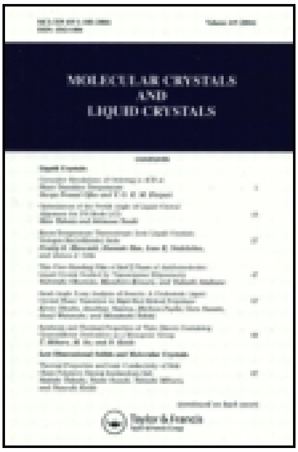


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dipole Association of Polar Mesogens in a Liquid Crystal Solvent

D. A. Dunmur [a] & K. Toriyama [a]

[a] Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, S3. 7HF, UK

To cite this article: D. A. Dunmur & K. Toriyama (1995): Dipole Association of Polar Mesogens in a Liquid Crystal Solvent, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 264:1, 131-144

To link to this article: http://dx.doi.org/10.1080/10587259508037307

Mol. Cryst. Liq. Cryst., 1995, Vol. 264, pp. 131 144
Reprints available directly from the publisher
Photocopying permitted by license only

Dipole Association of Polar Mesogens in a Liquid Crystal Solvent

D. A. DUNMUR and K. TORIYAMA

Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, S3, 7HF, UK

(Received April 29, 1994; revised received August 1, 1994)

This paper reports results of a detailed examination of the low frequency dielectric properties of dilute anisotropic solutions of two polar mesogens, 4-cyano-3-fluorophenyl-4′-propylbenzoate (C3FCN) and 4-cyanophenyl-4′-butylbenzoate (C4CN), as solutes in a non-polar liquid crystal solvent. At low concentrations the effects of dielectric screening are minimised, and the association of mesogens due to dipole-dipole forces can be studied. The measurements suggest that at very low concentrations the dipole-dipole interactions result in a small increase in the effective dipole moment, while at higher concentrations local antiferroelectric order becomes dominant. The results are fitted to an association model, which was originally developed to describe the dielectric behaviour of isotropic solutions of polar solutes (alcohols) in carbon tetrachloride solutions.

Keywords: Liquid crystals, dielectric properties, dipole correlation

INTRODUCTION

The dielectric properties of liquid crystals play an important role in determining the electro-optical response of liquid crystal-based devices. Many of the liquid crystal materials used have polar components, and the behaviour of device mixtures is influenced by dipolar interactions between the constituent molecular species.[1] As well as being of relevance in the development of new materials for applications, dipolar interactions in liquid crystals are also of interest as a new probe of intermolecular interactions. Our earlier studies[2-4] of the dielectric and optical properties of liquid crystal-forming solutes in isotropic solvents has revealed the importance of apolar association, which leads to both parallel and anti-parallel organization of molecular dipoles, the balance of which is determined by specific dipole-dipole interactions. The interaction of molecular dipoles in anisotropic environments such as liquid crystals introduces some new features such as an angle-dependent pair distribution function, and if the local rotational symmetry is broken,[5] long-range dipole-dipole energies vary as r^{-3} instead of r^{-6}. A recent model[6] for liquid crystal molecules interacting with a potential consisting of a hard ellipsoidal core with an imbedded dipole predicts that rod-like molecules with longitudinal dipoles will develop short-range antiparallel dipole order, while rod-like molecules with transverse dipoles will exhibit short-range ferroelectric order. Disc-shaped molecules having a dipole along the symmetry axis are predicted to order ferroelectrically, while if the dipole is in the plane of the disc, the short-range order will be antiferroelectric. Measurements on liquid crystals consisting of rod-like molecules confirm these predictions for both longitudinal dipoles[1-3] and transverse dipoles.[4] A recent study of a dipolar discotic liquid crystal[7] indicates that in spite of theoretical predictions, anti-parallel dipole organization is observed in both discotic nematic and columnar phases. This is explained by tilting of the molecules due to the location of dipolar groups at the edge of the core of the disc.

A new development in the study of dipolar interactions is the measurement of the dielectric properties of polar solutes in aligned, non-polar liquid crystalline solvents.[8] The advantage of such measurements is that dipole–dipole interactions can be measured in a low dielectric constant environment, so the effects of screening are reduced. Furthermore it is possible to measure the effective dipole moment for interacting molecules as a function of both concentration and temperature. The latter results enable the effect of the solvent order parameter on the dipolar organization to be investigated. In this paper, we report the result of a detailed study of the dielectric properties of two mesogens 4-cyano-3-fluorophenyl-4′-propylbenzoate (C3FCN) and 4-cyanophenyl-4′-butylbenzoate (C4CN) as solutes in a non-polar liquid crystal solvent. C3FCN has been reported[9,10] to show a very high dielectric anisotropy, suggesting the existence of ferroelectric dipole organization. The importance of the fluorine group in determining the dielectric properties of fluoro-esters is investigated by comparing the behaviour of C3FCN with a non-fluorinated analogue C4CN.

