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ELASTIC CONSTANT MEASUREMENT ON CHOLESTERIC MATERIALS

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ABSTRACT

A method of calculating elastic constants from C-V measurements on nematics has been extended to cholesteric liquid crystal materials using racemic mixtures. Calculations of elastic constants v. temperature obtained by this method are presented and discussed.

INTRODUCTION

Present evidence shows that the main structural difference between nematic and cholesteric liquid crystals is the presence of a chemical group in the latter which has the effect of replacing the cylindrical symmetry of the molecule by an enantiomeric pair of alternatives, the helical pitch depending inter alia on the balance of enantiomers present(1). This gives the bulk liquid crystal a twisted structure. The director, which in a nematic is that direction taken on average by the long axis of the molecules, is twisted into a spiral. The helical axis thus formed can be parallel or perpendicular to the enclosing cell plates, depending on the alignment treatment applied to these plates. It can be shown that cholesterics have the same elastic constants which are allowed in nematics(2); k_{11}(splay) k_{22}(twist) and k_{33}(bend). Continuum theory predicts another coefficient k_2, but this is associated with the permanent twist of the structure, τ, where

$$\tau = \frac{1}{p} \text{ (p is the helical pitch of the material)}$$

Elastic constants of nematics have frequently been measured by techniques in which a threshold of field-induced distortion is accurately determined optically or electrically. Calculation of elastic constants from the Maier-Saupe mean field theory does not give accurate results(3). Optical methods(4) of determining threshold voltages have the advantage of simplicity, but suffer the disadvantage of not showing as precise an onset of the transition as capacitive methods. This is particularly the case with the twisted nematic effect where a significant amount of distortion of alignment above threshold voltage occurs before the Mauguin limit(5) is approached and the guiding property of the off-state is sufficiently reduced to allow cells to turn on as preceived visually. An alternative method which has been used by Deuling(6) among others, involves the comparison of an experimental capacitance voltage curve with one calculated from continuum theory, and the use of curve fitting algorithm to compute values of k_{ii} which produce the best similarity between the two curves. This method is accurate and reproducible, but computationally more involved than threshold voltage methods. Dielectric permittivities ε_{11} and $\varepsilon_{\perp}$ must be calculated from cell capacitance(7), but the uncertainties of cell thickness inherent in the usual 'sandwich' construction of cells with mylar spacers does not affect the elastic constants thus calculated. Although simple in principle, this method requires a high level of experimental care as the difference between C-V curves for different elastic constants is not large.

Cholesteric materials of very long pitch, where a cholesteric liquid crystal has been added to a nematic, can often be assumed to have the elastic constants of the nematic, but this approximation is only valid for small concentrations of cholesteric dopant. The elastic constants of a mixture containing significant amounts of cholesteric dopant cannot easily be found due to the more complex nature of the coupled Euler-Lagrange equations, the effect of rounding errors of the required computations, the much higher applied fields which are required, the presence of disclination lines, and the tendency of other undesired textures (eg. focal conic) to nucleate. Furthermore, at the high fields necessary for distortion of short-pitch materials, conduction of ionised impurities can cause either hydrodynamic domains or the nucleation of focal conic texture. For all these reasons, measurements of k_{ii} of cholesteric materials have not been so well documented as those of nematics.

EXPERIMENT

It is well known that a mixture of two cholesterics of opposite chirality can produce nematic behaviour at the precise temperature at which the 'twisting powers' of the components are equal. It is therefore expected, as predicted by McDonnell(8) that a mixture of equal amounts of the two enantiomers of a single cholesteric compound will produce a racemic nematic with a temperature range, elastic constants, and dielectric properties identical to those of the individual enantiomers. Thus, the best available methods of elastic constant measurement can be used on these 'nematics' to find, by inference, the value of k_{ii} for the single enantiomer.

The materials used in this study were mixtures of E8 nematic, as supplied by BDH Ltd., and the racemic mixture of the CB-15 cholesteric liquid crystal enantiomers supplied by BDH. The method and the computer program used to calculate k_{ii} was kindly supplied by the RSRE Liquid Crystals group. E7 nematic material (BDH) was used as a test of accuracy, and the measured k_{ii} agreed closely with those obtained at RSRE.

