the square of the applied electric field were all linear within experimental error. Figure 6 shows solution Kerr constants, B_{12}, calculated using $B_{12} = \delta/(2\pi l E^2)$ for solutions of dl-camphor and $B_{12} = \alpha_{min}/(\pi l E^2)$ for solutions of d-camphor, plotted against the weight fraction of solute, w_2. Experimental errors associated with the determination of the solution Kerr constants are estimated to be not greater than $\pm 5\%$. We note that for solutions of d- and dl-camphor of equal concentration there is very little difference in their Kerr constants. Since the contribution of the solvent to the Kerr effect can be neglected for all but the most dilute solutions, it is convenient to discuss the experimental data in terms of the ratio of α_{min} (calculated using Eq. 10) to $\delta/2$. Thus, for $\delta = 2°$ the ratio, α_{min} (calc)/($\delta/2$), is calculated to be 1.02, 1.04 and 1.08 for $\beta = 10°$, 15°, and 20° respectively. Taking into consideration the experimental errors associated with B_{12} and the limited range of experimental values of δ and β, the data are consistent with the calculated ratios of $\alpha_{min}/(\delta/2)$ since values of α_{min} observed for solutions of d-camphor are very close to values of $\delta/2$ observed for solutions of dl-camphor of the same concentration.

Unfortunately, it was not possible, using solutions of camphor, to extend the measurements to the region where δ and β are both large and where α_{min} is predicted to be substantially different from $\delta/2$. This region will, however, be considered in a subsequent publication concerning the electro-optical properties of the liquid-crystal cholesteryl oleyl carbonate, which exhibits a very large Kerr effect and a high degree of optical activity in the isotropic phase when close to the isotropic-cholesteric transition point.

Appendix

Arbitrarily, choosing the first pair of optical elements in the Kerr cell to be a linear retarder followed by a rotator† the elliptical waveform emerging from these elements may be represented by two plane-polarised components

$$E_x^{(1)} = \mathscr{A}[\cos\Delta\beta\sin\omega t - \sin\Delta\beta\sin(\omega t - \Delta\delta)] \tag{1a}$$

$$E_y^{(1)} = \mathscr{A}[\cos\Delta\beta\sin(\omega t - \Delta\delta) + \sin\Delta\beta\sin\omega t] \tag{2a}$$

where the slow axis of the retarding element is parallel to Y component. By performing, in a recursive manner, the retardation and rotation operations implicit in Eqs. (1a) and (2a) on the X and Y components emerging from each successive pair of elements it can be readily shown that the final X and Y components leaving the Kerr cell may each be expressed as a series of N time-dependent sine functions whose arguments differ only in their phase.

$$E_x^{(N)} = \mathscr{A}\sum_{k=0}^{N}\mathscr{A}_{x,k}\sin(\omega t - k\Delta\delta) \tag{3a}$$

$$E_y^{(N)} = \mathscr{A}\sum_{k=0}^{N}\mathscr{A}_{y,k}\sin(\omega t - k\Delta\delta) \tag{4a}$$

For the case of quadratic detection the component of the electric vector of light transmitted by the analysing prism may be written as (see Figure 1)

$$E_Q^{(N)} = E_y^{(N)}\sin\Theta - E_x^{(N)}\cos\Theta \tag{5a}$$

Squaring Eq. (5a), after making substitutions from Eqs. (3a) and (4a), and integrating over time from $-\infty$ to $+\infty$, we finally obtain

$$I_Q = \frac{\mathscr{A}}{2}\sum_{k=0}^{N}\sum_{l=0}^{N}(\mathscr{A}_{y,k}\sin\Theta - \mathscr{A}_{x,k}\cos\Theta)(\mathscr{A}_{y,l}\sin\Theta - \mathscr{A}_{x,l}\cos\Theta) \times \cos[(k-l)\Delta\delta] \tag{6a}$$

for the intensity of transmitted light in the presence of an electric field. In the

† The order in which optical properties are assigned to the first pair of optical elements is immaterial provided that the sequence thereafter is alternating and the number of pairs of elements, N, is sufficiently large.

limit $N \to \infty$ Eq. (6a) becomes numerically equivalent to the asymptotic solution expressed by Eq. (4) of the text.

The analysis described above may be readily extended to the Sénarmont method of detection (described in Section B of the text) by recognising that the general forms of the components of light transmitted with electric vectors parallel and perpendicular to the slow axis of the quarter-wave retarder are given by

$$E_{\parallel}^{(N)} = -\mathscr{A} \sum_{k=0}^{N} \mathscr{A}'_{\parallel,k} \cos(\omega t - k\Delta\delta) \tag{7a}$$

and

$$E_{\perp}^{(N)} = \mathscr{A} \sum_{k=0}^{N} \mathscr{A}'_{\perp,k} \sin(\omega t - k\Delta\delta) \tag{8a}$$

respectively, where

$$\mathscr{A}'_{\parallel,k} = \mathscr{A}_{x,k} \cos\Theta - \mathscr{A}_{y,k} \sin\Theta$$

and

$$\mathscr{A}'_{\perp,k} = \mathscr{A}_{x,k} \cos\Theta + \mathscr{A}_{y,k} \sin\Theta$$

