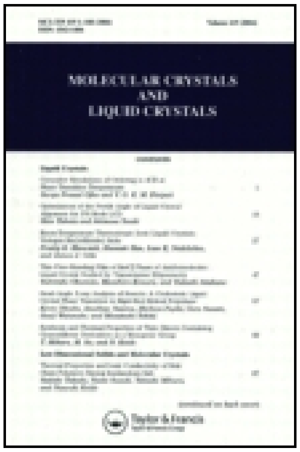

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A New Association Model for Nematogenic Systems—Its Significance for Liquid Crystal Materials Research

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A New Association Model for Nematogenic Systems—Its Significance for Liquid Crystal Materials Research

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The importance of molecular association is considered in relation to the physical properties of a number of nematogens. It is proposed that association leads to the formation of polar and apolar dimers, which influence the dielectric and electro-optic properties of nematic liquid crystals. Dielectric and light scattering measurements of polar and apolar correlation factors are reported for a series of dipolar mesogens, and interpreted in terms of a model for molecular association. Both the solute molecular structure and nature of the solvent influence the degree of association, and the good device properties of mixtures of positive and negative nematogens is tentatively attributed to the strong tendency of dipolar solutes to associate in negative nematic solvents.

Keywords: nematogenic system, molecular association, molecular light scattering, dipole correlation factor, quadrupole correlation factor

I. INTRODUCTION

The formation of orientationally ordered mesophases is a direct result of anisotropic intermolecular forces, but to relate the physical behaviour of liquid crystals to the properties of mesogenic molecules remains a formidable problem. The correlation of display performance with the molecular structure of mesogens is also difficult, but is an important subject of research for the improvement of liquid crystal display devices. Materials for twisted nematic liquid crystal displays (TN–LCD) have been developed by many workers since the early 1970's.[1–5] Many investigations[6–10] of the relationship between important parameters for display performance and material constants have been conducted. For example, correlation between the threshold sharpness, which is one of the most important parameters for multiplexability, and material constants has been extensively investigated in various material systems, and has been the subject of theoretical explanation.[11]

In the study of the relationship between molecular structure and mesophase properties, one firm conclusion that has emerged is that small changes in molecular structure can lead to dramatic changes in liquid crystal phase behaviour.[12,13] Since intermolecular forces are responsible for liquid crystal phase formation, the study of molecular interactions, associations and correlations is essential to understanding the properties of liquid crystals and the behaviour of LCD's. The Maier-Saupe mean-field theory of nematic liquid crystals replaces specific molecule-molecule interactions by an average pseudo-potential, which can be used to give a fair description of some physical properties of liquid crystals such as electric permittivities and refractive indices. The description of elastic and electro-optic properties of liquid crystals requires theories to allow for molecular interactions. Some such theories have been developed,[14–16] but it is usually difficult to test these experimentally. Evidence for molecular interaction, association or correlation from experimental studies tends to be rather indirect. X-ray measurements on both smectic and nematic mesophases show local translational order,[17] while strong depolarised light scattering[18] suggests long-range angular correlations over many molecular diameters.

Dielectric properties of nematic liquid crystals which consist of molecules with strongly polar end groups such as cyano- or nitro-, have been interpreted in terms of anti-parallel molecular association.[19] For these materials the temperature dependence of the mean permittivity above and below the nematic/isotropic transition temperature does not follow the expected Debye ($1/T$) behaviour. Also the magnitude of the permittivity in strongly polar mesogens is often considerably less than would be expected on the basis of free-molecule dipole moments. These effects have been explained in terms of anti-parallel dipole association, and can be quantitatively described by a Kirkwood correlation factor g_1. For anti-parallel association g_1 values are less than one, and results have been reported[20] as low as 0.45 for strongly polar mesogens such as Py.7 (5-*n*-heptyl-2-(4′-cyanophenyl)-pyrimidine). Weakly polar materials like MBBA (4-methoxybenzylidene 4′-*n*-butyl aniline) have g_1 values close to unity[19] indicating little dipole-dipole correlation.

The influence of anti-parallel local ordering on the elastic constants of polar mesogens has also been discussed,[21] and measurements on mixtures suggest that the effect of such ordering is to increase the bend : splay elastic constant ratio.[22] The observation of re-entrant smectic behaviour in polar nematogens, which can lead to problems in formulating device mixtures, has been explained in terms of an equilibrium between monomers and anti-parallel associated dimers.[23]

Molecular association has also been proposed to explain the properties of certain device mixtures. One of the authors[24] has proposed that mixtures of dielectrically positive materials (Np) as guests and dielectrically negative materials (Nn) as hosts give good display performances with respect to threshold sharpness and small viewing angle dependence of the threshold voltage, both of which are important factors for high multiplexability. A sharp threshold value in Nn plus Np mixture systems has been attributed to their small bend : splay elastic constant ratio,[7,11] and some authors have explained this in terms of an equilibrium between monomers and anti-parallel associated dimers of Np in an Nn solvent.[22,25] Another example is the small threshold voltage and small temperature dependence of the threshold observed in systems of Np molecules with a laterally substituted halogen mixed with Nn hosts.[26,27] An attempt to explain the results in terms of an unstable anti-parallel dimer association of substituted Np molecules was given by one of the authors.[27]

Although dipole-dipole interactions are important in determining some mesophase and device properties, they do not appear to play a significant role in contributing to mesophase stability. Nematic/isotropic transition temperatures cannot be correlated with changes in dipole moment,[13] and there is no evidence for any long-range ferro-electric or anti-ferro-electric order in nematic phases. There is however plenty of evidence[28–30] to show that molecular orientations are correlated over long distances in mesophases, and in isotropic phases close to mesophase transition temperatures. This correlation should result in both parallel and anti-parallel local ordering of molecules, and this observation has led us to reconsider the usual model for anti-parallel dipole association in mesogens and mesogenic solutions. Clearly dipole-dipole forces will play a secondary role in fixing the relative amounts of parallel and anti-parallel dipole association, but both types of dipole ordering should be considered in describing the properties of liquid crystals and liquid crystal device mixtures.