The cell was housed in a screened metal box resting on insulating material, and all electrical connections leading outside this box were screened. Capacitance measurements were made using a Marconi TF2700 Universal Bridge, and the A.C. bias voltage applied using an Advanced J2E L.F. oscillator set at 1 kHz (checked by oscilloscope) and feeding the 'External A.C.' jack socket of the bridge. (This bridge possessed the advantage that an external oscillator was not greatly attenuated at the capacitor terminals, so no further amplification of the output of the J2E was necessary.) To measure the bias voltage being applied, a high-impedance unity-gain buffer amplifier was constructed from a circuit given in National Semiconductors Linear Data Book, p(3.12). The apparatus is shown in Fig.(1).

Control of temperature inside the box containing the cell was maintained using two Feedback Instrument modules. The Feedback PT326 Process Trainer, fitted with a variable temperature air blower, was modified by the replacement of the existing assembly with the cell container, suitably ventilated to allow free passage of air, connecting leads, and thermometer leads. Three-term control of temperat was provided by linking this apparatus to the 'controller' section of a Feedback PCS-327 Process Control Simulator. Thermal equilibrium was assumed when no detectable variation of temperature has occurred in thirty minutes. Because the exact temperature at which the system stabilised was not a simple function of control positions, and the accuracy of the internal thermometer was poorer than ± 3°C, an auxiliary Digitron 1754 digital thermometer was used to record the temperature at which the system had stabilised. The lowest temperature of the system, claimed as 30°C by the manufacturers but in reality dependent on the ambient temperature, could be decreased further by placing the apparatus in a reduced-temperature room of ambient temperature 6°C - 10°C.

RESULTS

The initial E7 calibration is shown in Fig.(2); the lines were obtained by Raynes et al$^{(9)}$ and the points using the present apparatus. As temperature approaches T_{ni}, the difference between the two sets of results increases, and this is most probably attributable to slightly different ambient conditions for the estimation of T_{ni}. Graphs of k_{ii} against reduced temperature T/T_{ni} were plotted for each mixture used (Fig.3-5). The effect of increasing concentration of CB-15 is observed in all three cases as a decrease in elastic constant at any given value of T/T_{ni}. However, as the curves approach a common zero at $T/T_{ni} = 1$, the combined effects of errors in elastic constant and T_{ni} may lead to masking of this concentration effect. From these graphs, elastic constants at the value $T/T_{ni} = 0.8$ were plotted against concentration of CB-15 in E8 (Fig.6); in the concentration range studied, the decrease in k_{ii} is linear with concentration.

CONCLUSION

The results show clearly the decrease in elastic properties as the temperature approaches T_{ni}, due to decrease in order parameter. This also explains the fall in k_{ii}, at any specified temperature, with concentration of CB-15 present in the mixture. Because the transition temperature of CB-15 is much lower than that of E8 (in fact at room temperature CB-15 is isotropic), the fall in T_{ni} with increases in concentrations of CB-15 brings the specified temperature closer to T_{ni} of the mixture. It must therefore be noted that results within five degrees of T_{ni} are more prone to systematic errors due to inaccurate temperature settings and higher random errors due to fluctuation of temperature. For all elastic constants the temperature gradients of k_{ii} are large and increase asymptotically as T_{ni} is approached.

The results show a distinct linear fall in the values of all elastic constants with increasing CB-15 concentration at constant reduced temperature.

The method of computation includes a least-squares fit of experimental data on to the theoretical curves for a certain set of k_{ii}, and the sum of the squares of the error between calculated and predicted curves at each point is one guide to the quality of the results. However, it is doubtful whether a slow change in cell temperature, of the order of 0.1° per hour and therefore not apparent thermometrically, would manifest itself as a large sum of squares (although in principle, residuals could be tested for non-randomness to show if such a systematic error is present). The most probable effect of this perturbation would be seen as a different shape of the C-V curve, substantially changing at least one of the elastic constants. Slight errors in the measurement of empty cell capacitance (a parameter of the order of 30 picofarads) could contribute towards errors in measured permittivities, but in practice the errors in k_{ii} due to deliberately changing the values of permittivities by up to 5% were larger in the 'sum of squares' than in the values of k_{ii}.