Using Eqs. (7a) and (8a) we may proceed, in a straightforward manner, to derive an expression for the intensity of light transmitted by the analysing prism set at an azimuthal angle α. We finally obtain

$$\begin{aligned} I_s = \frac{\mathscr{A}}{4} \sum_{k=0}^{N} \sum_{l=0}^{N} & (\mathscr{A}'_{\parallel,k}\mathscr{A}'_{\parallel,l} + \mathscr{A}'_{\perp,k}\mathscr{A}'_{\perp,l})\cos[(k-l)\Delta\delta] \\ & + (\mathscr{A}'_{\parallel,k}\mathscr{A}'_{\parallel,l} - \mathscr{A}'_{\perp,k}\mathscr{A}'_{\perp,l})\cos[(k-l)\Delta\delta]\cos 2\alpha \\ & \pm (\mathscr{A}'_{\parallel,k}\mathscr{A}'_{\perp,l} - \mathscr{A}'_{\parallel,l}\mathscr{A}'_{\perp,k})\sin[(k-l)\Delta\delta]\sin 2\alpha \end{aligned} \tag{9a}$$

The double sign appearing before the sin 2α term in Eq. (9a) denotes the two permissible orientations of the quarter-wave retarder (see text).

The value of α corresponding to minimum transmission of light is obtained by differentiating Eq. (9a) with respect to 2α, setting the derived function equal to zero and solving for α. The required solution is then given by

$$\alpha_{\min} = \tfrac{1}{2}\tan^{-1}\left(\pm \frac{\sum_{k=0}^{N}\sum_{l=0}^{N} (\mathscr{A}'_{\parallel,k}\mathscr{A}'_{\perp,l} - \mathscr{A}'_{\parallel,l}\mathscr{A}'_{\perp,k})\sin[(k-l)\Delta\delta]}{\sum_{k=0}^{N}\sum_{l=0}^{N} (\mathscr{A}'_{\parallel,k}\mathscr{A}'_{\parallel,l} - \mathscr{A}'_{\perp,k}\mathscr{A}'_{\perp,l})\cos[(k-l)\Delta\delta]}\right) \tag{10a}$$

The intensity of light transmitted by the analysing prism for quadratic detection was calculated for various combinations of δ, β and N using a digital computer to evaluate Eq. (6a). The intensity of transmitted light was

TABLE I

Normalised intensity of light, 10^2 I, for quadratic detection, calculated using Eq. (6a). Values of I corresponding to $N \rightarrow \infty$ were calculated using Eq. (4) of the test. The top line of entries in the table were calculated using the relationship $I = \sin^2 \delta/2$.

		Phase Retardation δ						
β	N	5	10	20	40	60	80	100
0	—	0.1903	0.7596	3.015	11.69	25.00	41.32	58.68
10	5	0.1848	0.7377	2.928	11.36	24.30	40.18	57.11
10	50	0.1829	0.7302	2.899	11.25	24.05	40.93	56.54
10	100	0.1828	0.7297	2.898	11.24	24.04	39.75	56.51
10	∞	0.1827	0.7293	2.895	11.23	24.02	39.72	50.47
20	50	0.1621	0.6473	2.570	9.982	21.38	35.43	50.42
20	100	0.1617	0.6456	2.564	9.957	21.32	35.34	50.40
20	∞	0.1613	0.6440	2.557	9.932	21.27	35.25	50.28
30	50	0.1317	0.5259	2.089	8.130	17.47	29.09	41.77
30	100	0.1309	0.5228	2.077	8.082	17.37	28.93	41.53
30	∞	0.1301	0.5196	2.064	8.034	17.26	28.76	41.28
40	50	0.0969	0.3870	1.539	6.012	13.00	21.87	31.81
40	100	0.0958	0.3825	1.521	5.944	12.86	21.63	31.47
40	∞	0.0947	0.3780	1.504	5.876	12.71	21.39	31.13
50	100	0.0619	0.2472	0.9853	3.884	8.527	14.65	21.88
50	200	0.0612	0.2446	0.9752	3.845	8.444	14.51	21.69
50	∞	0.0606	0.2422	0.9652	3.806	8.362	14.37	21.50

also calculated using the exact expression given in Eq. (4) of the text. The results of these calculations are shown in Table I. We note that as the number of optical elements, representing the Kerr cell, is increased the intensity of light calculated using the approximate expression (Eq. 6a) rapidly approaches the exact value calculated using Eq. (4). For the range of values of δ and β shown in Table I the intensities calculated using Eq. (6a), were found to be insensitive to the number of pairs of optical elements. Thus, for $\delta = 100°$ and $\beta = 50°$ the approximate intensity, calculated using Eq. (6a) with $N = 100$ is within 2% of the exact value.

An interesting feature of the lamellar model of Jones, with regard to the Kerr effect of chiral molecules, is that it should provide a very good description of the electro-optic properties of a mixture of molecules in which molecules of one type contribute to the intrinsic Kerr effect, but are achiral, and molecules of another type are chiral, but contribute only a little to the intrinsic Kerr effect. Solutions of d-camphor, or any other suitable chiral molecule, in nitrobenzene would be an example of a system of this type.

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