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Light scattering and dielectric studies of molecular association in mesogenic solutions

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Results are reported of light scattering and dielectric measurements on solutions of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-pentyl-4′-cyanobicyclohexane (5CCH). Correlation factors g_1 and g_2 are deduced from the measurements, and are discussed in terms of a model for molecular association. It is concluded that at low concentrations the association between 5CB molecules is substantially greater than that between 5CCH molecules.

1. Introduction

The formation of orientationally ordered mesophases is a direct result of anisotropic intermolecular forces, but to make the connection between the thermodynamic properties of liquid crystal mesophases and the properties of mesogenic molecules remains a formidable problem. In a formal sense the anisotropic interactions can be categorized as electrostatic, dispersion and hard core repulsive forces, and it is generally accepted [1, 2] that coupling between the latter two is largely responsible for the formation of thermotropic nematic liquid crystals. Other factors such as molecular flexibility and the distribution of interaction centres within a molecule are also important and add to the complexity of the problem. One firm conclusion that has emerged from studies of the mesophase properties of many different types, is that relatively small changes in molecular structure can lead to dramatic changes in the liquid crystal phase behaviour [3, 4].

Since intermolecular forces are responsible for liquid crystal phase formation, the study of molecular interactions, associations and correlations will provide the key to understanding the properties of liquid crystals. The highly successful molecular field theory of nematic liquid crystals due to Maier and Saupe replaces specific molecule–molecule interactions by an average pseudo-potential, which can be suitably scaled to give a fair description of single particle properties in nematics. Various theoretical approaches [5, 6] have been developed to take account of specific molecular interactions in the statistical theory of liquid crystals, but it is usually difficult to test these experimentally. A novel description of molecular correlation in nematics has been proposed by Faber [7], based on his fluctuation theory of liquid crystals, which compares well with the results of computer simulation experiments [8].

Experimental probes of molecular correlation in liquid crystals tend to be rather indirect. X-ray measurements on both smectic and nematic mesophases show local translational order [9], while long range angular correlations over many molecular diameters result in relatively large differential scattering cross sections for visible light

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[10]; the characteristic torsional elastic properties of liquid crystals are also due to long range angular correlations. Dielectric properties of some polar nematic liquid crystals have been interpreted in terms of anti-parallel molecular association [11], which has also been invoked to explain certain elastic properties of materials [12] and re-entrant phase behaviour [13]. By studying the properties of solutions of mesogenic molecules over a range of concentrations, it is possible to obtain information on the progressive association of molecules and its effect on physical properties. In many cases the liquid crystal phase is anticipated by the properties of an isotropic solution, for example through anomalous light scattering intensity [14, 15] or electric birefringence [16], and so measurements on solutions can be expected to provide valuable information on the formation of the orientationally ordered mesophase. An earlier paper ([17]—hereafter referred to as I) introduced a new model for molecular association, which was used to explain the dielectric properties of mesogenic solutions. This model postulated the existence of parallel and anti-parallel dimers in such solutions, and it was suggested that the relative concentrations of these dimers reflected the importance of polar/apolar association. By restricting attention to pairwise association the model is limited to describing the properties of relatively dilute solutions, however a clear understanding of the differences between mesogenic and non-mesogenic solutions should aid the development of theories of the ordered mesophase. In this paper new measurements are presented for the depolarized light scattering from solutions of two liquid crystals, and values are derived for the quadrupolar correlation factor g_2. These results are discussed in terms of our model for molecular association, and compared with earlier results for the dipolar correlation factor g_1.

2. Theoretical background

There is an extensive literature on the effects of molecular association on various physical properties. However the association that is believed to be important in liquid crystal mesophases is of a particular type. Since these phases are characterized by correlation of molecular orientations over long distances, we wish to consider the extent to which interacting molecules are mutually aligned. We shall restrict attention to pair correlations, and so the results of this treatment will only be strictly valid for relatively dilute solutions: clearly many-body cooperative interactions are important in determining the behaviour of pure mesophases.