DIELECTRIC PROPERTIES OF NEMATIC SOLUTIONS

Our approach to the interpretation of static dielectric measurements on aligned nematic solutions of polar solutes in non-polar liquid crystalline hosts has been given in previous papers.[8] It is based on the Maier and Meier equations for the principal permittivities of a nematic, assumes an isotropic internal electric field, and results in an expression for the effective mean square dipole moment ($\mu_{\text{eff}}^{(i)2}$) of the solute for directions parallel ($i = \parallel$) or perpendicular ($i = \perp$) to the director, this equation is given below, and corrects an earlier typographical error [ref. 8, Eq. (4)]:

$$\mu_{\text{eff}}^{(i)2} = \frac{9\varepsilon_0 kT(2\varepsilon + n_2^2)^2}{N_A x_2 (n_2^2 + 2)^2 (2\varepsilon + 1)} \left[\frac{(\varepsilon_i - 1)[x_1 M_1 + x_2 M_2]}{\varepsilon d} - \frac{3x_1 M_1(\varepsilon_{1i} - 1)}{d_1(2\varepsilon + \varepsilon_1)} - \frac{3x_2 M_2(n_{2i}^2 - 1)}{d_2(2\bar{\varepsilon} + n_2^2)} \right] \quad (1)$$

Subscripts 1 and 2 refer to the solvent and solute respectively: M, ε, n, d and x are molecular weight, permittivity, refractive index, density and mole fraction; variables without number subscripts are for the solution. The effective moment can be expressed in terms of anisotropic Kirkwood correlation factors ($g_1^{(i)}$) defined by:

$$\mu_{\text{eff}}^{(\parallel)^2} = g_1^{(\parallel)}[\mu_l^2(1 + 2S) + \mu_t^2(1 - S)]$$

$$\mu_{\text{eff}}^{(\perp)^2} = g_1^{(\perp)}[\mu_l^2(1 - S) + \mu_t^2(1 + S/2)] \tag{2}$$

where S is the orientational order parameter of the solute defined as:

$$S = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle \tag{3}$$

θ is the angle between the major molecular axis and the director, and μ_l and μ_t are dipole moment components parallel to and transverse to the major molecular axis. For flexible molecules a fixed major molecular axis cannot be defined, and the order parameter is in some sense defined by the technique used to measure it. In this work we use measurements of refractive indices to determine the order parameter, which therefore relates to a conformationally averaged axis of maximum polarizability. The dipole correlation factors parallel and perpendicular to the director refer to the correlation between the molecular dipole components projected onto laboratory fixed axes, they can be defined in terms of the appropriate dipole correlation functions as:

$$g_1^{(i)} = 1 + V^{-1}\int \frac{\langle \mu_i(0)\mu_i(\mathbf{r})\rangle}{\langle \mu_i(0)\mu_i(0)\rangle}\,\mathrm{d}\mathbf{r} \tag{4}$$

where (i) refers to the parallel and perpendicular directions.

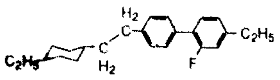
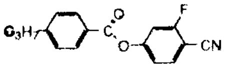
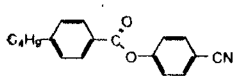
EXPERIMENTAL AND RESULTS

Information on the solutes and solvent used in this work is listed in Table I. The solutes were dipolar mesogens that we have previously studied as dilute isotropic solutes[1–3], so that information was available on the free-molecule dipole moments; dielectric and optical properties of the solvent have been reported in an earlier paper.[11] Measurements of principal permittivities, refractive indices and densities of solutions of the mesogens in the non-polar liquid crystal solvent, I22, were carried out as a function of temperature and composition using methods previously described.[8,11] The solvent I22 is particularly suitable for studies of dipolar interactions in anisotropic environments since it has a low mean permittivity of 3.0, thereby minimising the dielectric screening between solute molecules, and a permittivity anisotropy of zero, so that the dielectric anisotropy resulting from the solute is readily measurable even at low concentrations.

Our result for the free molecule dipole moment of C3FCN is in good agreement with other experimental results ($\mu_0 = 6.6$D[9]), and also with a calculated value of $\mu_0 = 6.59$D based on group dipole moments.[12] Similarly our measured free molecule dipole moment for C4CN of 5.77D is also in good agreement with a previous recorded value

TABLE I

Materials studied and molecular dipole moments

structure and acronym	Transition temperatures – T/°C					Dipole moment/Debyes		
	K		N		I	μ_0	μ_l	μ_t
 I22	*	13	*	64.0	*	1.38	0.8	1.36
 C3FCN	*	70.3		(18)	*	6.59	6.2	2.16
 C4CN	*	68		(42)	*	5.77	5.52	1.68

*temperatures in brackets indicate a monotropic nematic-to-isotropic transition
1 Debye = 3.336 × 10^{-30} C m

of 5.8 D.[9] In order to obtain the correlation factors from measurements of the effective dipole moments through Equation 2, it was necessary to determine the order parameter S. The order parameters of the solutions were obtained by fitting measured refractive indices to a mean field expression using the Tough-Bradshaw procedure.[11] It was also necessary to assume that the solute order parameter was equal to that derived from solution measurements; in practice the derived order parameters were independent of concentration for equal reduced temperatures, indicating that the solute had little effect on the orientational order of the solvent. At the low concentrations used in this work, there was only a small change in the nematic-to-isotropic transition temperatures of the solutions from the pure solvent value, indicating that solvent-solute interactions were relatively unimportant.

Results of permittivity measurements for solutions of various compositions are given in Figures 1 and 2, and the corresponding values for the Kirkwood correlation factors ($g_1^{(0)}$, $g_1^{(1)}$) calculated from Equation 2 are given in Figures 3 and 4 as a function of composition. For both C3FCN and C4CN, the factor $g_1^{(0)}$ shows an unexpected behaviour against concentration: for concentrations less than 0.1 mole-fraction $g_1^{(0)} > 1$ which indicates the presence of parallel dipole association, but with increasing concentration this parallel association apparently decreases giving $g_1^{(0)} < 1$ at higher concentrations. The correlation factor $g_1^{(1)}$, which is less accurately determined, is less than 1 over the concentration range investigated. Equation 2 indicates that there should be a linear dependence of μ_{eff}^2 on the order parameter, but this neglects the possible temperature dependence of $g_1^{(0)}$ and $g_1^{(1)}$. Results for μ_{eff}^2 normalized by μ_0^2 are given as a function of order parameter in Figure 5 for C3FCN and in Figure 6 for C4CN. For the materials studied $\mu_{\mathrm{eff}}^2/\mu_0^2$ varies approximately linearly with order parameter as predicted; also plotted on the figures are theoretical results assuming no correlation.

