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Determination of Nematic Liquid Crystal Elastic and Dielectric Properties from the Shape of a Capacitance-Voltage Curve

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This paper shows how capacitance-voltage curves can be used to determine nematic liquid crystal dielectric and elastic constants and surface tilt angles. Careful analysis of the C-V curves reveals that distortion free energy theory is useful up to a V/V_c of about two. A detailed curve of tilt angle as a function of SiO deposition angle is also presented along with temperature variation in liquid crystal properties. Pentylcyanobiphenyl (5CB) was used throughout the study.

INTRODUCTION

A method was described in an earlier paper[1] whereby nematic liquid crystal elastic and dielectric properties could be determined from birefringence experiments using parallel LC cells. This paper shows how the same properties (k_{11}, k_{33}, ε_{11}, $\varepsilon_{\perp}$) plus surface tilt angle can be determined from capacitance-voltage curves obtained using the same parallel cell construction. A typical C-V curve appears in Figure 1. A shorter version of this paper was presented in a talk given at the 6th International LC Conference. Also included are the affects of surface alignment on the parameters, their temperature variation, and the maximum V/V_c for which accurate property determinations can be made. The latter constraint provides a measure of the range over which distortion-free energy theory applies.

Basically the calculation procedure involves adjusting the above mentioned parameters, contained in the appropriate mathematical model, so as to minimize the sum of squares (SS) of the measured (C_m) and calculated (C_c) capacitances for N-data points.

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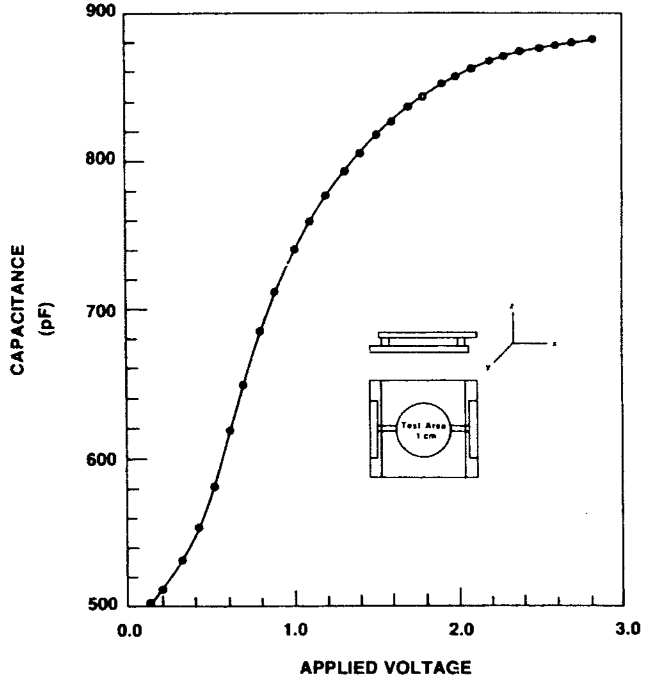


FIGURE 1 A typical capacitance-voltage curve for 5CB obtained from a cell with one cm^2 indium oxide electrodes and parallel molecular orientation.

$$SS = \sum_{1}^{N} [C_m - C_c]_i^2 \tag{1}$$

Parameter values corresponding to the minimum *SS* are then assumed to be the best estimates of the *LC* material properties.

Details of the calculation procedure can be found in the original work,[1] and a brief description of the mathematical model used in this study is contained in the next section.

MODEL

By minimizing the sum of elastic and dielectric free energies appropriate expressions for director orientation, capacitance (C_c), and applied voltage (V) for a *LC* cell of parallel molecular orientation can be obtained. In integral form, these equations are:

$$V = \frac{2}{\sqrt{\varepsilon_0}} \int_{\theta_0}^{\theta_m} \frac{d\theta}{E(\theta)\sqrt{F(\theta)}} \tag{2}$$

$$C_c = 2\varepsilon_0 \left(\frac{A}{d}\right) \frac{\displaystyle\int_{\theta_0}^{\theta_m} \frac{E(\theta)d\theta}{\sqrt{F(\theta)}}}{\displaystyle\int_{\theta_0}^{\theta_m} \frac{d\theta}{\sqrt{F(\theta)}}}, \tag{3}$$

with the following definitions and symbols:

$F(\theta) \equiv \left[\frac{1}{E(\theta)} - \frac{1}{E(\theta_m)}\right] K(\theta)^{-1}$

$E(\theta) \equiv \varepsilon_{11} \sin^2 \theta + \varepsilon_\perp \cos^2 \theta$