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

$$\begin{aligned} G_1(\mathbf{r}) &= \frac{\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(\mathbf{r})\rangle}{\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(0)\rangle}, \\ &= \langle P_1[\cos\theta(\mathbf{r})]\rangle; \end{aligned} \tag{1}$$

here $\boldsymbol{\mu}(\mathbf{r})$ is the dipole moment of a molecule at position $\mathbf{r}$ within the fluid and the angular brackets denote an ensemble average. Integration of $G_1(\mathbf{r})$ over a macroscopic volume gives the Kirkwood correlation factor g_1 as

$$\begin{aligned} g_1 &= V^{-1}\int G_1(\mathbf{r})\,d\mathbf{r}, \\ &= 1 + \sum_{j\neq 1}\langle P_1(\cos\theta_{1j})\rangle, \end{aligned} \tag{2}$$

where θ_{1j} is the instantaneous angle between two interacting dipoles on molecules 1 and j. The permittivity of an isotropic liquid is related to g_1 by [18]

$$g_1\mu^2 = \frac{9\varepsilon_0 kT}{N}\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} \tag{3}$$

where ε is the relative permittivity, n is the refractive index, N is the molecular number density and μ is the free-molecule dipole moment. The correlation function $G_1(\mathbf{r})$ is an odd function of the angle between interacting molecules, and anti-parallel ordering of molecular dipoles results in values of $g_1 < 1$.

A measure of the correlation of molecular axes independent of dipole direction is given by the correlation function $G_2(\mathbf{r})$

$$G_2(\mathbf{r}) = \langle P_2[\cos\theta(0)]\,P_2[\cos\theta(\mathbf{r})]\rangle; \tag{4}$$

$P_2[\cos\theta(\mathbf{r})]$ is the second Legendre polynomial evaluated at point $\mathbf{r}$ in the fluid for a particular molecular axis making an angle of θ with a laboratory fixed direction. The integral of $G_2(\mathbf{r})$ over a macroscopic volume gives the correlation factor g_2

$$\begin{aligned} g_2 &= V^{-1}\int G_2(\mathbf{r})\,d\mathbf{r}, \\ &= 1 + \sum_{j\neq 1}\langle P_2(\cos\theta_{1j})\rangle. \end{aligned} \tag{5}$$

The most direct experimental route to g_2 is to measure the intensity or narrow Rayleigh spectrum of depolarized light scattered by an isotropic fluid. The relationship between the depolarized intensity (I_{VH}) and the correlation factor for axially symmetric molecules is [19]

$$I_{\mathrm{VH}} = \frac{\text{const.}\ N(\Delta\alpha)^2}{\lambda^4}\left(\frac{n^2 + 2}{3}\right)^4\left(\frac{\gamma}{\Delta\alpha}\right)^2 g_2. \tag{6}$$

In equation (6) $\Delta\alpha$ is the isolated-molecule polarizability anisotropy, while γ is the effective anisotropy of a molecule interacting with its environment. The constant includes geometrical factors related to the scattering angle, the size of the scattering volume and the distance from the scattering volume to the detector. Various models have been considered for γ, and its importance is that it relates to the local structure of the fluid. Corrections due to the internal field are taken account of by the term $[(n^2 + 2)/3]^4$, which is based on the Lorentz model. Expressions (3) and (6) that relate g_1 and g_2 to experimental quantities are for pure fluids, and require modification to describe solutions and associating systems, but before dealing with that aspect of the problem a model for the association of mesogenic molecules in solution will be discussed.

In I we have outlined a model for dipole association based on the assumption that both parallel and anti-parallel correlation of molecular axes may occur in solutions of mesogenic molecules. Restricting our attention to dimer formation we have the equilibria

$$2M \rightleftharpoons M_{2\mathrm{a}}, \quad 2M \rightleftharpoons M_{2\mathrm{p}}, \tag{7}$$

with equilibrium constants K_{a} and K_{p} for anti-parallel and parallel dimers respectively. Defining the equilibrium constants in terms of mole fractions, we can relate the concentrations of monomer (x_m) parallel (x_p) and anti-parallel (x_a) dimers by

$$x_m = \frac{[1 + 4x_2(2 - x_2)(K_a + K_p)]^{1/2} - 1}{2(2 - x_2)(K_a + K_p)}, \tag{8}$$

with $K_a = x_a/x_m^2$, $K_p = x_p/x_m^2$ and x_2 is the total solute mole fraction.