In an earlier paper[31] we introduced a new model for molecular association, which was used to explain the dielectric properties of mesogenic solutions. This model postulates the existence of parallel and anti-parallel dimers and the relative concentrations of these dimers reflects the importance of polar/apolar association. This paper reviews the model and its application to dielectric and light scattering measurements on mesogenic solutions. Values are derived for the dipole (polar) correlation factor g_1 and for the quadrupole (apolar) correlation factor g_2, and these are discussed in terms of our model for molecular association. The microscopic behaviour of Np plus Nn binary systems is reconsidered on the basis of our newly proposed model. Implications of the model for the interpretation of device properties and the formulation of new device mixtures are also discussed.

II. DIELECTRIC STUDY OF MOLECULAR ASSOCIATION

2.1. Theoretical background

The correlation of molecular dipoles on interacting molecules can be described in terms of a dipole correlation function defined by:

$$G_1(\mathbf{r}) = \frac{\langle \boldsymbol{\mu}(\mathrm{o}) \cdot \boldsymbol{\mu}(\mathbf{r}) \rangle}{\langle \boldsymbol{\mu}(\mathrm{o}) \cdot \boldsymbol{\mu}(\mathrm{o}) \rangle} = \langle P_1(\cos\theta(\mathbf{r})) \rangle \qquad (1)$$

where $\boldsymbol{\mu}(\mathbf{r})$ is the dipole moment of a molecule at position $\mathbf{r}$ within the fluid. The angular brackets denote an ensemble average. Integration of Eq. (1) over a macroscopic volume gives the Kirkwood correlation factor g_1 as:

$$g_1 = \frac{1}{V} \int G_1(\mathbf{r}) d\mathbf{r} = 1 + \sum_{j \neq 1} \langle P_1(\cos\theta_{1j}) \rangle \qquad (2)$$

where θ_{1j} is the instantaneous angle between two interacting dipoles on molecules 1 and j. The correlation function $G_1(\mathbf{r})$ is an odd function of the angle between the molecules, and anti-parallel ordering of dipoles gives rise to values of g_1 less than unity. Results for g_1 can be obtained from measurements of the permittivity of an isotropic liquid by using:

$$g_1\mu^2 = \frac{9\epsilon_0 kT}{N}\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \tag{3}$$

ϵ is the relative permittivity, n the refractive index, N the number density of molecules and μ is the free molecule dipole moment. Expressions relating the dipole correlation factors to the permittivity components for anisotropic fluids are given in Reference (19). For a solution of polar molecules mole fraction (x_2) in a non-polar solvent mole fraction (x_1), g_1 is given by:[32]

$$g_1 = \frac{9kT\epsilon_0(2\epsilon + n^2)^2}{\mu^2 N_A x_2(n^2 + 2)^2(2\epsilon + 1)}\left\{\frac{\epsilon - 1}{\epsilon}\left[\frac{x_1M_1 + x_2M_2}{d}\right] - \frac{3x_1M_1(\epsilon_1 - 1)}{d_1(2\epsilon + \epsilon_1)} - \frac{3x_2M_2(n^2 - 1)}{d_1(2\epsilon + n^2)}\right\} \tag{4}$$

ϵ, d and n are the permittivity, density and refractive index of the solution, while ϵ_1 and d_1 refer to the pure solvent; M_1 and M_2 are the molecular weights of solvent and solute molecules.

We now consider the possibility that in addition to monomeric species in solution, there may also be parallel and anti-parallel dimers, the concentrations of which are determined by the equilibria:

$$\begin{gathered} 2M \rightleftharpoons M_{2a} \\ 2M \rightleftharpoons M_{2p} \end{gathered} \tag{5}$$

K_a and K_p are the equilibrium constants for the formation of anti-parallel and parallel dimers respectively, defined in terms of the mole fractions as:

$$K_a = x_a/x_m^2; \quad K_p = x_p/x_m^2 \tag{6}$$

x_a, x_p and x_m are the anti-parallel dimer, parallel dimer and monomer mole fractions, and these are related by:

$$X_m = \frac{[1 + 4x_2(2 - x_2)(K_a + K_p)]^{1/2} - 1}{2(2 - x_2)(K_a + K_p)} \tag{7}$$

where x_2 is the total solute mole fraction. If there are a number of associated solute species present, the apparent dipole correlation factor becomes:[33]

$$g_1 = \frac{1}{\mu_m^2} \sum_k N_k \mu_k^2 \Big/ \sum N_k \tag{8}$$

In our model we restrict attention to monomers, parallel and anti-parallel dimers, in which case the expression for g_1 becomes:

$$g_1 = \frac{1}{x_2(1 + x_a + x_p)} \left[x_m + x_a \left(\frac{\mu_a}{\mu_m}\right)^2 + x_p \left(\frac{\mu_p}{\mu_m}\right)^2 \right] \tag{9}$$

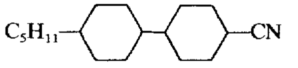
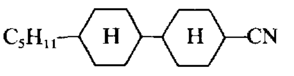
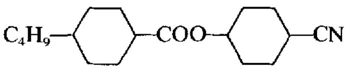
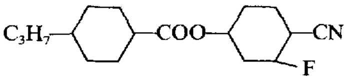
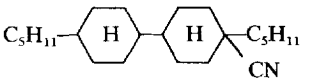
From Eq. (9) g_1 may be calculated knowing the relative concentrations and dipole moments of monomers (μ_m) anti-parallel dimers (μ_a) and parallel dimers (μ_p). Alternatively, as described in this paper, measured values of g_1 may be fitted to Eq. (9) to yield values for the equilibrium constants K_a and K_p.