$K(\theta) \equiv k_{11} \cos^2 \theta + k_{33} \sin^2 \theta$

θ_0, θ_m = director tilt angles at $z = 0$, $d/2$ respectively

(A/d) = cell area – thickness ratio

k_{11}, k_{33} = splay and bend elastic constants

$\varepsilon_{11}, \varepsilon_\perp$ = parallel and perpendicular dielectric constants

$\varepsilon_0 = 8.854 \times 10^{-12}$ farads/meter

V = applied voltage

$R_c \equiv \frac{V}{V_c}$ = critical voltage ratio

Adjustable parameter set: $k_{11}, k_{33}, \varepsilon_{11}, \varepsilon_\perp, A/d, \theta_0$

Standard deviation

$$\sigma = \left[\frac{SS}{N - p}\right]^{1/2} \tag{4}$$

p = number of parameters (6) in the model.

As presented in Eq. (3), the capacitance integral is nothing more than an averaging integral for the $\sin^2(\theta)$ and $\cos^2(\theta)$ over a distribution of tilt angles in a cell of thickness d. These averages when multiplied by the appropriate constants give the capacitance. Equation (3) can also be written in terms of the average value of the z-component of the dielectric constant $(\bar{\varepsilon}_z)$.

$$C_c = \varepsilon_0 \bar{\varepsilon}_z \left(\frac{A}{d}\right) \tag{5}$$

EXPERIMENTAL

Parallel cells of one sq. cm active area, Figure 1, containing pentylcyanobiphenyl ($T_{KN} = 24.2$ C, $T_{NI} = 36.4$ C) were used throughout this study. Surface alignment was achieved by evaporating 300 Å of silicon monoxide at various grazing angles onto the indium electrodes over the range from six to thirty degrees between the source and plane of the substrate.

Cell thickness was determined by placing an empty cell into a UV-visible spectrophotometer and scanning through a wavelength range chosen to give several reflection extremum. Thickness was then calculated using the following relationship:

$$d_m = \frac{n}{2}\left(\frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}\right) = \text{measured cell thickness} \tag{6}$$

n = number of maxima or minima between wavelengths λ_1 and λ_2.

Cell thickness can also be determined from the curve-fitting procedure by dividing the parameter (A/d) into the known electrode area, 1 cm^2. Comparing this value to the thickness determined using Eq. (6) provides an independent check of the curve-fitting procedure. Table I contains thickness values thus determined. Agreement is generally good and on the average $d_c > d_m$. The latter is to be expected as electrode patterns on opposite sides of a cell cannot be aligned exactly. As a consequence active cell area is less than 1 cm^2.

Test cells used for R_c and temperature variation studies were aligned by depositing silicon monoxide at a six degree angle measured between the source and the plane of the substrate (84 degrees to the substrate normal).

TABLE I

Cell thickness as measured using a spectrometer compared to that calculated using the curve-fitting program

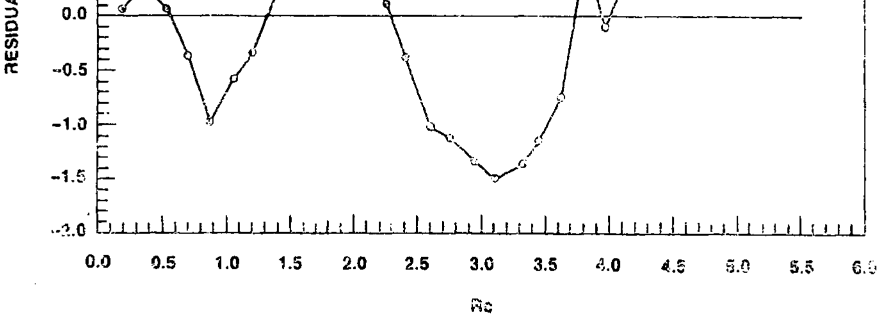
Measured	Calculated	% Difference
17.44 μ	16.78	3.78
19.82	19.99	−0.86
24.77	23.79	3.96
21.74	22.07	−1.52
22.15	20.81	5.78
21.09	20.27	3.89
19.20	18.67	2.76
16.62	17.08	−2.77
21.83	21.65	0.82
16.56	16.59	0.18
		avg = 1.57

VOLTAGE LIMITATIONS

So as to minimize errors in parameter estimates consideration must be given to the voltage range over which Eqs. (2) and (3) apply. The normalized residuals $[C_m - C_c]\sigma^{-1}$ should be random when plotted against R_c. Any systematic or non-random error appearing in such a plot can be associated with lack of fit to Eqs. (2) and (3) inadequately describing the experiment.