For a solution of polar molecules in a non-polar solvent g_1 is given by [18, p. 261]

$$g_1 = \frac{9kT\varepsilon_0(2\varepsilon + n^2)^2}{\mu^2 N_A x_2(n^2 + 2)^2(2\varepsilon + 1)}\left\{\frac{\varepsilon - 1}{\varepsilon}\left[\frac{x_1 M_1 + x_2 M_2}{d}\right] - \frac{3x_1 M_1(\varepsilon_1 - 1)}{d_1(2\varepsilon + \varepsilon_1)} - \frac{3x_2 M_2(n^2 - 1)}{d_1(2\varepsilon + n^2)}\right\}. \tag{9}$$

Here ε, d and n^2 are the permittivity, density and refractive index of the solution respectively, 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. If there are a number of solute multimers (k) present, then g_1 may be defined as [20]

$$g_1 = \mu_m^{-2} \sum_k N_k \mu_k^2 \Big/ \sum_k N_k \tag{10}$$

and for a system containing monomers, parallel and anti-parallel dimers, equation (7) becomes

$$g_1^{\text{calc}} = [x_2(1 + x_a + x_p)]^{-1}\left[x_m + x_a\left(\frac{\mu_a}{\mu_m}\right)^2 + x_p\left(\frac{\mu_p}{\mu_m}\right)^2\right]. \tag{11}$$

Knowing the relative concentrations of the monomer and associated species together with their dipole moments it is therefore possible to calculate g_1. Alternatively measured values of g_1 obtained from equation (9) for a range of concentrations may be fitted to equation (11) and the equilibrium constants K_a and K_p can be determined.

The influence of molecular association on the angular correlation factor g_2 can be obtained, in principle, from measurements of the intensity of depolarized light scattered by solutions of anisotropic molecules in an isotropic solvent. There are, however, complications in the analysis of these measurements because the polarizability of a molecule is considerably influenced by interactions with its neighbours, even if they are optically isotropic. This particular situation was analysed in detail by Keyes and Ladanyi [21]; they concluded that for a two component system of an anisotropic solute in a solvent of isotropic molecules, the depolarized scattered intensity can be written as

$$I_{VH} = \frac{\text{const.}\ (\Delta\alpha_2)^2}{\lambda^4}\left(\frac{n^2 + 2}{3}\right)^4 g_2 N_2 \left(\frac{\gamma_2}{\Delta\alpha_2}\right)^2, \tag{12}$$

where

$$\frac{\gamma_2}{\Delta\alpha_2} = 1 + \frac{L}{\Delta\alpha_2}$$

and

$$L = \frac{6}{5}\left[N_1(\alpha_1\alpha_2 + \tfrac{1}{3}\alpha_1\Delta\alpha_2)\,\tau_{20}^{(2,1)} + N_2\left((\alpha_2^2 + \tfrac{1}{3}\alpha_2\Delta\alpha_2 + \tfrac{2}{9}\Delta\alpha_2^2)\,\tau_{20}^{(2,2)} - \frac{1}{15}\left(\alpha_2\Delta\alpha_2 + \frac{\Delta\alpha_2^2}{3}\right)\tau_{22}^{(2,2)}\right)\right]\Big/ 4\pi\varepsilon_0, \tag{13}$$