The largest experimental scatter and the highest disagreement with other results on nematic E7, occurred for k_{22} values. This can be attributed to the fact that the information which has most effect on k_{22} is the measurement of the threshold voltage for a twisted cell (V_T), whereas k_{11} and k_{33} depend on a total of at least ten experimental points. Furthermore, the calculation of k_{22} depends on the values of k_{11} and k_{33}, thus increasing the size of the final error in k_{22}. V_T was measured from the capacitance-voltage curve of the twisted cell by extrapolation of experimental readings in the range 1.0 V_T - 1.5 V_T, to the $\varepsilon_{\parallel} = \varepsilon_{\perp}$ line. In the small range of the curve studied, a straight line approximation could usually be seen to possess resonable accuracy, but the difference between inclusion and exclusion of a particular experimental point could produce 1% shift in the value of V_T, which gave a relatively large 5% change in computed k_{22}. It must be noted that the present results used 25µ mylar for both parallel and twisted cells whereas previous studies(9) prefer a 50µm cell for V_T measurements. The latter thickness will produce a sharper threshold, tending to reduce the type of error here experienced, albeit with the disadvantage of longer 'settling times' at voltages near the threshold.

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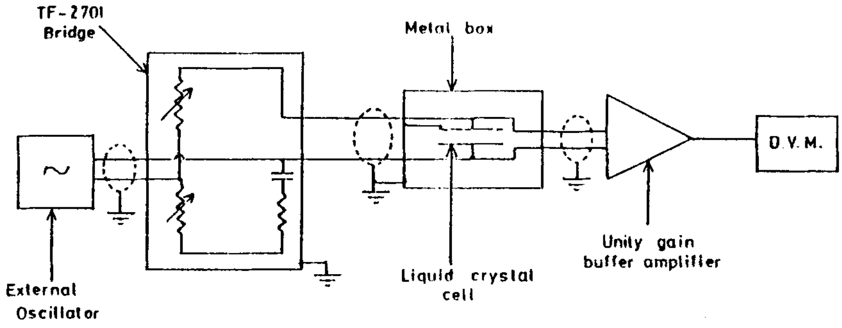