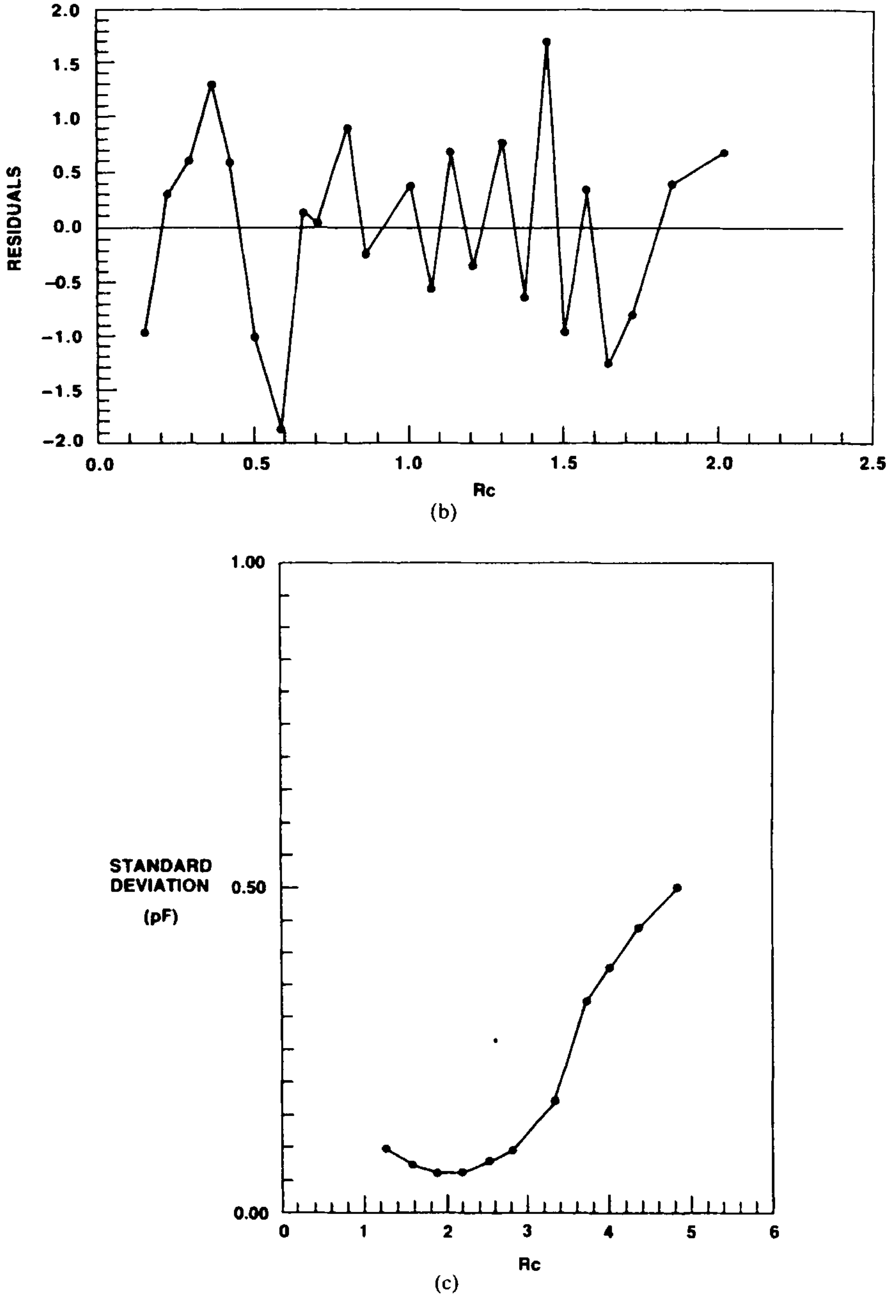
A plot of normalized residuals, Figure 2a, covering R_c values up to 4.86 reveals that a systematic deviation between theory and experiment does exist which is similar in appearance to an undamped periodic function. Starting at $R_c = 4.86$ and reducing R_c by removing points from the data set gradually reduces the systematic error and permits determination of the maximum allowable R_c in the context of Eqs. (2) and (3). Residuals shown in Figure 2b resulting from this procedure are more nearly random and indicate the maximum R_c is about two. The average residual, Figure 2b, is 0.004; whereas the average is -0.04 for the data appearing in Figure 2a. If the error were purely random the average residual would be zero. However 0.004 probably represents a practical approach to zero, and further indicates that an $R_c = 2$ is a maximum value for distortion-free energy theory.

In terms of the standard deviation, Figure 2c, a minimum is seen to occur at $R_c = 2$ which is consistent with the residual data. Increasing σ below $R_c = 2$ is a result of the quantity $(N - p)$, Eq. (4), becoming too small. The latter condition can be negated by merely taking more data in the range $0 < R_c < 2$.