α_1, α_2 and $\Delta\alpha_2$ are the polarizabilities and polarizability anisotropy of the solvent (1) and solute (2) species. The quantities $\tau_{20}^{(i,j)}$ and $\tau_{22}^{(i,j)}$ take account of the polarization of a central molecule due to the angular dependence of the radial distribution function of its neighbours. For example $\tau_{20}^{(2,1)}$ describes the polarization of an anisotropic solute molecule in a cavity of isotropic solvent molecules; if the central molecule is assumed to do nothing but exclude solvent molecules from an ellipsoidal molecular volume then,

$$\tau_{20}^{(2,1)} = \frac{10\pi\delta}{3}, \tag{14}$$

where δ is the anisotropy in the depolarization factor for an ellipsoid. The dimensions of the ellipsoid will depend on the shape and size of the anisotropic solute molecule. The coefficient $\tau_{22}^{(2,2)}$ results from interactions between two anisotropic solute molecules giving rise to anisotropy in the radial distribution; it vanishes at infinite dilution and will be neglected in our calculations. Equations (12) and (13) together with values for the solution concentration and refractive index and molecular polarizabilities for solute and solvent permit the calculation of the angular correlation factor g_2 from measured intensities of the depolarized scattered light.

Our model for molecular association postulates the existence of parallel and anti-parallel dimers of anisotropic solute molecules in the solution. These will contribute to the scattered light intensity, and we wish to relate the concentration and polarizabilities of these dimers to the g_2 value calculated from equation (12). This is a difficult problem because light scattering probes the properties of molecules *and* the correlations between them. However in moderately dilute solutions as a first approximation we may treat separately the contributions of different species to the scattered light intensity and write

$$I_{\mathrm{VH}} = \frac{\text{const.}}{\lambda^4}\left(\frac{n^2+2}{3}\right)^4 \sum_K N_k(\Delta\alpha_k)^2\left(\frac{\gamma_k}{\Delta\alpha_k}\right)^2, \tag{15}$$

where γ_k is the effective polarizability anisotropy for species k in solution. To proceed, a model has to be adopted for the different associated molecular species present in solution, i.e. anti-parallel dimers and parallel dimers. Simple additivity would suggest that the polarizability anisotropy of a dimer is twice that of the monomer, but a more realistic estimate which takes account of the structure of the dimers could be obtained from a dipole–dipole calculation based on the Silberstein model [22]. Comparison of equations (12) and (15) leads to an expression for a calculated g_2^{calc} for the association model, such that

$$g_2^{\text{calc}} = \sum_k N_k(\Delta\alpha_k)^2\left(\frac{\gamma_k}{\Delta\alpha_k}\right)^2 \Big/ N_2\left[1+\frac{L}{\Delta\alpha_2}\right]^2(\Delta\alpha_2)^2. \tag{16}$$

Although a simple model for dimer polarizabilities can be constructed, the effect of association on the solute–solute interactions and the effective polarizability is not yet understood. In order to compare theory with experimental results we assume that $\gamma_k/\Delta\alpha_k$ is the same for all species present, so that the correlation factor g_2 is determined only by the number densities of the multimers.

3. Results

3.1. *Dielectric measurements*

The dipole correlation factors g_1 for 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-pentyl-4′-cyanobicyclohexane (5CCH) were obtained from measurements of the electric permittivity, refractive indices at 633 nm and densities of solutions in *p*-xylene. All measurements were made at 25·0 ± 0·3°C, and details of our experimental techniques are given in an earlier paper [23]. Values for g_1 at different concentrations are obtained from equation (9), and the free-molecule dipole moment, μ, can be found by extrapolation to low concentrations when g_1 is equal to 1. Results are given in table 1 and figure 1; a noteworthy feature is that $g_1 < 1$ for both materials, consistent with predominant anti-parallel association, but the more dipolar mesogen (5CB) shows significant association at low concentrations, while for 5CCH the association develops more slowly as the concentration increases. The full line in figure 1 is obtained by fitting the experimental values for g_1 to equation (11), setting $\mu_a/\mu_m = 0$ and $\mu_p/\mu_m = 2$; the best fit values for the dipole correlation factors are also listed in table 1.