Fig.1 C-V MEASURING APPARATUS

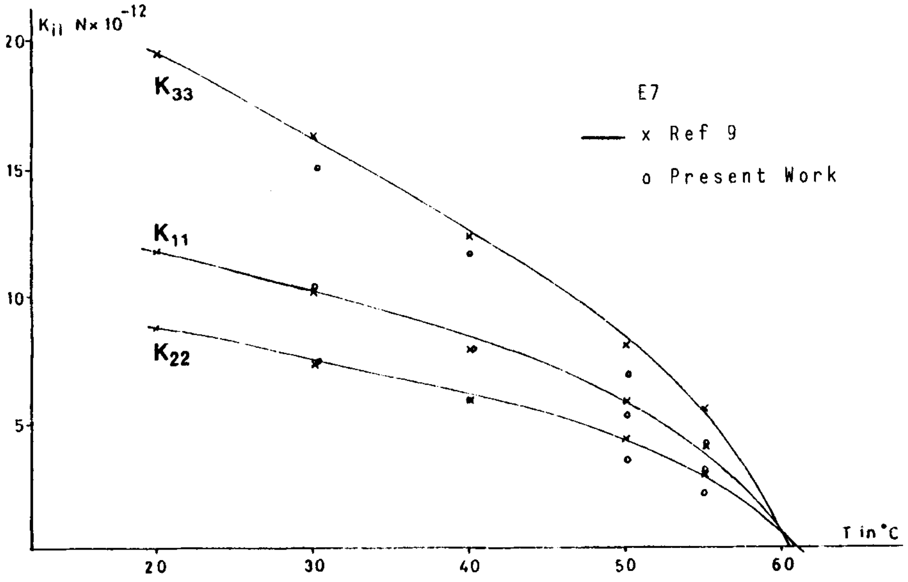


Fig.2 k_{ii} AGAINST TEMPERATURE

Fig.3: Graph of K_{11} of E8/±CB15 mixtures against reduced temperature T/T_{ni}

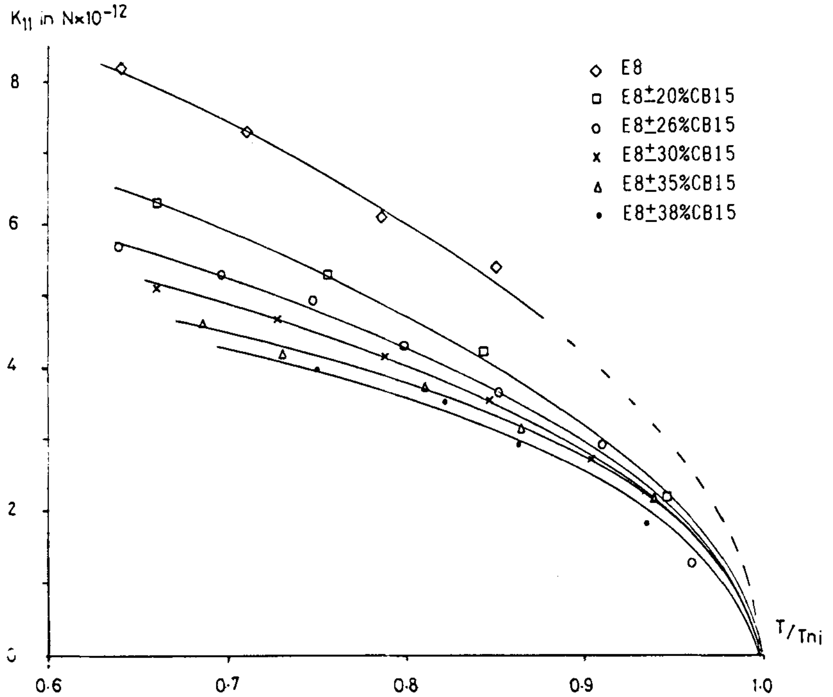


Fig.4: Graph of K_{22} of E8/±CB15 mixtures against reduced temperature T/T_{ni}

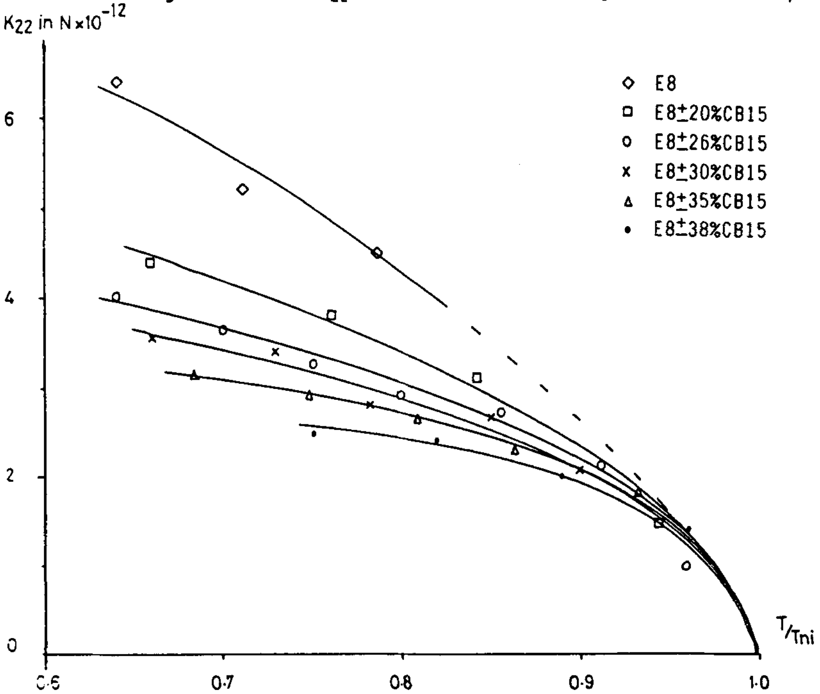


Fig. 5: Graph of K_{33} of E8/±CB15 mixtures against reduced temperature T/T_{ni}