(a)

FIGURE 2(a) Residuals $[C_c - C_m]\sigma^{-1}$ from a test conducted at a maximum R_c of 4.86.



(b)

(c)

FIGURE 2(b) Residuals for $R_c = 2.01$ exhibiting a more random pattern. (c) Standard deviation showing a minimum at $R_c = 2$.

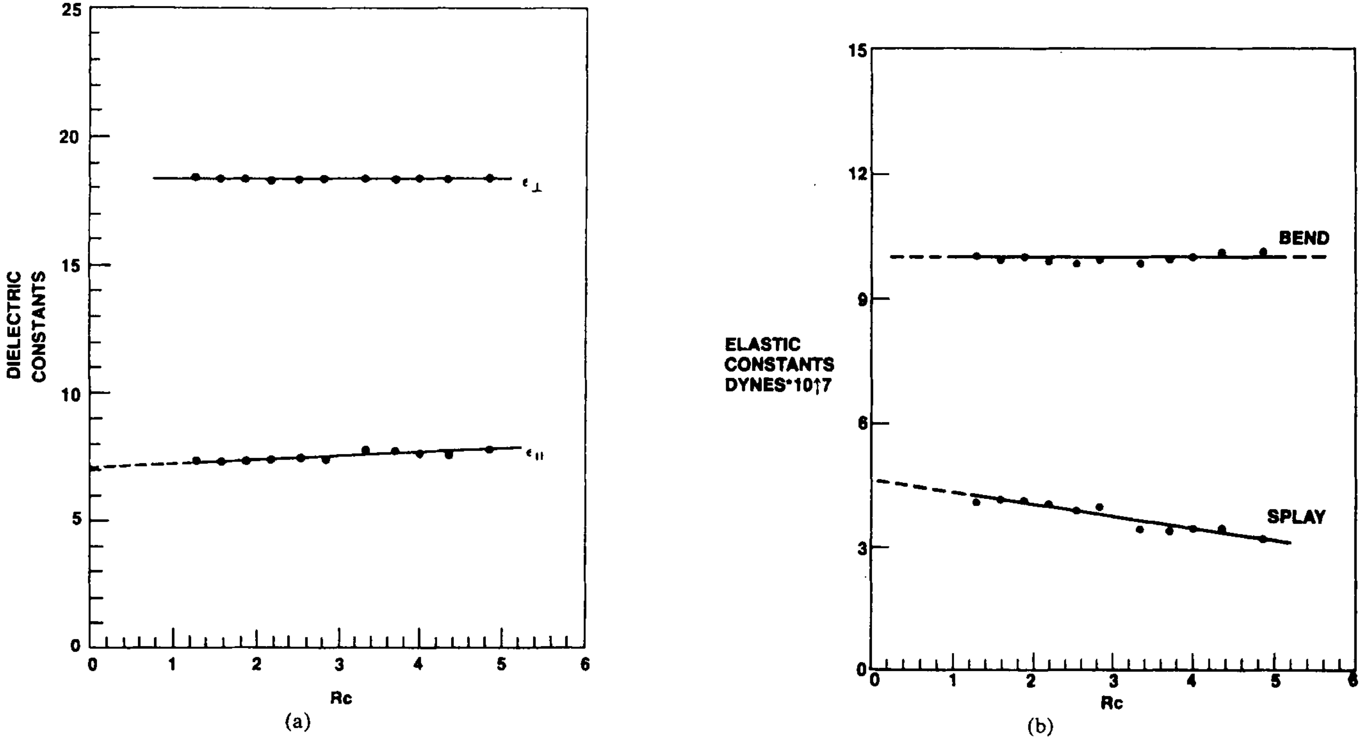


FIGURE 3(a) Dielectric constants of 5CB as a function of R_c. (b) Elastic constants.