2.2. Dielectric results

The materials studied are listed in Table I. Dipole correlation factors were obtained from measurements of the electric permittivity, refractive indices at 633 nm and densities of the materials in xylene solutions at 25.0 ± 0.3°C, using Eq. (4). Details of our experimental techniques are given in an earlier paper.[34] Our results are presented in Figure 1. In order to obtain information on the association in these solutions, the next stage in the analysis is to evaluate the equilibrium constants K_a and K_p. To do this we need to have a model for the dipole moments of the dimeric species. For approximately cylindrical molecules such as CB5 and CCH5 with axial dipoles it is reasonable to set $\mu_a = 0$ and $\mu_p = 2\mu_m$, but for molecules with transverse dipole components, there are a number of possibilities. Strong coupling between both longitudinal and transverse components of the molecular dipoles would give the same result as for axial dipolar molecules. However our picture of associated molecules envisages much weaker dipole-dipole interactions with relatively free rotation of the molecules about their longitudinal axes. We therefore assume that the transverse components of the dipoles are uncorrelated, but the longitudinal components are strongly correlated and will cancel in the anti-parallel dimers. Values for the component dipoles for the molecules of this investigation have been obtained from bond moment calculations. Using these values we have obtained the equilibrium constants for association listed in Table II, by fitting the experimental g_1 values of Eqs. (7) and (9).

TABLE I

Materials studied

		Nematic/isotropic transition temperature (T_{NI})	Isotropic permittivity at T_{NI}
	(CB5)	35.2°C	11.1
	(CCH5)	88.0°C	5.7
	(C4CN)	41.5°C	19.3
	(C3FCN)	(18°C)	(33.0)
	(CCN55)	66.4°C	—

Our results indicate that there are considerable differences in association behaviour between the materials studied. For the axial molecules CB5 and CCH5 anti-parallel dimers predominate with $K_a/K_p \sim 10$, but the strength of association is much greater for CB5. With CCH5 the association develops more slowly as the concentration increases, which is consistent with the smaller polarisability anisotropy of CCH5.[13] The approximately equal proportions of parallel to anti-parallel dimers for CB5 and CCH5 suggests that the dipole-dipole interactions are very similar in both materials, and that the difference in their dielectric behaviour is due to differences in apolar association.

The esters C4CN and C3FCN are both strongly associated, which presumably reflects their high polarisabilities, however the relative proportion of anti-parallel to parallel dimers is less than with the axial molecules CB5 and CCH5. A probable explanation of this is the distribution of dipole centers and molecular shapes of the esters which prevent strong dipole-dipole correlation. The results for CCN55[41,42] are surprising in that they show an increase in the effective dipole moment with concentration, corresponding to g_1 values greater than one. On the basis of the proposed dimer structures illustrated in Figure 2, we set $\mu_a = 0$ and $\mu_p = 2\mu_m$. Fitting the dielectric results for xylene solutions of CCN55 to our association model gives $K_a/K_p \sim 0.25$ suggesting a predominance of parallel dimers. Unfortunately we have not yet made depolarised light scattering measure-

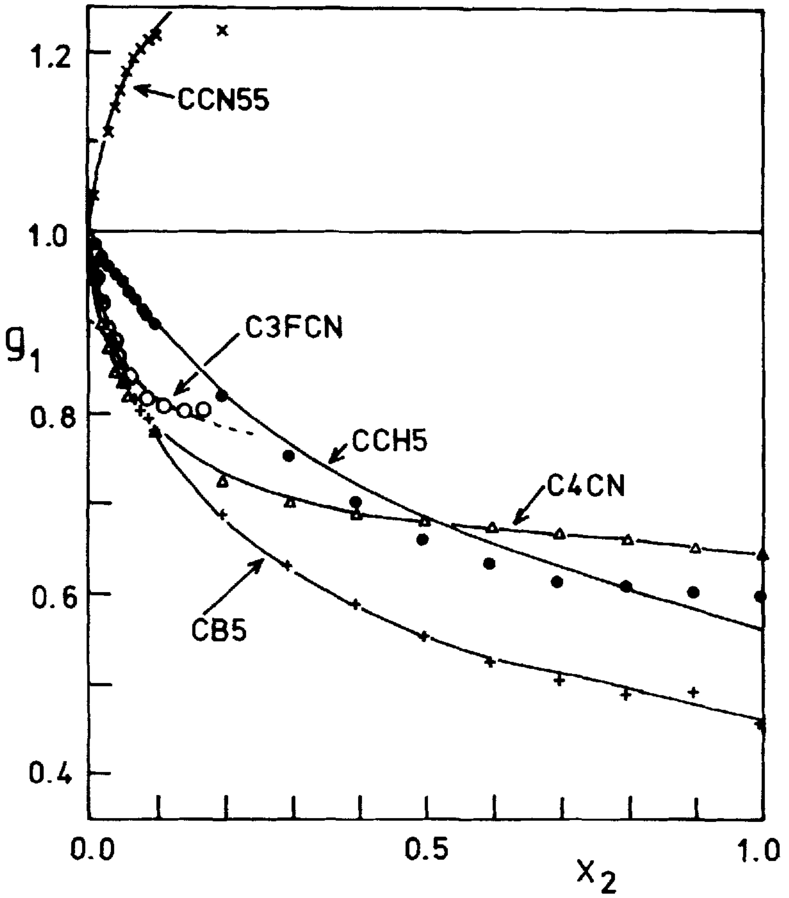


FIGURE 1 Dipole correlation factors g_1 as a function of mole fraction for *p*-xylene solutions of mesogens.

ments on solutions of CCN55, but they will provide valuable information on this interesting material.