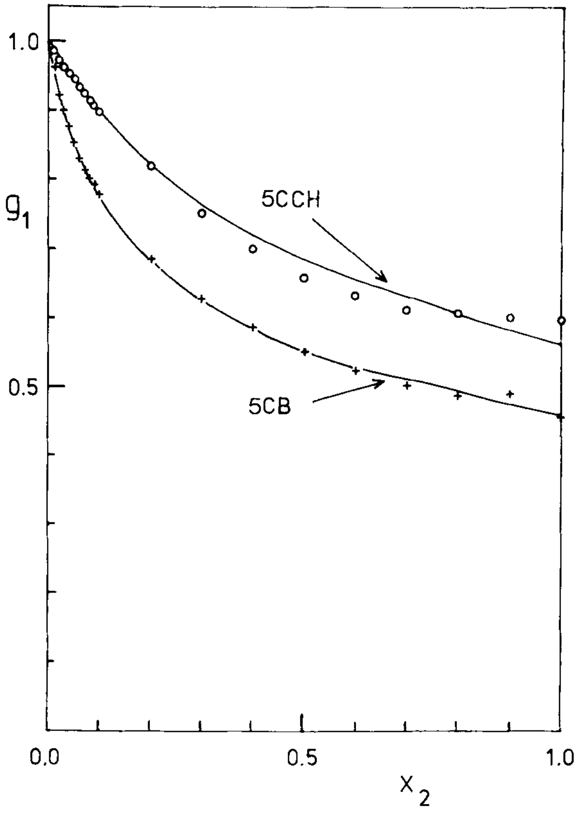


Figure 1. Dipole correlation factors as a function of solute concentration x_2. Experimental points are marked, the full lines are the best fit to equation (11).

3.2. *Light scattering measurements*

The intensity of depolarized light scattered by solutions of mesogens was measured using a Malvern Instruments light scattering spectrometer. Measurements

Table 1. Dipole correlation factors.

Mole fraction in *p*-xylene	5CB		5CCH	
	Calculated	Experimental	Calculated	Experimental
0·02	0·93	0·92	0·97	0·97
0·04	0·87	0·88	0·95	0·96
0·06	0·83	0·83	0·93	0·94
0·08	0·80	0·80	0·91	0·92
0·10	0·78	0·78	0·89	0·90
0·20	0·69	0·69	0·82	0·82
0·30	0·63	0·63	0·76	0·75
0·40	0·59	0·59	0·72	0·70
0·50	0·56	0·55	0·69	0·66
0·60	0·53	0·52	0·66	0·64
0·70	0·51	0·51	0·63	0·62
0·80	0·49	0·49	0·61	0·61
0·90	0·47	0·49	0·49	0·60
1·00	0·46	0·46	0·57	0·60

were normalized with respect to the incident laser power ($\lambda = 633\,\mathrm{nm}$), and all intensities were measured with a type K8023 photon counter. A 90° scattering geometry was used, and computer control of the experiment caused the detector to measure the polarized and depolarized scattered intensities consecutively. When making measurements a large number of data points were accumulated and subjected to statistical analysis so any non-random fluctuations in the scattered light intensity were eliminated. In spite of the large polarizability anisotropies of the mesogenic molecules studied, their dilute solutions scattered only weakly and so it was necessary to minimize scattering from the solvent. For this reason carbon tetrachloride was chosen as solvent, which has a very low depolarization ratio. In order to carry out the analysis according to the theory given in the previous section, it was also necessary to measure the refractive indices and densities of the solutions; all measurements were made at 23·0 ± 0·1°C. Results for the depolarized light scattering intensity (in arbitrary units) for solutions of 5CB and 5CCH are given in figure 2.