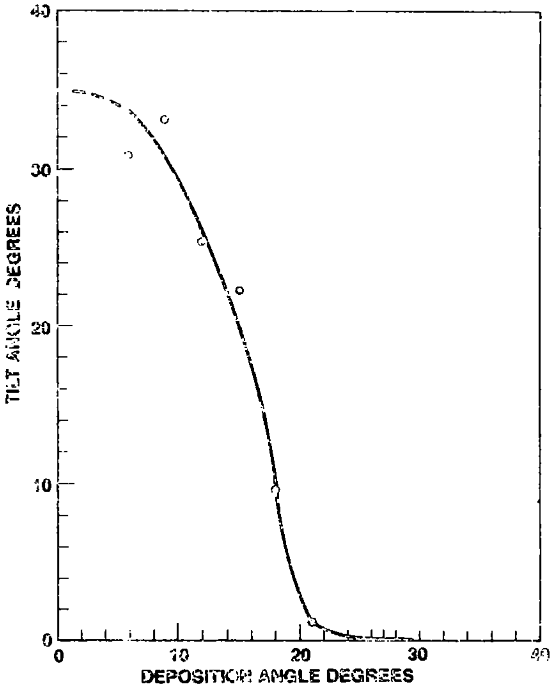
Parameter estimates also vary with R_c as shown in Figures 3a and b. $\varepsilon_\perp$ and k_{11} are seen to vary slightly while ε_{11} and k_{33} are insensitive to changes in R_c. While not crystal clear from the data, there is a hint that both $\varepsilon_\perp$ and k_{11} level out below $R_c = 2$ obviating the necessity to extrapolate to zero. Best estimates for k_{11} and $\varepsilon_\perp$ are then the ones obtained at a critical ratio of two. While not shown, surface tilt angle varies inversely with R_c. The foregoing tests were conducted at 22°C.

All subsequent results represented herein are based on data taken and analyzed for R_c values near two.

SiO DEPOSITION ANGLE

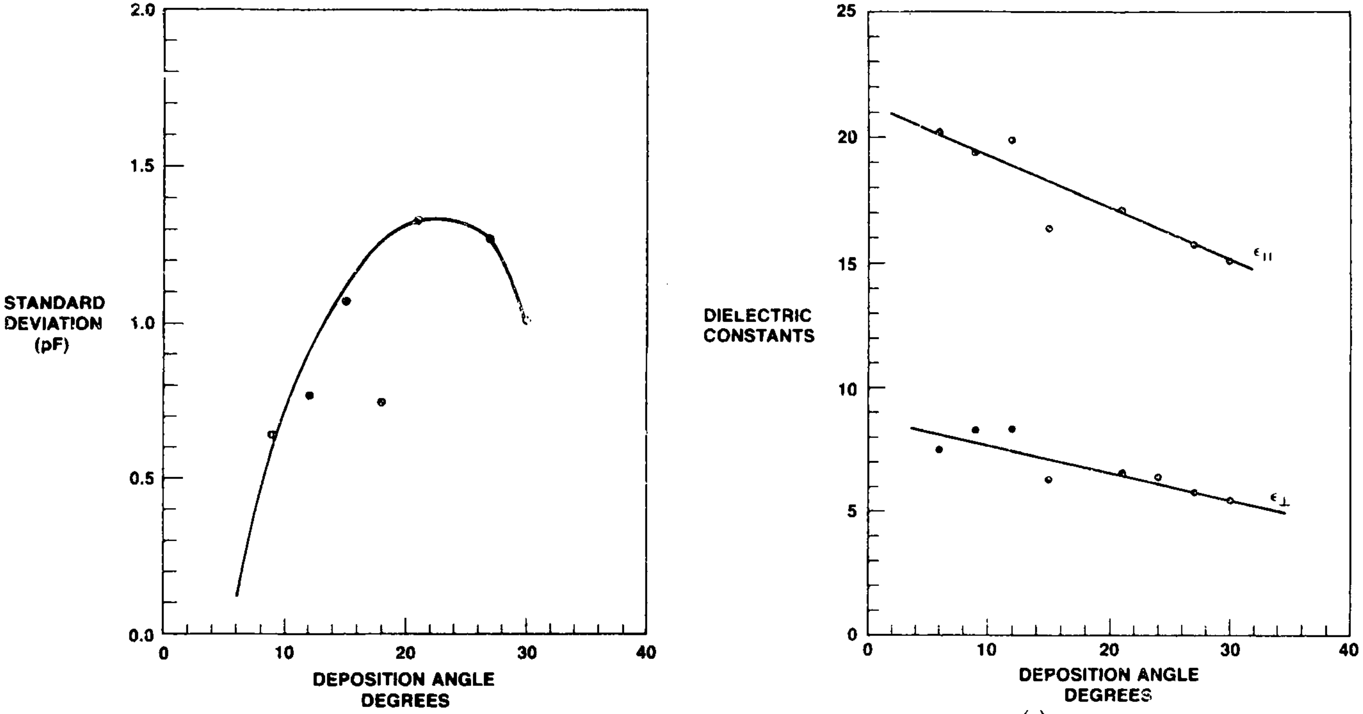
Only small variations in parameter values were detected as a function of R_c; however variation with alignment, established by oblique SiO deposition, is much greater.