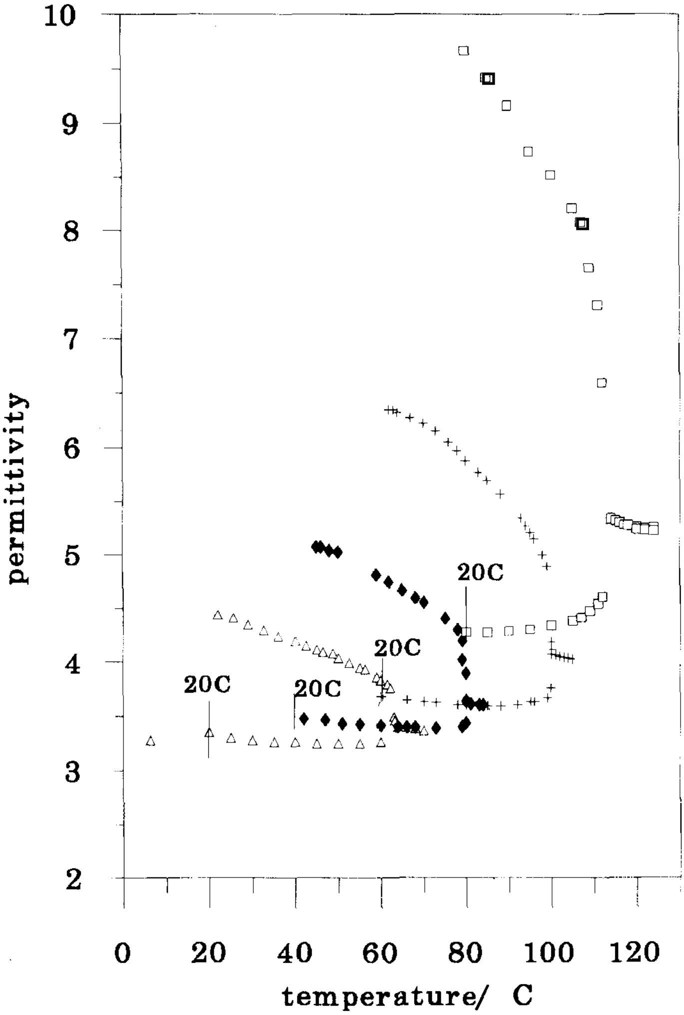


FIGURE 1 Permittivity components (parallel and perpendicular) of C3FCN/I22 solutions for different weight fractions. For clarity the temperature scales for different solutions are shifted, successively by 20°. In reality the nematic-to-isotropic transition temperatures are very nearly equal for all solutions.
(Δ): $w/w = 0.0268$, (◆): $w/w = 0.0401$, (+): $w/w = 0.0635$, (□): $w/w = 0.1304$.

The effect of fluorine-substitution ortho to the nitrile group is to increase the transverse dipole component and dielectric anisotropy of C3FCN relative to C4CN. Dipole correlation factors measured for C3FCN show a larger concentration dependence, which suggests that the fluorine atom is influencing the intermolecular interactions and association rather strongly. Overall there seems to be less association of C4CN molecules in I22 since the *g*-factors tend to their uncorrelated values at low temperatures and high concentrations.

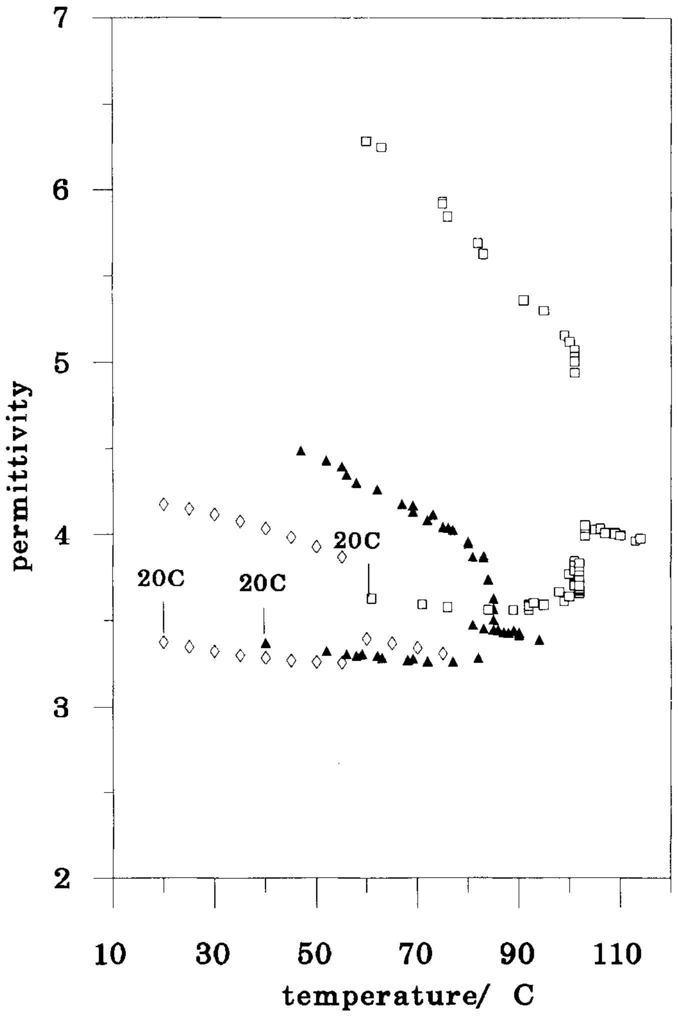


FIGURE 2 Permittivity components (parallel and perpendicular) of C4CN/I22 solutions for different weight fractions. (◇): $w/w = 0.0265$, (▲): $w/w = 0.0344$, (□): $w/w = 0.0795$