The correlation factor g_2 for a particular solution concentration (solute number density N_2) can be obtained from

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

but to evaluate this expression requires a knowledge of the free-molecule and effective polarizability anisotropies, $\Delta\alpha_2$ and γ_2. The former has been obtained from measurements of the Kerr effect in dilute solution [4], while γ_2 can be calculated from equation (13) using the approximate equation (14) for $\tau_{20}^{(2,1)}$. In the absence of absolute intensity measurements it is not possible to obtain the free-molecule polarizability anisotropy from I_{VH}, hence the need to rely on electric birefringence measurements. However by comparing the results for two mesogens, we can obtain a self-consistency requirement for the ratio of the free-molecule polarizability anisotropies

$$\left(\frac{\Delta\alpha_2^{\mathrm{I}}}{\Delta\alpha_2^{\mathrm{II}}}\right)^2 = \lim_{N_2 \to 0} \left[\frac{I_{\mathrm{VH}}}{(n^2 + 2/3)^4 N_2 (\gamma_2/\Delta\alpha_2)^2}\right]^{\mathrm{I}} \Bigg/ \lim_{N_2 \to 0} \left[\frac{I_{\mathrm{VH}}}{(n^2 + 2/3)^4 N_2 (\gamma_2/\Delta\alpha_2)^2}\right]^{\mathrm{II}}; \qquad (18)$$

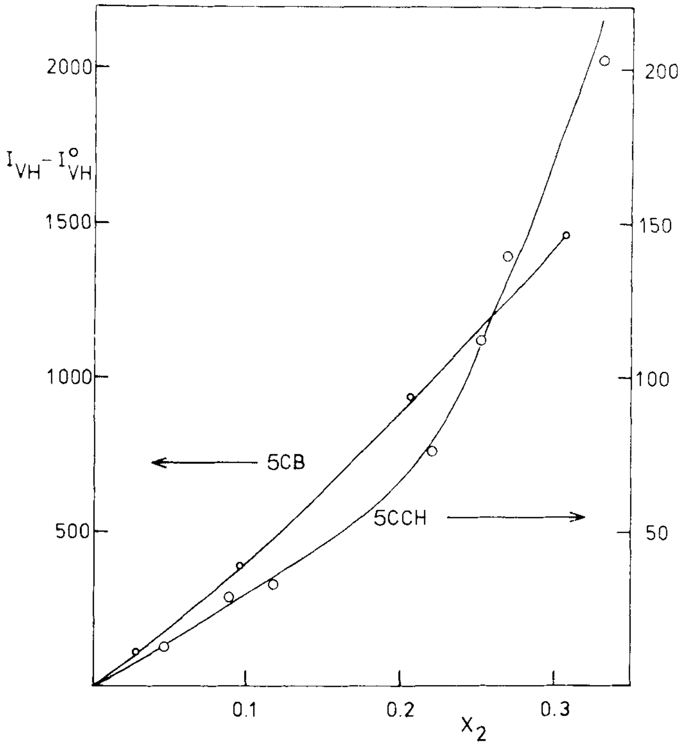


Figure 2. Depolarized scattered intensities (in arbitrary units) as a function of solute concentration x_2; I^0_{VH} is the residual depolarized scattering of the pure solvent.

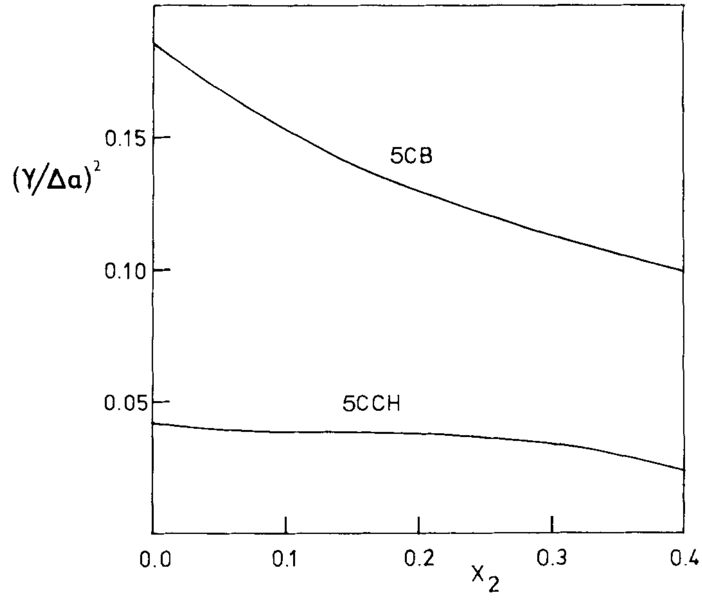
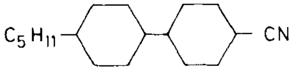
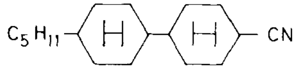


Figure 3. The square of the effective polarizability anisotropy from equation (13) as a function of solute concentration.