III. LIGHT SCATTERING STUDY OF MOLECULAR ASSOCIATION

3.1. Theoretical background

The correlation of molecular axes independent of dipole direction can be described by the correlation function:

$$G_2(\mathbf{r}) = \langle P_2(\cos\theta(\mathrm{o})) \cdot P_2(\cos\theta(\mathbf{r}))\rangle \qquad (10)$$

TABLE II

Dipole-dipole association parameters

	Dimer dipole moments		Dimer association constants	
Mesogen	μ_a/μ_m	μ_p/μ_m	K_a	K_p
CB5	0.0	2.0	(a) 2.65 ± 0.12	0.38 ± 0.02
			(b) 1.79 ± 0.08	0.22 ± 0.01
CCH5	0.0	2.0	(a) 0.85 ± 0.10	0.09 ± 0.01
C4CN	0.42	2.0	(a) 7.86 ± 0.82	2.70 ± 0.28
			(b) 7.21 ± 0.75	1.93 ± 0.20
C3FCN	0.61	1.9	(a) 10.60 ± 2.20	4.75 ± 0.98
CCN55	0.0	2.0	(a) 0.92 ± 0.06	3.79 ± 0.23

(a) *p*-xylene solution
(b) PCH32 solution

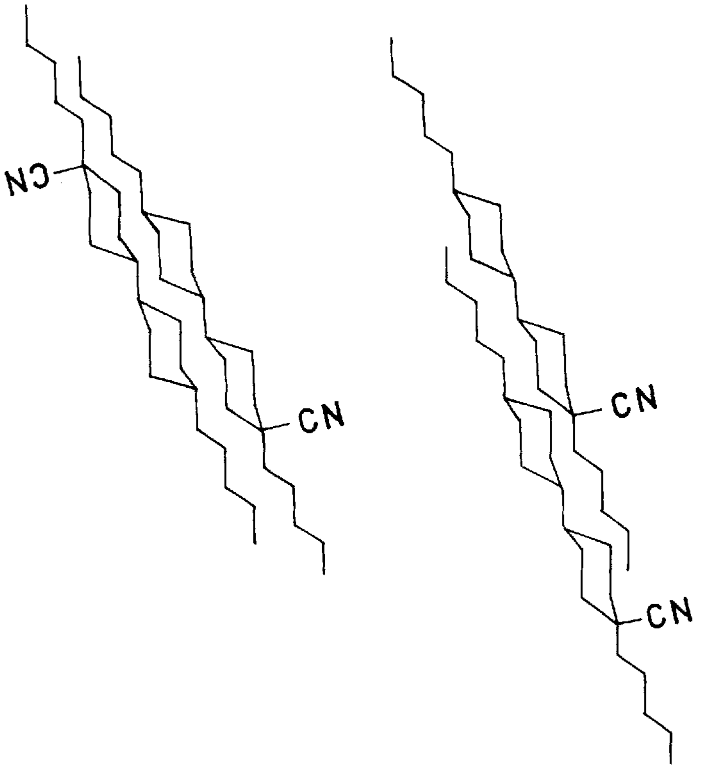


FIGURE 2 Proposed structures for parallel and anti-parallel dimers of CCN55.

$P_2(\cos\theta(\mathbf{r}))$ is the second Legendre polynomial evaluated at point $\mathbf{r}$ in the fluid for a particular molecular axis making an angle θ with a laboratory fixed direction. This correlation function may be written[35] as an exponential function of distance such that:

$$G_2(\mathbf{r}) = \frac{\text{const}}{r} \cdot \exp - r/\xi \qquad (11)$$

where ξ is a coherence length. Integrating over a macroscopic volume gives the quadrupole correlation factor g_2, and a relation between g_2 and the coherence length:

$$g_2 = \frac{1}{V}\int G_2(\mathbf{r})d\mathbf{r} = 1 + \sum_{j \neq 1} \langle P_2(\cos\theta_{1j})\rangle = \text{const} \cdot \xi^2 \qquad (12)$$

Values of g_2 and ξ have been measured[28–30] for a few mesogens: both diverge as the nematic/isotropic temperature is approached from above, and at temperatures close to T_{NI}, $g_2 \sim 100$ and $\xi \sim 100\text{Å}$, indicating a substantial degree of apolar orientational correlation which undoubtedly persists in the nematic phase. The most direct probe of g_2 is depolarised light scattering, the intensity of which (I_{VH}) is related to the quadrupolar correlation factor by:[36]

$$I_{\mathrm{VH}} = \frac{\text{const}\ N(\Delta\alpha)^2}{\lambda^4}\left(\frac{n^2+2}{3}\right)^4\left(\frac{\gamma}{\Delta\alpha}\right)^2 g_2 \qquad (13)$$

$\Delta\alpha$ is the isolated molecule polarisability anisotropy, while γ is the effective anisotropy of a molecule interacting with its environment: γ takes account of the local structure of the fluid. Corrections due to the internal field are accounted for by $((n^2 + 2)/3)^4$, and the constant in Eq. (13) includes geometrical factors related to the scattering angle and scattering volume. For parallel or anti-parallel correlation of molecules g_2 is greater than one, but if molecules prefer to align mutually perpendicular then g_2 becomes less than one. This situation may be realised in binary mixtures of rod-like and plate-like mesogens.[37,38]