DISCUSSION AND CONCLUSIONS

An important observation from our results is that both C3FCN and C4CN solutions in the nematic solvent I22 have a markedly different behavior from their solutions in isotropic solvents. As we have already reported in our previous studies,[1-3] the Kirkwood correlation factor g_1 for those cyano-ester compounds (C3FCN & C4CN) in *p*-xylene has a strong concentration dependence, rapidly decreasing from unity at very low concentrations and reaching a relatively constant value (0.7

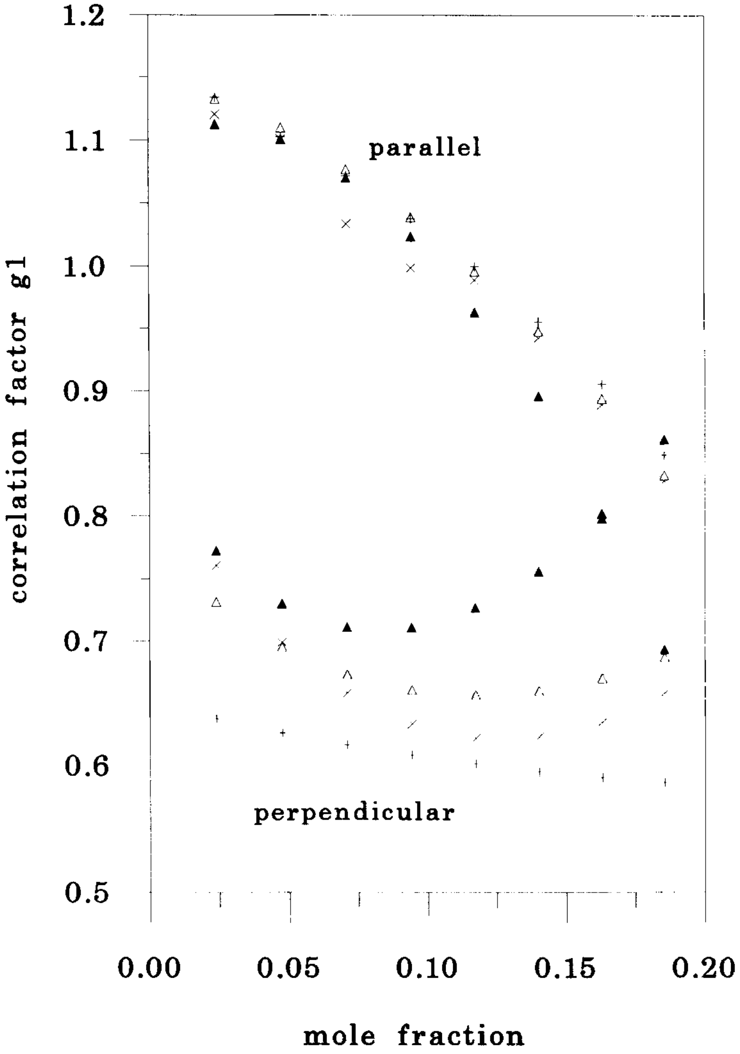


FIGURE 3 Kirkwood correlation factor of C3FCN solutions as a function of mole-fraction in I22 solutions at different temperatures. (+): 20°C, (×): 30°C, (△): 40°C, (▲): 50°C

for C4CN and 0.8 for C3FCN) for concentrations greater than 0.2 mole-fraction (see Figure 1 in Ref. 2). This behaviour is in contrast to that of weakly associating cyano-mesogens such as alkylcyanobicyclohexanes (CCHn),[13] for which g_1 decreases slowly with increasing concentration.[2] The association behaviour of mesogens in isotropic solutions can be interpreted by a model which proposes the existence of both parallel and anti-parallel associated dimers having different equilibrium constants.