Table 2. Molecular properties.

	Mean polarizability $10^{-40}J^{-1}C^2m^2$	Polarizability anisotropy $10^{-40}J^{-1}C^2m^2$	Dipole moment $10^{-30}Cm$	Shape anisotropy (a/b)†
 5CB	37·5	20·2‡	15·9	2·7
 5CCH	35·5	12·1‡	12·6	2·6
Solvent (CCl_4)	11·7	—	—	

† Calculated (assuming an ellipsoidal shape) from molecular lengths for 5CB and 5CCH of 18 Å and measured molar volumes.

‡ These values have been corrected from our earlier paper [4] to satisfy the self-consistency relation (equation 19). The new values are within the error limits previously quoted.

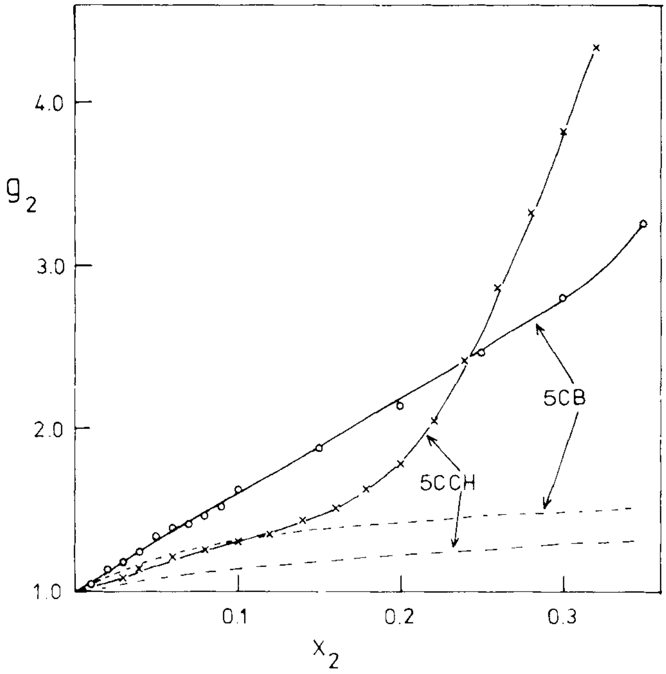


Figure 4. Correlation factors g_2 as a function of solute concentration x_2. Full lines are experimental results, broken lines are calculated from monomer/dimer concentrations.

this ratio must equal the ratio of anisotropies used in the calculation of L^{I} and L^{II} from equation (13).

Calculated values for $(\gamma_2/\Delta\alpha_2)^2$ are plotted as a function of solute concentration in figure 3; the molecular parameters used are listed in table 2. It is clear that the

Table 3. Experimental g_2.

Mole fraction in CCl_4	5CB	5CCH
0·02	1·14	—
0·04	1·25	1·15
0·06	1·40	1·21
0·08	1·47	1·26
0·10	1·63	1·32
0·15	1·89	1·48
0·20	2·15	1·79
0·25	2·48	2·65
0·30	2·81	3·83