Measurements of the depolarised scattered light intensity from solutions of associating molecules in an isotropic solvent can in principle be used to obtain values for g_2. However there are complications in the analysis of these measurements because the polarisability anisotropy of a solute molecule may be considerably influenced by interactions with isotropic solute molecules. In our analysis we use the results of the theory of Keyes and Ladanyi,[39,40] which gives:

$$I_{VH} = \frac{\text{const }(\Delta\alpha_2)^2}{\lambda^4}\left(\frac{n^2+2}{3}\right)^4 g_2 N_2 \left(\frac{\gamma_2}{\Delta\alpha_2}\right)^2 \tag{14}$$

where $\gamma_2/\Delta\alpha_2 = 1 + L/\Delta\alpha_2$, and

$$L = \frac{6\tau_{20}}{20\pi\epsilon_0}\left[N_1\left(\alpha_1\alpha_2 + \frac{1}{3}\alpha_1\Delta\alpha_2\right) + N_2\left(\alpha_2^2 + \frac{1}{3}\alpha_2\Delta\alpha_2 + \frac{2}{9}\Delta\alpha_2^2\right)\right] \tag{15}$$

α_1 is the mean polarisability of the solvent, α_2 and $\Delta\alpha_2$ are the polarisability and polarisability anisotropy of the solute molecule. The quantity τ_{20} takes account of the polarisation of a solute molecule due to a non-spherical shell of solvent/solute neighbours. Assuming that the solute cavity may be represented as an ellipsoid of revolution whose volume is equal to the solute molecular volume, then:

$$\tau_{20} = \frac{10\pi\delta}{3} \tag{16}$$

where δ is the anisotropy in the depolarisation factor for an ellipsoid.

Since the measurement of absolute intensities is difficult, values for g_2 are obtained from Eq. (14) by extrapolation to zero solute concentration using:

$$g_2 = \left[\frac{I_{VH}}{\left(\frac{n^2+2}{3}\right)^4 N_2\left(\frac{\gamma_2}{\Delta\alpha_2}\right)^2}\right] \Bigg/ \lim_{N_2\to 0}\left[\frac{I_{VH}}{\left(\frac{n^2+2}{3}\right)^4 N_2\left(\frac{\gamma_2}{\Delta\alpha_2}\right)^2}\right] \tag{17}$$

3.2. Light scattering measurements

Measurements of the depolarised light scattered by solutions of mesogens in carbon tetrachloride were made using a Malvern Instruments Light Scattering Spectrometer with a He–Ne laser light source (λ = 633 nm). All measurements were made at a temperature of 23.0 ± 0.1°C: refractive indices of the solutions were also measured at the same temperature to obtain the local field correction. Results for the scattered intensity from solutions of CB5 and CCH5 are given in Figure 3. In order to derive values for g_2 from the intensities, the effective polarisability factors L had to be calculated using Eq. (15), and values for the free molecule mean polarisabilities and polarisability anisotropies of the solvent and solute molecules.[13] The derived values for the quadrupolar correlation factor are plotted in Figure 4, where it is seen that at low concentrations the correlation of CCH5 molecules is less than that of CB5 molecules. This result is consistent with the conclusions of the dielectric measurements and lends some support to our theory of polar/apolar association in these systems. At concentrations of CCH5 greater than 0.25 mole fraction the light

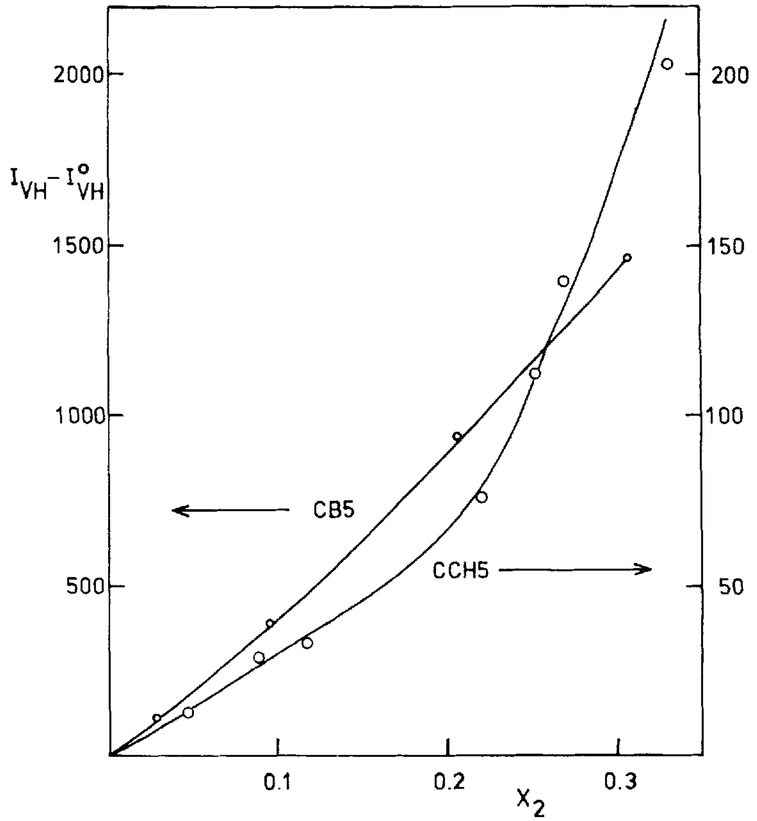


FIGURE 3 Depolarised scattered light intensities (in arbitrary units) for solutions of CB5 and CCH5.