$$2M \rightleftharpoons M_{2a}$$

$$2M \rightleftharpoons M_{2p} \qquad (5)$$

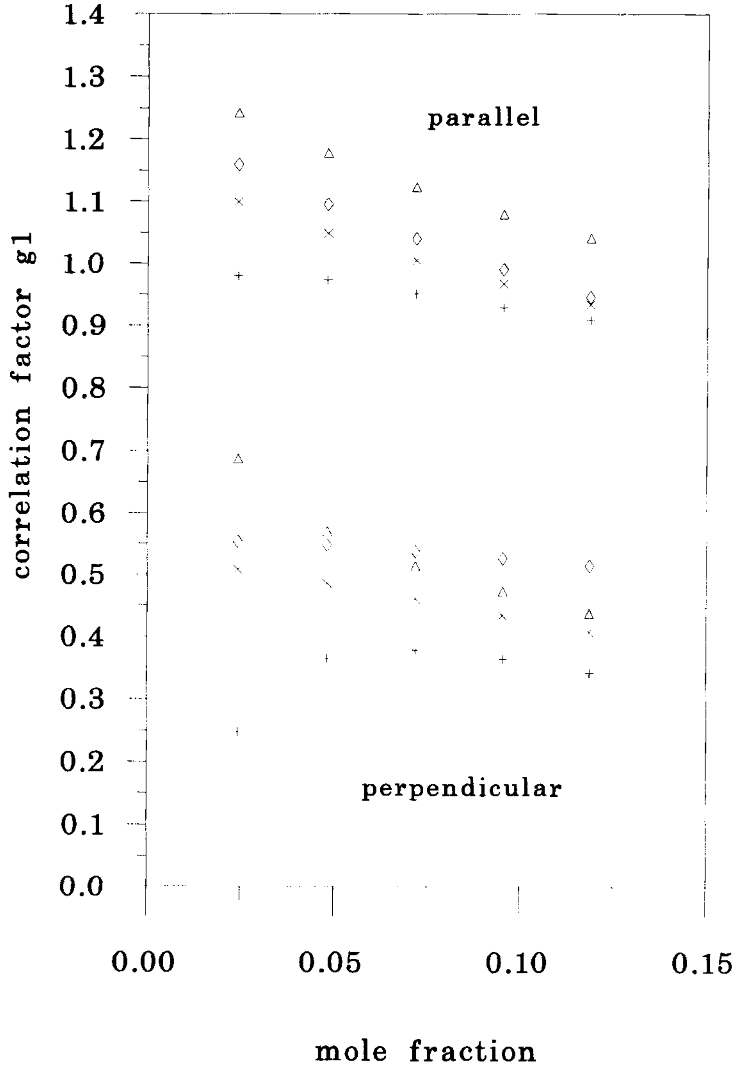


FIGURE 4 Kirkwood correlation factor of C4CN solutions as a function of mole-fraction in I22 solutions at different temperatures. (+): 20°C, (×): 30°C, (△): 40°C, (◇): 50°C

The equilibrium constants for these dimerizations, K_a (antiparallel) and K_p (parallel), are large for C3FCN and C4CN e.g. for C3FCN: $K_a = 10.60$, $K_p = 4.75$, but are much smaller for weakly associating mesogens such as CCH5 ($K_a = 0.85$ and $K_p = 0.09$). The predominance of antiparallel over parallel dimers is determined by the ratio of K_a/K_p. To understand the behaviour when an isotropic solvent is replaced by a nematic solvent, we need to know how these equilibria are modified.

Our earlier results on compounds having large dipole moments perpendicular to the long molecular axis (4HENO4 and 6HENO4[4,8]) indicated a non-linear dependence of

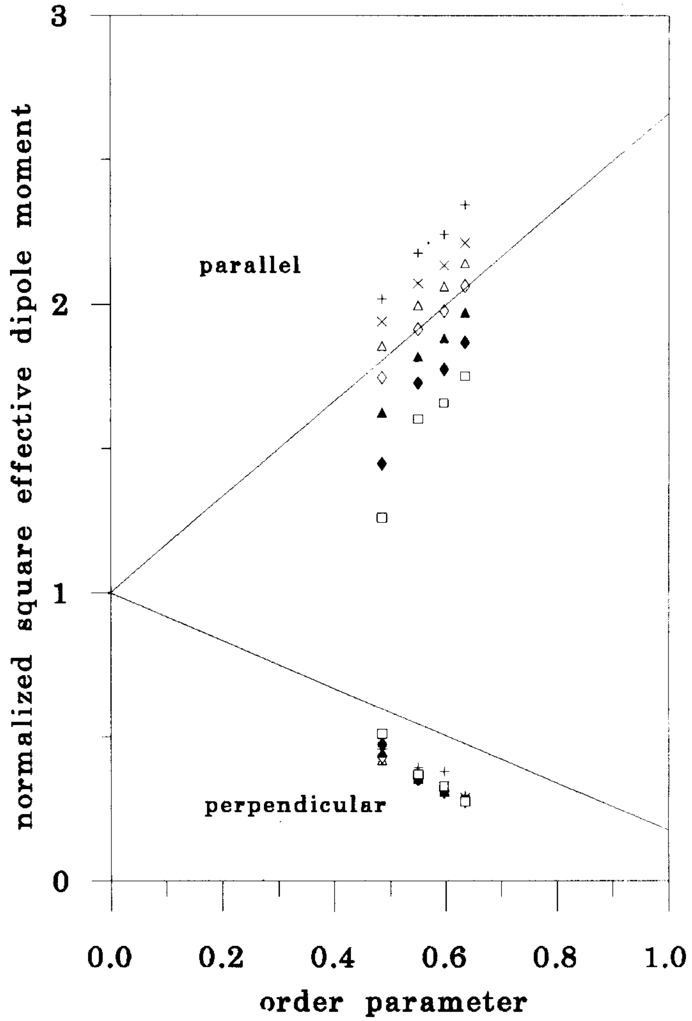


FIGURE 5 $[\mu_{eff}/\mu_0]^2$ as a function of order parameter S for C3FCN for different weight fractions (w/w): the full lines are those calculated from Equation 2 assuming $g_1 = 1$. (+): w/w = 0.02; (×): w/w = 0.06; (△): w/w = 0.08; (◇): w/w = 0.1; (▲): w/w = 0.12; (◆): w/w = 0.14; (□): w/w = 0.18

g_1 on concentration in both isotropic and anisotropic solvents. This was particularly marked in nematic solutions even at very low concentrations (< 0.01 weight-fractions) where g_1 increases rapidly from 1 to 2, and then remained fairly constant, increasing slowly above 0.2 *w/w*. Dilute anisotropic solutions of the compounds C3FCN and C4CN, which have large dipole components parallel to the long molecular axis, also have g_1 values which differ from unity, however for these materials we observed a change in sign of $(g_1 - 1)$, indicating a change from a predominance of parallel to antiparallel dipole organization. The simple equilibrium model developed for isotropic