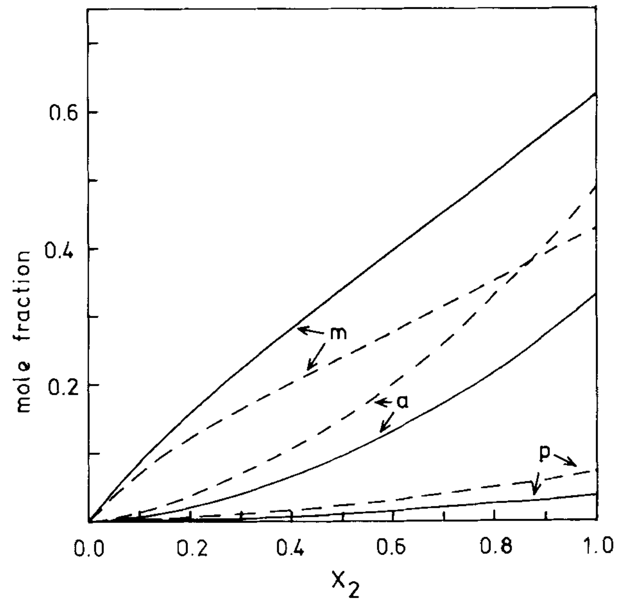


Figure 5. Monomer (m), anti-parallel dimer (a) and parallel dimer (p) mole fractions as a function of total solute mole fraction from equation (8). Broken lines are results for 5CB with $K_a = 2·65$ and $K_p = 0·38$; full lines are for 5CCH with $K_a = 0·85$ and $K_p = 0·09$.

effective polarizability of 5CB is much more dependent on concentration than that of 5CCH, but the magnitude of the solvent effect is great for the latter. Both observations can be explained in terms of the relative polarizabilities of solute and solvent species. For 5CB both the isotropic and anisotropic parts of the polarizability tensor are larger than the isotropic polarizability of the solvent, thus the effect of a solvent cavity on the depolarized scattering of the solute molecule within the cavity is reduced, but varies rapidly with concentration as solute molecules replace solvent molecules in the cavity shell. However for 5CCH the isotropic solvent polarizability is very similar to the solute anisotropy, so the effect of the solvent is greater but not so dependent on concentration. Values for g_2 calculated from the depolarized intensities using equations (12), (13) and (17) are presented in figure 4 and listed in table 3.

The effect of molecular association on depolarized light scattering can be demonstrated by calculating the effective g_2 for a solution of monomers and dimers through equation (16). It must be emphasized that such calculations will be valid only at low concentrations since only interactions between pairs of molecules are considered and no account is taken of interactions between different species. The mole fractions of monomers, parallel and anti-parallel dimers, as determined from the dielectric measurements, are plotted in figure 5. Assuming that the polarizability anisotropy of parallel and anti-parallel dimers is just twice that of the monomers gives results for g_2^{calc}, plotted in figure 4 as broken lines.

4. Discussion and conclusions

There have been few previous attempts to investigate molecular correlation in solutions of mesogens. Gierke and Flygare [14] have studied the depolarized Rayleigh scattering from solutions of 4-methoxybenzylidene-4′-*n*-butylaniline in carbon tetrachloride and reported measurements over a range of concentrations and temperatures. They found that g_2 was significantly greater than unity, even at low molecular concentrations. In their work the important contributions from the local fluid structure were neglected but the final values obtained for the correlation factor are similar to the results reported in this paper. At low concentrations our results suggest that there is less angular correlation between 5CCH than 5CB molecules, which is consistent with weaker association in 5CCH solutions; for mole fractions $> 0{\cdot}25$ the angular correlation in 5CCH increases rapidly. Dielectric measurements show that dipole–dipole association occurs at low concentrations in 5CB solutions but at higher concentrations for 5CCH, which again suggests that the association constants for 5CB are greater.

The model for molecular association proposed in I is based on parallel and anti-parallel dimerization in solution. By fitting the results of dielectric measurements to the theory we have obtained estimates of the equilibrium constants for dimerization in solutions of 5CB and 5CCH. We conclude that for the strongly dipolar molecules studied in this work there are about ten times more anti-parallel dimers than parallel dimers in solution but that the strength of association is weaker for 5CCH than for 5CB. These conclusions from dielectric measurements are supported by our light scattering studies, which show that at low concentrations the angular correlation between 5CB molecules is significantly greater than between 5CCH molecules. The results for g_2 are consistently higher than the predictions of the association model, which indicates that the association does influence the effective polarizabilities, and this aspect of the problem is now under investigation.

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