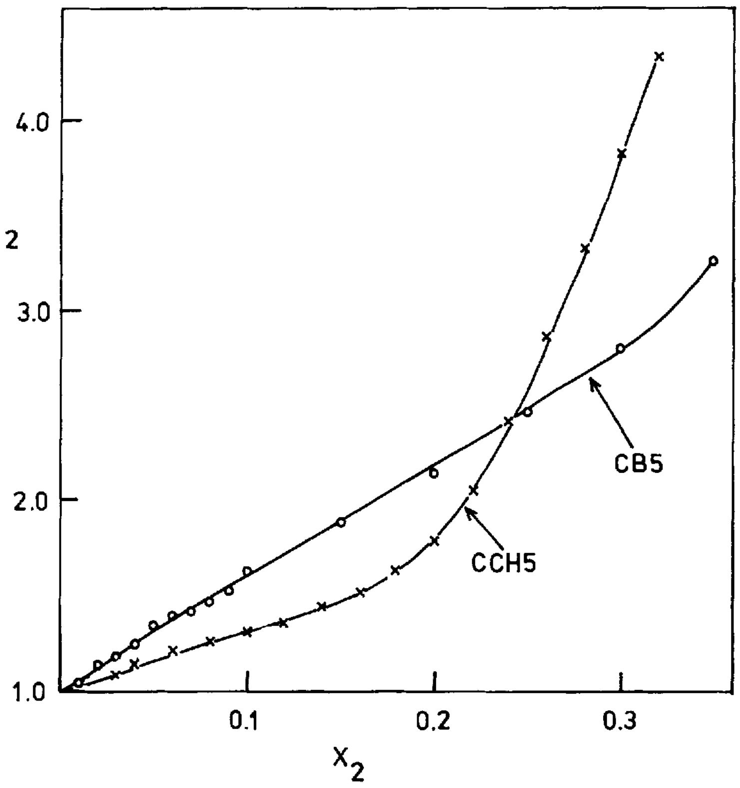


FIGURE 4 Quadrupolar correlation factors g_2 as a function of mole fraction for solutions of CB5 and CCH5.

scattering intensity increases rapidly indicating clustering of molecules: our theory as presently constituted only allows for dimerisation and cannot therefore account for the rapid increase in g_2.

IV. APPLICATION TO BINARY SYSTEMS OF POSITIVE AND NEGATIVE NEMATOGENS

As explained in the introduction systems of Np molecules as guests in Nn hosts have been investigated as device mixtures.[24,26,27] Among many types of Np molecules such as cyanobiphenyls (CBn), cyano cyclohexyl benzenes (PCHn), 4-cyano benzene-4′*n*-alkylbenzoates (CnCN) and others, we have found that 4-cyano-3 fluorophenyl-4′*n*-alkylbenzoates (CnFCN) have low threshold voltages and very little temperature dependence of the threshold in Np + Nn mixtures.[27] From our studies of Np nematogens it is evident that in non-polar solvents such as xylene Np molecules undergo polar and apolar association leading to parallel and anti-parallel ordering of molecular dipoles. We have also found that there are substantial differences between the association behaviour of different cyanonematogens, dependent on their molecular shape and polarisabilities.

In an attempt to extend our ideas to mixtures of positive and negative nematogens, we have simulated the binary mesophase systems by investigating a cyanonematogen solute (Np) in 4-trans-(4-propyl) cyclohexylethylbenzene (PCH32) solvent which acts like an Nn host. Figure 5 gives experimental values of the Kirkwood correlation factor g_1 of CB5 in both *p*-xylene and PCH32 solvents as a function of CB5 mole fraction. Apparently the association in the Nn

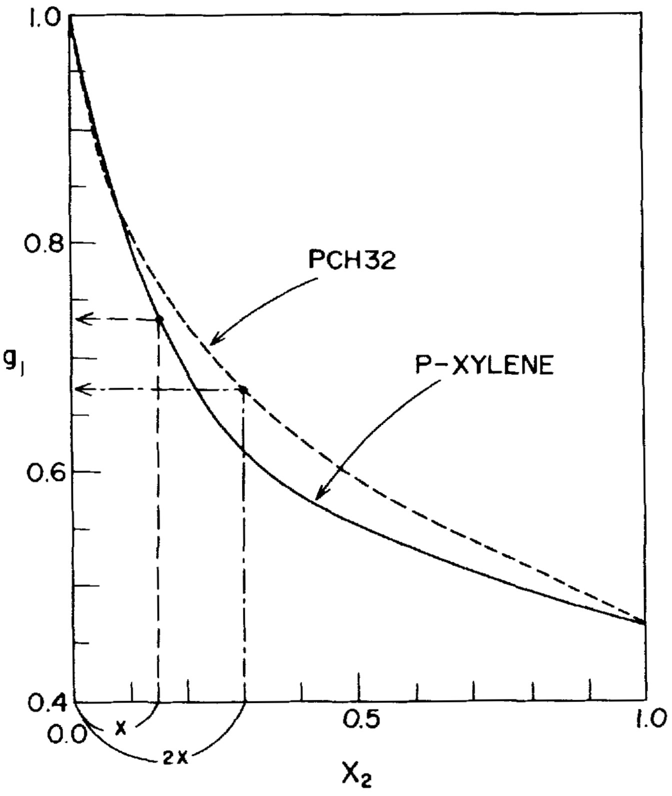


FIGURE 5 Dipole correlation factors as a function of solute (CB5) mole fraction in solvents *p*-xylene and PCH32.

solvent is less, but it must be remembered that the PCH32 solvent molecule has nearly twice as large a molecular volume as compared to the *p*-xylene molecule. As illustrated in Figure 6, one PCH32 molecule may correspond to two *p*-xylene molecules with respect to the occupation of host molecule sites surrounding a solute molecule. That is to say a mole fraction of x of solute in *p*-xylene solution may be equivalent to a mole fraction $2x$ of solute in PCH32 solution, at least to a first degree of approximation in moderately dilute solutions. This may explain the apparent difference in g_1 dependence on mole fraction for *p*-xylene and PCH32 solvents as shown in Figure 5. If we go a step further, we expect one PCH32 solvent molecule to act as a solvating shell as effectively as two *p*-xylene molecules, therefore in Figure 7 the g_1 values for CB5 are plotted as a function of volume fraction of solute. On this basis we conclude that CB5 molecules correlate more strongly in PCH32 solvent than in *p*-xylene. A similar behaviour was observed for C4CN solute molecules, as shown in Figure 8. By fitting the g_1 results to Eqs. (7) and (8) we can obtain some quantitative measure of the change in association, expressed as equilibrium constants in Table II.