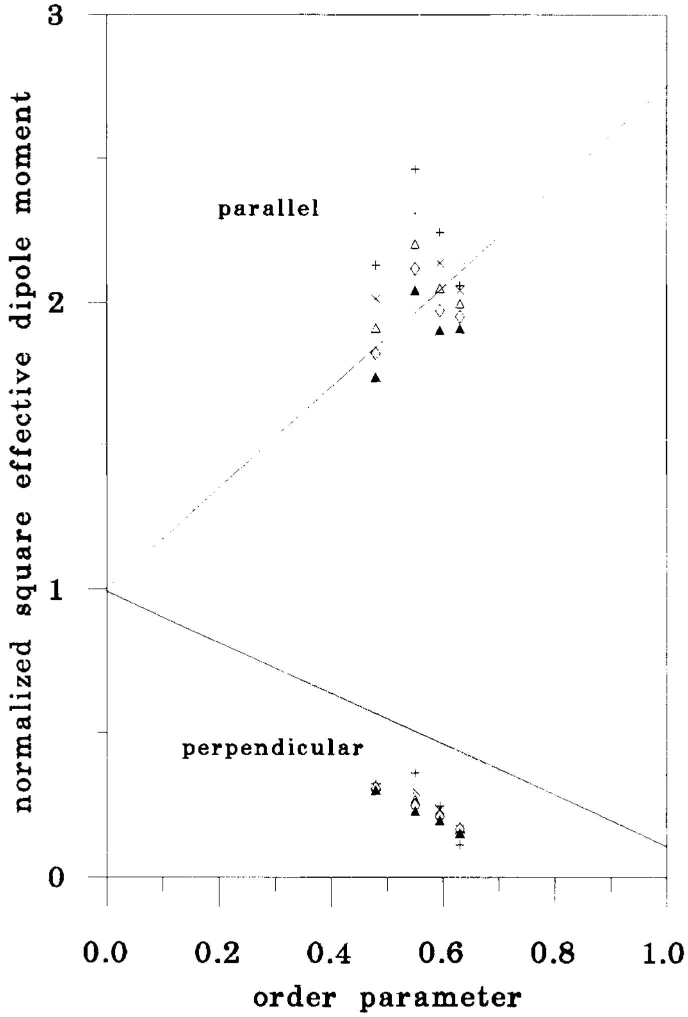


FIGURE 6 $[\mu_{eff}/\mu_0]^2$ as a function of order parameter S for C4CN: the full lines are those calculated from Equation 2 assuming $g_1 = 1$. (+): w/w = 0.02; (×): w/w = 0.04; (△): w/w = 0.06; (◇): w/w = 0.08; (▲): w/w = 0.1

solutions cannot predict a change from parallel to antiparallel association, and so does not appear to be applicable to anisotropic solutions. The limiting value for g_1 extrapolated to zero concentration has to be unity, so a change in sign of $(g_1 - 1)$ from positive to negative implies the existence of a maximum in g_1 at low concentrations. The dielectric properties of very dilute solutions (less than 2 mole per cent) of alcohols in non-polar solvents were investigated in references 14–16, and a maximum in g_1 was observed. This result was explained by proposing the existence of small multimers having a large dipole moment, while at increased concentrations, higher multimers with a smaller dipole moment become dominant. The implication of these results is that the equilibria between various kinds of multimers depend on the concentration, and it is not possible to use concentration-independent equilibrium constants. We may conclude that the behaviour of strongly polar mesogens in non-polar solvents has some similarities with other strongly polar systems,

One possible source of concentration dependent g-factors could be through the anisotropic electric permittivity of the solution i.e. long-range screening effects. The dipole–dipole interaction energy for an isotropic environment can be written as:

$$u_{12} = -\frac{\mu_1\mu_2}{4\pi\varepsilon r^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi) \tag{6}$$

where θ_1, θ_2 and ϕ are as defined in Figure 7, and ε is the isotropic permittivity. In anisotropic solutions the result for the pair interaction energy is more complicated,[20] since the screening from the solution permittivity is angle dependent. For example the screening between dipoles interacting perpendicular to the intermolecular vector will be different from that for dipoles parallel to the intermolecular vector. Increasing the solution permittivity results in a decrease in the dipole–dipole energy, but for solutions at low concentration the dielectric screening will enhance the electrostatic interactions associated with the anisotropic radial distribution function.