A rapidly decreasing tilt angle is shown in Figure 4a as a function of the SiO deposition angle (α). Up to $\alpha = 21$ degrees, θ_0 decreases rapidly from



(a)

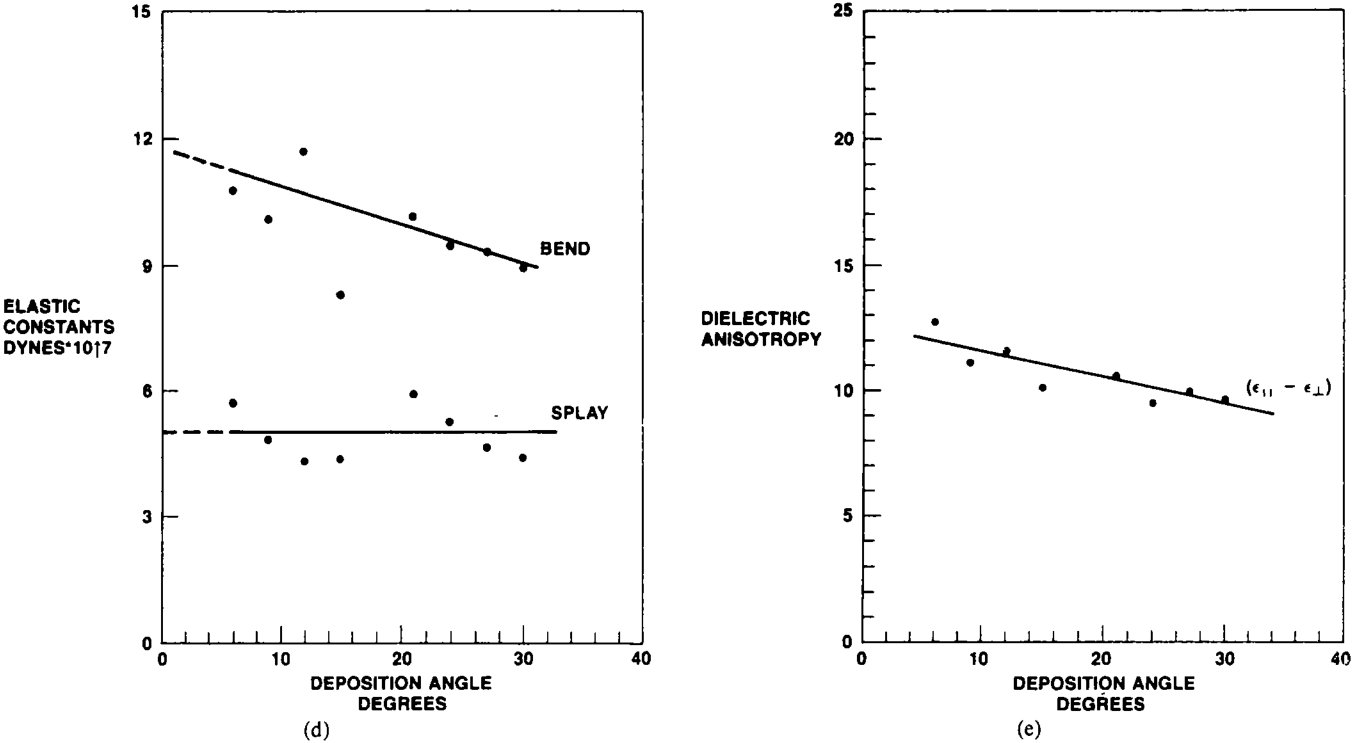
FIGURE 4(a) Surface tilt angle of 5CB as a function of SiO deposition angle.



(b)

(c)

FIGURE 4(b) Standard deviation showing a maximum at 21 degrees deposition angle. (c) Dielectric constant.



(d) (e)

FIGURE 4(d) elastic constant variation with deposition angle. (e) Dielectric anisotropy.

about 35 degrees to one degree. For α's in the 21 to 30 degree range, θ_0 decreases from about 1 to 0.02 degrees. More extensive tests using the biphenyl mixture E-7[7] produced results which are similar to those shown in Figure 4a for 5CB. In both cases large variations in tilt angles have been observed for deposition angles in the 15 to 21 degree range.

Visual examination of cells prepared by depositing SiO in the 15 to 21 degree range revealed non-uniform alignment with a high density of disclinations. Assuming director rotation follows a curve similar in shape to that exhibited by θ_0, Figure 4a, then non-planar alignments would be expected around $\alpha = 18$ degrees. Above $\alpha = 21$ and below 15 degrees, alignment quality as evaluated by examination under polarized light was always uniform and parallel.

Lack of uniform planar alignment around $\alpha = 18$ degrees is also reflected in the standard deviation as shown in Figure 4b. Increasing σ with α indicates an increasing disparity between theory and experiment. Some recovery of planar alignment is indicated by a decrease in σ above $\alpha = 21$ degrees, however.