From the above experiments it can be concluded that cyanonematogens (Np) associate strongly in the non-polar nematogenic solvent (Nn) in the isotropic and presumably nematic state. The molecule C3FCN is particularly effective as an Np guest in an Nn host presumably because of its strong tendency to associate as indicated in Section 2. Studies of the electro-optic properties of binary nematogenic systems of Np plus Nn (Table III) show that with C3FCN at fairly high concentrations (0.25 weight fraction) the temperature dependence of the threshold 1/V (dV/dT) is small compared with other Np materials such as CB5 and C4CN. This may be attributed to the very high association constants found for C3FCN. There is of course a problem in interpreting the results at high concentrations in terms of a dimer model. Light scattering studies reported here show that Np materials tend to form clusters in non-polar solvents at moderate concentrations, and allowing for these many body effects in explaining the temperature dependence of the threshold voltage in binary systems of Np and Nn nematogens is likely to be difficult.

V. CONCLUSIONS

In this paper we have presented a review of molecular association in some nematogenic systems, and have attempted to show how studies

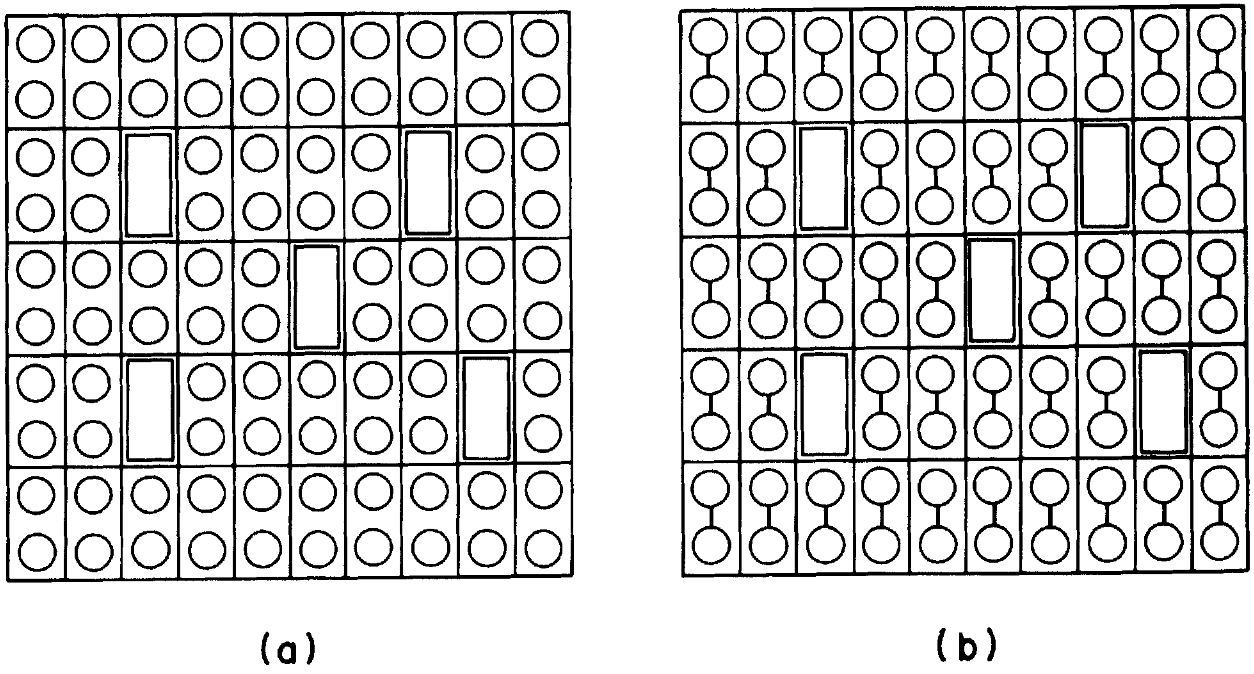


FIGURE 6 Solvation by (a) *p*-xylene and (b) PCH32 illustrating the effect of solvent molecular volume on the solute mole fraction.

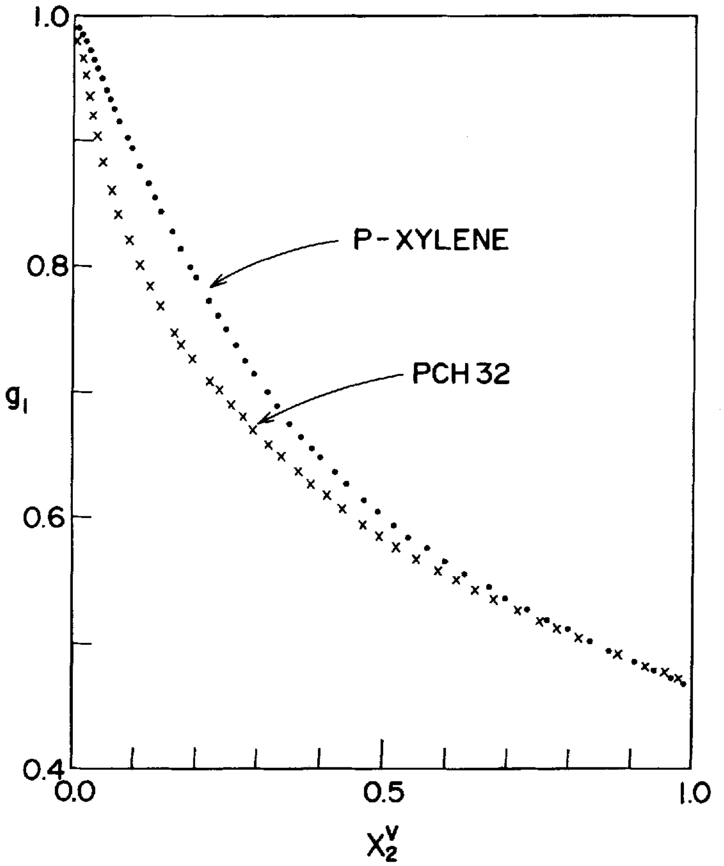


FIGURE 7 Dipole correlation factors as a function of solute (CB5) volume fraction (x_2^v) in solvents *p*-xylene and PCH32.