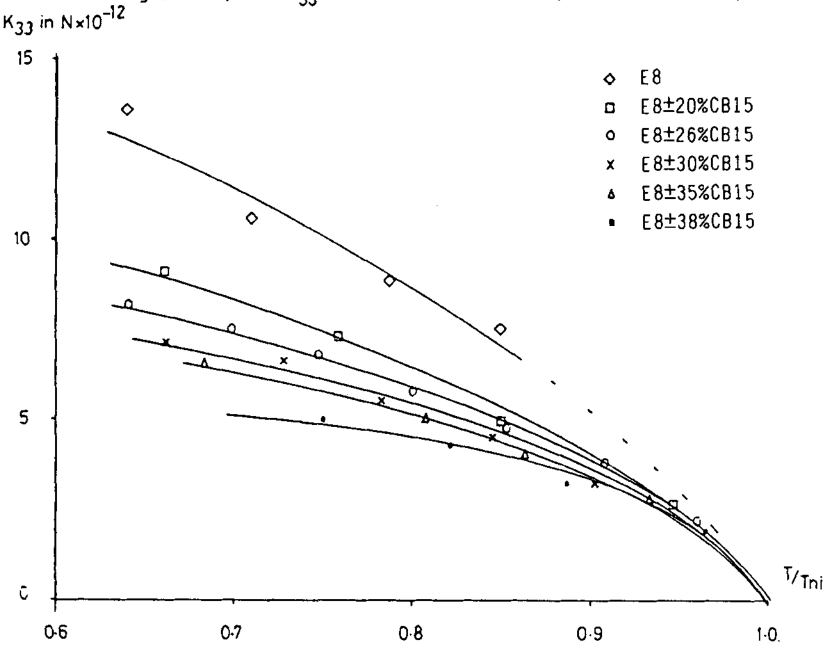
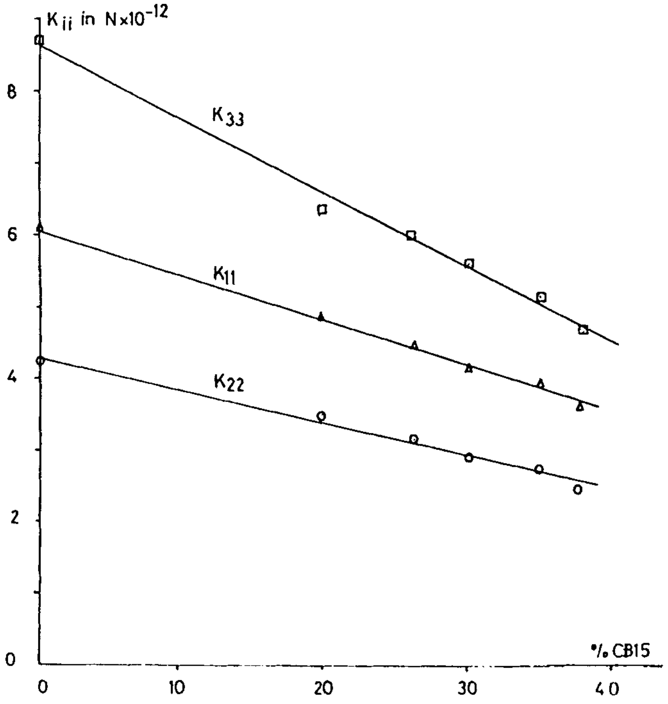


Fig.6: Graph of K_{ii} against concentration of ±CB15 in E8
T/T_{ni} = 0·8



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