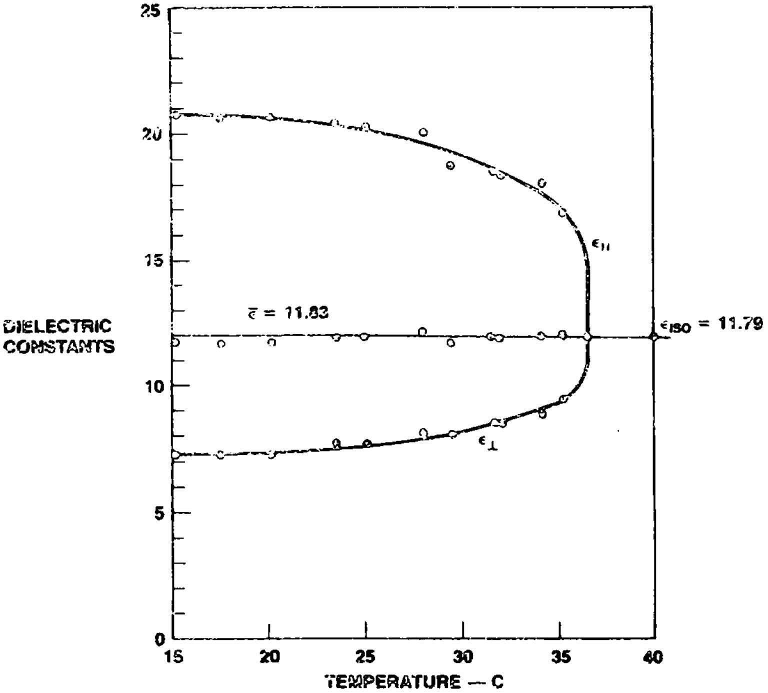
The combination of relatively large σ at $\alpha \geq 15$ and a uniform appearance in the alignment indicates that visual examination may not be a good indication of alignment quality.

Dielectric and elastic constants show considerable scatter in the non-aligned region, Figures 4c and d, and an overall linear variation with deposition angle. This scatter is postulated to be caused by a splay dispersion in the plane of the substrate for molecules on and near the surface. This splay in the x–y plane results in a molecular twist which propagates some distance in the z-direction. Since twist energy is not accounted for in the planar model, its presence in test cells will cause parameter estimates to be inaccurate and show considerable scatter. Dielectric anisotropy, Figure 4e, is not as sensitive to poor alignment as are either $\varepsilon_{\parallel}$ or $\varepsilon_{\perp}$. Both elastic constants are quite sensitive to alignment uniformity, however.

TEMPERATURE VARIATION OF PARAMETERS

A cell aligned by depositing SiO at six degrees was used to study temperature variation of the model parameters.

Dielectric constant varies in the expected manner, Figure 5a, and the isotropic value of ε (11.8 ± 0.3) measured at 40°C is the same as the average of all ε_{avg} points appearing in Figure 5a. Other determinations[5,6] of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for 5CB have resulted in measurable differences between ε_{iso} and ε_{avg}. These differences may be due to dipole–dipole interactions in the nematic state which are not present above T_{NI}.



(a)

FIGURE 5(a) Temperature variation of dielectric constants.