of molecular interactions may be used to understand the physical characteristics of device mixtures. Molecular correlation may be measured in terms of the dipolar correlation factor g_1 and the quadrupolar correlation factor g_2. In Section 2 we have reported measurements of the Kirkwood correlation factor g_1 for solutions of polar nematic liquid crystals which consist of molecules with the strong polar cyano- end group. These experimental results have been interpreted in terms of polar and apolar association between molecules leading to both parallel and anti-parallel ordering of molecular dipoles in mesogenic solutions. Furthermore it was found that there are substantial differences between the association behaviour of different polar mesogens, dependent on the molecular shape and polarisability.

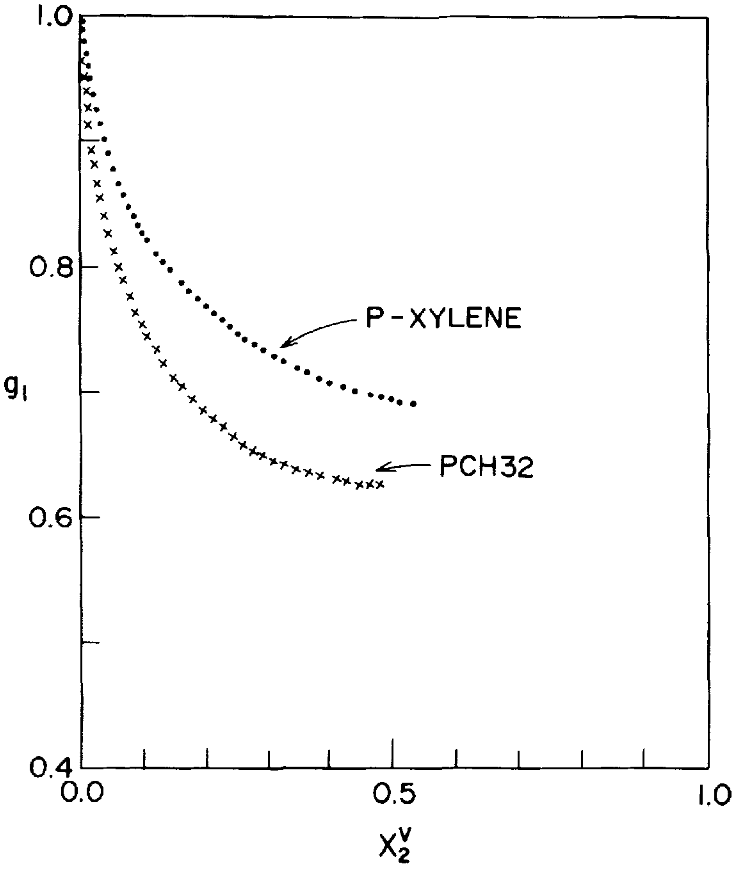


FIGURE 8 Dipole correlation factors as a function of solute (C4CN) volume fraction in solvents *p*-xylene and PCH32.

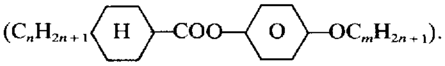
To confirm the importance of apolar association of mesogens, we have applied the theory of Keyes and Ladanyi[39] of depolarised light scattering to obtain measurement of g_2 from light scattering intensity measurements of mesogenic solutions. Results are given for two typical polar nematogens, CB5 and CCH5, and we find that there is less angular correlation between CCH5 molecules at low concentrations than between CB5 molecules. Dielectric measurements also show that association occurs at lower concentrations in CB5 solutions than in CCH5 solutions. From these measurements we conclude that there are about ten times more anti-parallel dimers present than parallel dimers. More polar molecules like C4CN and C3FCN show stronger correlation, with different proportions of parallel and anti-parallel

TABLE III

Temperature dependence ΔV^{T}[a] of threshold voltage for various N_p (guest) plus a N_n[b] (host) mixed systems

wt % / N_p material	10	20	30
CBn	4.5 (105°C)[c]	6.1 (93°C)	6.7 (84°C)
CnCN	3.8 (104°C)	4.5 (96°C)	5.4 (89°C)
CnFCN	3.5 (100°C)	3.0 (89°C)	3.0 (80°C)

[a] ΔV^{T} is defined as $\Delta V^{T} = \{(V_{\text{th, 0°C}} - V_{\text{th, 40°C}})/(V_{\text{th, 0°C}} + V_{\text{th, 40°C}})\} \times 100$

[b] The host Nn material consists of homologous members of cyclohexane carboxylic acid phenylesters ().

[c] Values in parentheses are nematic-isotropic transition temperatures.

dimers. Of particular interest is the behaviour of the Nn material CCN55, which has a strong association with parallel dipole dimers predominating.

In Section 4 we have applied our ideas of association to a model binary system of a polar nematogen (Np) and non-polar nematogen (Nn). We have found that in PCH32 both CB5 and C4CN molecules associate strongly, more so than in *p*-xylene if allowance is made for the differences in solute molecular volumes. The strong tendency of C3FCN molecules to associate, as shown by our dielectric results, leads to good display performance of mixtures of C3FCN (Np) in Nn hosts, as illustrated by the temperature dependence of the threshold voltage.

It is hoped that further studies along the lines indicated in this paper on many more systems will provide further evidence for the importance of both polar and apolar molecular association is determining the properties of LCD mixtures.

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