In an earlier paper[6] we have developed a mean-field theory of short-range dipole-dipole correlation in anisotropic fluids. The basis of this theory is that angle dependent repulsive forces favour particular configurations of interacting dipoles:

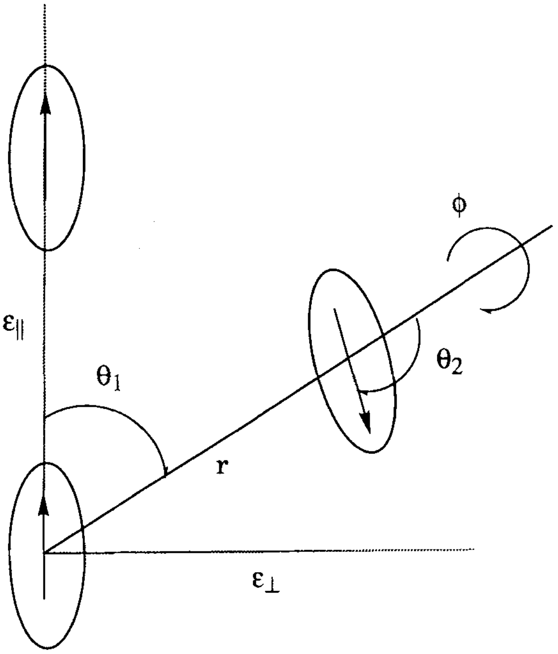


FIGURE 7 Interaction of two dipoles in an anisotropic environment: dipole 1 is assumed arbitrarily to be along the director – θ_1 and θ_2 are the angles between the molecular dipoles and the intermolecular vector, and $\varepsilon_\parallel$ and $\varepsilon_\perp$ are permittivities of the solution parallel and perpendicular to the director.

for calamitic molecules with longitudinal dipoles, anti-parallel dipole–dipole association is predicted, while for transverse dipoles a parallel organization is preferred. Our experimental results show that at low concentrations, $g_1 > 1$ indicating parallel association of dipoles, while at higher concentrations the anisotropic short-range radial distribution of the dipolar solute molecules asserts itself, and the resultant behaviour is anti-parallel dipole association, as predicted by the theory. Clearly at higher concentrations, multimer interactions must also be considered, and it is no longer sufficient to describe the dielectric properties in terms of pair correlations between dipolar solute molecules or simple equilibria between monomers and dimers. In order to explain the change from $g_1 > 1$ at low concentrations to $g_1 < 1$ at high concentrations it is necessary to introduce an additional mechanism for dipole-dipole interactions. At low enough concentrations we can neglect short-range repulsion between solute molecules, and the resultant isotropic electrostatic interactions will not favour parallel or anti-parallel dipole organization. However the solute molecules are surrounded by an anisotropically polarizable solvent medium, and an indirect dipole interaction can result through the induced dipole of the solvent molecules: the so-called triple dipole interaction. This is predicted to result in a parallel dipole configuration,[17] which is consistent with our experimental results. At higher concentrations the direct dipole–dipole interaction becomes more important, including the effects of dipole-screening, and the predicted anti-parallel organization results.

To explain the experimental observations that at a certain concentration the sign of $(g_1 - 1)$ changes from plus to minus, we cannot use a model with equilibrium constants independent of solute concentration. Instead we propose a simplified model which includes a mechanism for the reduction of the para-dimer species either through interaction of the para-dimers themselves or with other monomers. We postulate that at very low concentrations parallel dimers are formed, analogous to the association of 1-heptanol in carbon tetrachloride.[16] The para-dimers may be plate-ike rather than rod-like[18] and with increasing concentration they should favour a parallel, head-to-tail alignment analogous to the case in the dielectric polarization of small plate-shaped molecules in the gas phase.[19] However at higher concentrations this type of local ferroelectric organization must be internally compensated since so far there is no experimental evidence for ferroelectric nematics. Two mechanisms for the reduction in ferroelectric order are available: the screening effect of the dielectric medium and the long-range dipole–dipole interaction discussed above. At some critical concentration c_0 corresponding to $g_1 = 1$, there is no preference for parallel or antiparallel dipole correlation. This concentration can be estimated from the permittivity versus concentration curves: a deviation from a linear dependence at a certain concentration (typically around 0.1 mole-fraction) is observable, which is close to the concentration at which $g_1 - 1$ changes sign. A possible microscopic model which can explain the change in sign of $(g_1 - 1)$ around the concentration c_0 involves a competition between the screening effect which destabilises the parallel dimer, and association between the dimer and other monomers resulting in a reduced effective dipole. Such a model involves equilibria described by the following relations:

$$x_d = K_d x_m^2 \quad \text{and} \quad x_p = K_p x_d^n \tag{7}$$

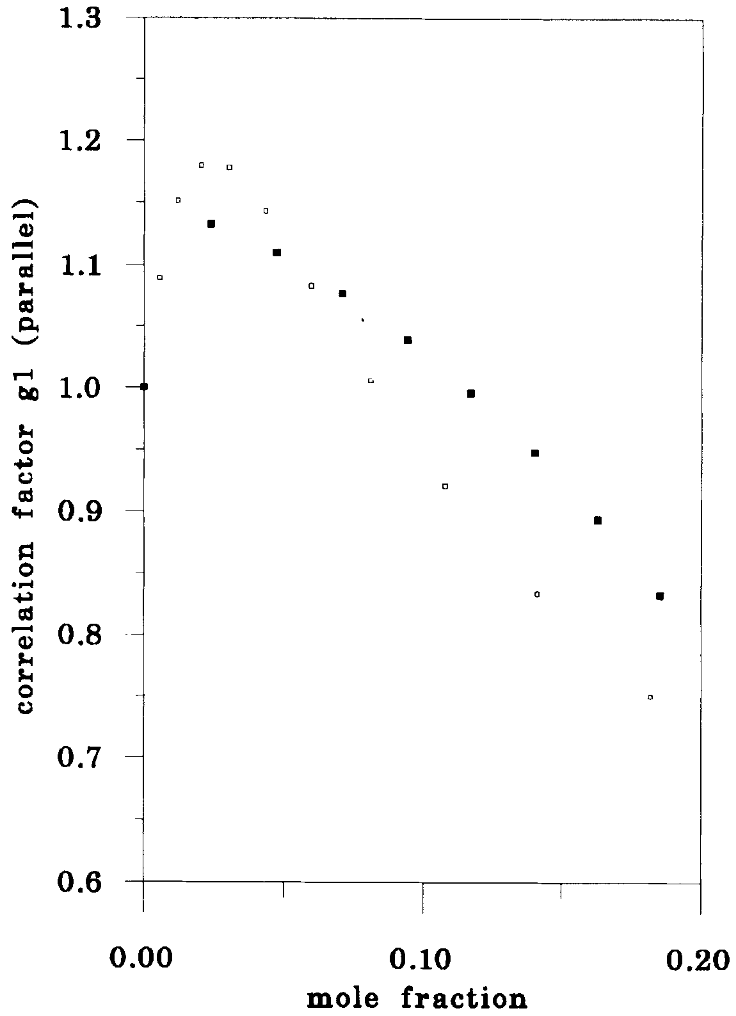


FIGURE 8 Kirkwood correlation factor of C4CN as a function of mole-fraction in I22 solutions at 40°C (■) and calculated values (□) from Equation 9.

where, x_m, x_d, x_p, are mole-fractions of the monomer, paradimer, and multimer, respectively, and K_d and K_p are equilibrium constants for the associations. It is possible to estimate the contribution of this association to the effective dipole moment as follows. Assuming that $n = 2$ it is possible to derive a relation between the total solute concentration (mole fraction x) and the concentration of contributing species as:

$$x = \frac{x_m + 2x_d + 4x_p}{1 + x_d + 3x_p} \tag{8}$$

and for the normalised effective dipole moment defined by g_1:

$$g_1 = \frac{x_m\left(\frac{\mu_m}{\mu_0}\right)^2 + x_d\left(\frac{\mu_d}{\mu_0}\right)^2 + x_p\left(\frac{\mu_p}{\mu_0}\right)^2}{x(1 + x_d + 3x_p)} \tag{9}$$

Thus given the solute concentrations it is possible to calculate the corresponding correlation factors. Fitting the above equations to our results for the C3FCN-I22 solution, with $K_d = 6$ and $K_p = 30$ as parameters, gives the results plotted as a theoretical curve in Figure 8. From these results the concentration at which $g_1 = 1$ can be estimated, and for the systems studied in this work it corresponds approximately to the experimentally observed weight fraction of $c_0 = 0.1$.

In conclusion, we have demonstrated that even at low concentrations, there is evidence of dipole–dipole association in liquid crystal solutions. The fact that such systems are anisotropic means that extra information can be obtained from dielectric measurements, and further investigation of the effects of anisotropic screening, and the effects of different solute molecular shapes and the phase of the liquid solutions could lead to a detailed understanding of dipole–dipole interactions in fluids.

Acknowledgement

This work is part of the research programme "Molecular organisation in liquid crystals resulting from particular intermolecular interactions" funded through the European Union Human Capital and Mobility Programme (contract No. CHRX-CT93-0161).

References

1. K. Toriyama and D. A. Dunmur, *Mol. Cryst. Liq. Cryst.*, **139**, 123 (1986).
2. K. Toriyama and D. A. Dunmur, *Mol. Phys.*, **56**, 478 (1985).
3. D. A. Dunmur and K. Toriyama, *Liq. Cryst.*, **1**, 169 (1986).
4. K. Toriyama and D. A. Dunmur, *Liq. Cryst.*, **5**, 1001 (1989).
5. D. J. Photinos, C.-D. Poon, E. T. Samulski and H. Toriumi, *J. Phys. Chem.*, **96**, 8176 (1992).
6. D. A. Dunmur and P. Palffy-Muhoray, *Mol. Phys.*, **76**, 1015 (1992).
7. T. J. Phillips, J. C. Jones and D. G. McDonnell, *Liq. Cryst.*, **15**, 203 (1993).
8. D. A. Dunmur and K. Toriyama, *Mol. Cryst. Liq. Cryst.*, **198**, 201 (1991).
9. D. G. McDonnell, E. P. Raynes and R. A. Smith, *Liq. Cryst.*, **6**, 515 (1989).
10. M. Bremer and K. Tarumi, *Adv. Mater.*, **5**, 842 (1993).
11. D. A. Dunmur, D. A. Hitchin and Hong Xi Ju, *Mol. Cryst. Liq. Cryst.*, **140**, 303 (1986).
12. R. T. Klingbiel, D. J. Genova, T. R. Criswell and J. P. Van Meter, *J. Amer. Chem. Soc.*, **96**, 7651 (1974).
13. R. Eidenschink, D. Erdmann, J. Kraus and L. Pohl, *Angew. Chem., Int. Ed. Engl.*, **17**, 133 (1987).
14. D. A. Ibbitson and L. F. Moor, *J. Chem. Soc. Chem. Commun.*, **15**, 339 (1965).
15. D. A. Ibbitson and L. F. Moor, *J. Chem. Soc.*, **B1967**, 76, 80.
16. P. Bordewijk, M. Kunst and A. Rip, *J. Phys. Chem.*, **77**, 548 (1973).
17. B. M. Axilrod and E. Teller, *J. Chem. Phys.*, **11**, 299 (1943).
18. M. R. Wilson and D. A. Dunmur, *Liq. Cryst.*, **5**, 987 (1989).
19. C. L. Kong, *J. Chem. Phys.*, **53**, 1522 (1971).
20. P. Palffy-Muhoray and D. A. Dunmur, to be published.