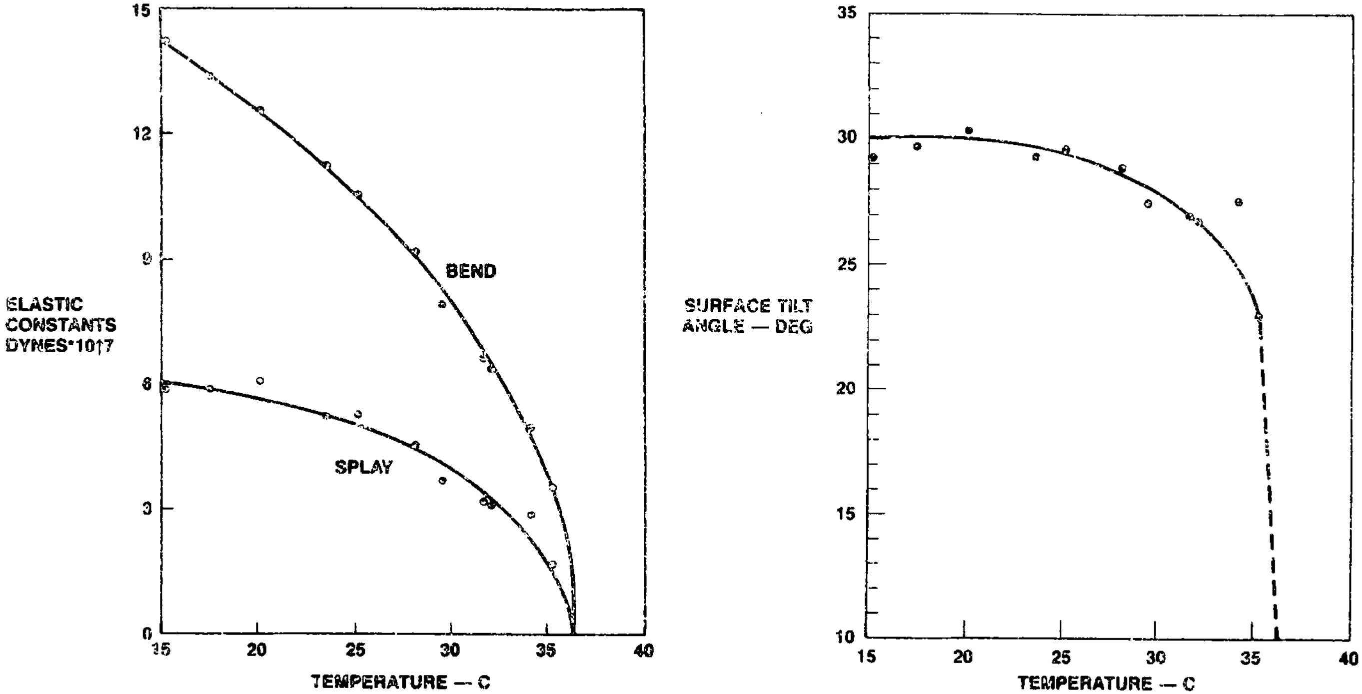
Elastic constants, Figure 5b, decrease to zero at T_{NI} following relationships similar to those found for PAA and MBBA.[4]

Surface tilt angle, Figure 5c, also decreases with increasing temperature, and becomes increasingly non-linear as T approaches T_{NI}. The magnitude of the decrease is more than expected, and based on the curve shape, further substantial decreases can be expected as $(T - T_{NI})$ approaches zero. Extrapolation of the tilt angle to zero at T_{NI} is tempting; however, the data does not justify such action.

COMPARISON TO OTHER METHODS

Many questions always arise concerning the validity of parameter estimates obtained by curve-fitting compared to similar results obtained by rising more direct experimental methods.[5,6]

Usually direct methods rely on large applied fields and surface alignment control to orient the liquid crystal for the purpose of determining elastic and



(b)

(c)

FIGURE 5(b) Temperature variation of elastic constants, and (c) the surface tilt angle.

dielectric constants. Capacitance of the aligned sample is measured to determine either ε_{11} or $\varepsilon_{\perp}$, and elastic constants are determined by detection of a particular critical field. Direct experimental methods depend on establishing limiting conditions in terms molecular orientation and are therefore restrictive with respect to the information available. By contrast curve-fitting uses many data points taken over a range of applied fields, and only one experiment is needed to obtain estimates for several parameters. However, one experiment per parameter is required when using direct methods.

Consider the cell represented by the curve shown in Figure 1, ε_{11} from the curve-fitting algorithm gives a capacitance of 938 pF. This value is well above the maximum shown in Figure 1, and extrapolation to 938 pF given the shape of that curve would be difficult. ε_{11} obtained by direct experiment[5] results in a capacitance of 903 pF, still well above the maximum shown in Figure 1. The difference in ε_{11} obtained by the two methods is only 3.3 percent (18.3 vs. 17.7); however the numerical result shows how reliance on saturation of capacitance is inaccurate.

CONCLUSIONS

Simple isothermal capacitance–voltage curves obtained from cells of parallel orientation can be used to determine several nematic liquid crystal properties. Care must be taken to obtain uniform alignment, SiO evaporated at six degrees has been found to be satisfactory, and R_c should not exceed two by more than a few tenths.

Although alignment in the range of 15–21 degrees SiO deposition angle is non-uniform, C–V curves can still be analyzed to ascertain tilt angles. Considerable scatter in the data will occur and several duplicate tests must be performed so as to arrive at a reasonable average result. Non-uniform surface alignment influences the parameter estimates by introducing unwanted twist energy into the planar structure which is a result of director splay in the plane of the substrate. The effect is not small as ε_a varies from 9.5 to 12 over a range of SiO deposition angles of thirty to six degrees, respectively.

Analyzing a C–V curve, up to $R_c = 2$, gives better parameter estimates than can be obtained by just relying on large applied fields and surface alignments to orient LC materials.

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